PRECAMBRIAN ORGANIC COMPOUNDS FROM THE KETILIDIAN OF SOUTH-WEST GREENLAND

Part IV

BY

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WITH 49 FIGURES AND 3 TABLES IN THE TEXT

Abstract

Organic compounds have been extracted from Ketilidian sedimentary rocks (nearly 2000 m.y. old). The results are compared with the previously published data obtained on material from the Ketilidian low metamorphic (greenschist facies) supracrustals and with results from graphite from the Nagssugtoqidian fold belt of West Greenland.

Organic compounds have been extracted from two dolomitic samples and a graphite sample of respectively about 15 kg, 7 kg, and 8.5 kg. A grey dolomitic shale is the only dolomitic sample in which monoterpenoid compounds were found, and it is different from the others in the lack of normal alkanes, or at least they are present only in trace amounts. A dark dolomitic sample is shown to contain normal alkanes of the range C_{11} to C_{20} and a graphite from a high-grade metamorphic gneiss (amphibolite facies) has a content of normal alkanes (C_{14} to C_{18}), normal fatty acids from C_{12} to C_{18} and monounsaturated acids from C_{15} to C_{19} besides branched C_{13}-, C_{14}-, and C_{15}-acids. The three samples contain branched-cyclic, aliphatic compounds and various aromatic substances, especially the homologous benzene, naphthalene, and phenanthrene compounds.

The organic compounds extracted from the Ketilidian supracrustals are from graphitic and dolomitic rocks of different types deposited under rather different conditions. By comparison it is seen that low-grade metamorphosed samples yield the highest amounts of organic material per kilogram, and that monoterpenoids are present preferentially in coal–graphite samples while only one dolomitic sample contains detectable amounts of monoterpenoid compounds. The variation in the accumulation of organic material was perhaps dependent on the rate of production of organic material and/or on the deposition conditions. There was possibly also a difference in the biological activity, perhaps with different types of organisms, depending on other conditions in the area.
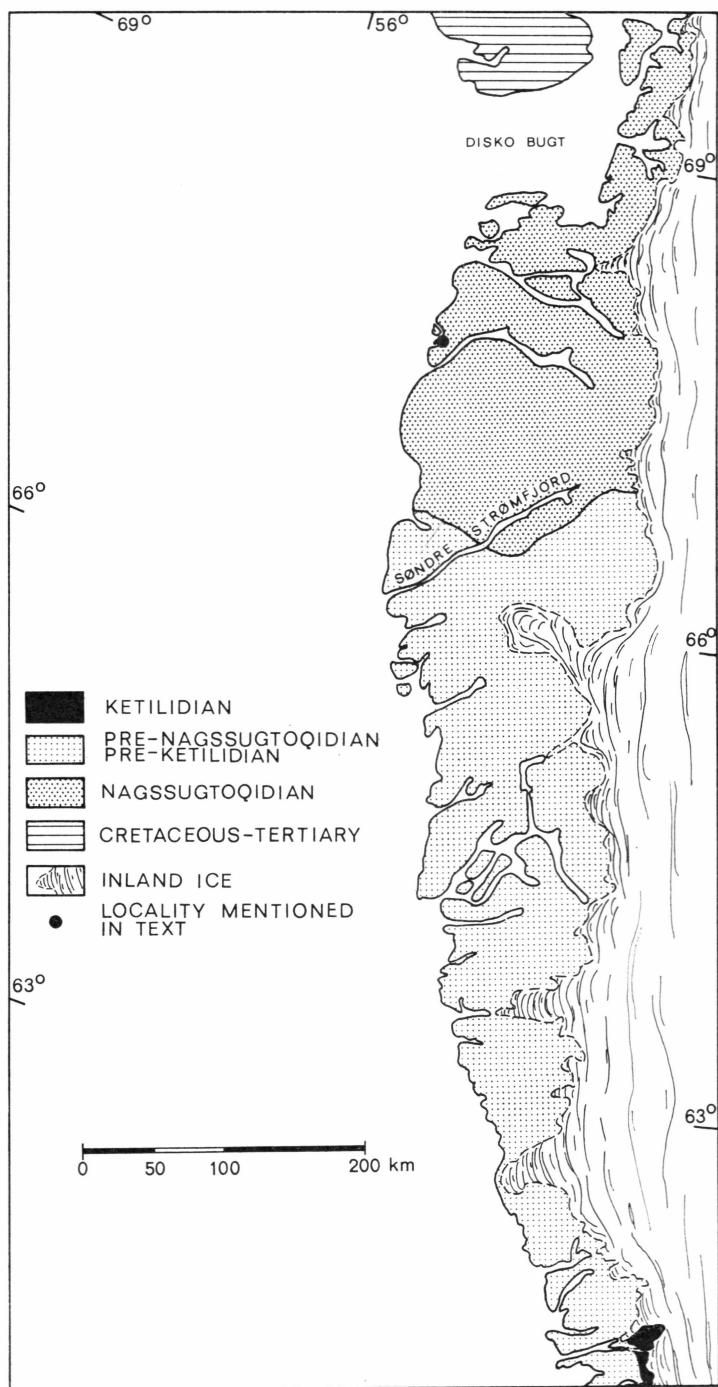
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1*

Fig. 1. Map of West Greenland showing the position of the Agto area in the Nagssugtoqidian and Grænseland area in the southern part of the Ketilidian.

INTRODUCTION

The examinations described in this work have been carried out by the writers at the Chemical Institute (J. LAM) and at the Geological Institute (K. RAUNSGAARD PEDERSEN) of the University of Aarhus.

The organic material dealt with in this paper has been extracted from Precambrian low-grade metamorphic rocks of the Ketilidian fold belt of Grænseland, South-West Greenland, and from Precambrian metamorphic rocks from the Nagssugtoqidian fold belt of West Greenland.

Organic material from the Ketilidian of Grænseland has been treated in three previous publications (RAUNSGAARD PEDERSEN & LAM, 1968, 1970; LAM & RAUNSGAARD PEDERSEN, 1968) and the micro- and macroscopic fossil structures found in some of the sediments have been described by RAUNSGAARD PEDERSEN (1966, 1967 & 1968) and BONDE-SEN et al., 1967. This organic material was extracted from a dark dolomite with small macrofossils and microfossils, and from a coal–graphite. Both types of rock gave rather small amounts of organic compounds, but extraction of large samples of rocks gave a sufficient amount of organic material with many different organic compounds.

The organic material from two samples of dark dolomite with fossils was investigated. In one of them we have shown the presence of normal and branched alkanes with chain lengths from C_{10} to C_{20} and various aromatic hydrocarbons; in the other alkanes from C_{10} to C_{32} and fatty acids are present.

The organic material of the coal–graphite was dominated by aliphatic (straight chain, branched and cyclic) hydrocarbons. The material revealed many saturated straight chain hydrocarbons with n-C_{15} alkane as the most abundant among the normal alkanes, ranging from C_{12} to about C_{21} and various isoalkanes and anteisoalkanes. Saturated cyclic hydrocarbons like alkyl cyclohexanes, and homologous series of alkyl benzenes and alkyl naphthalenes were present. Also monoterpenoid compounds were present together with fatty acids and methyl esters of fatty acids.

The samples treated in this publication contain hydrocarbons in a varied mixture, but none of them show signs of alkanes with more than about twenty C-atoms in any detectable amount. In this paper the previously described geological samples and their organic compounds are compared with the new material.
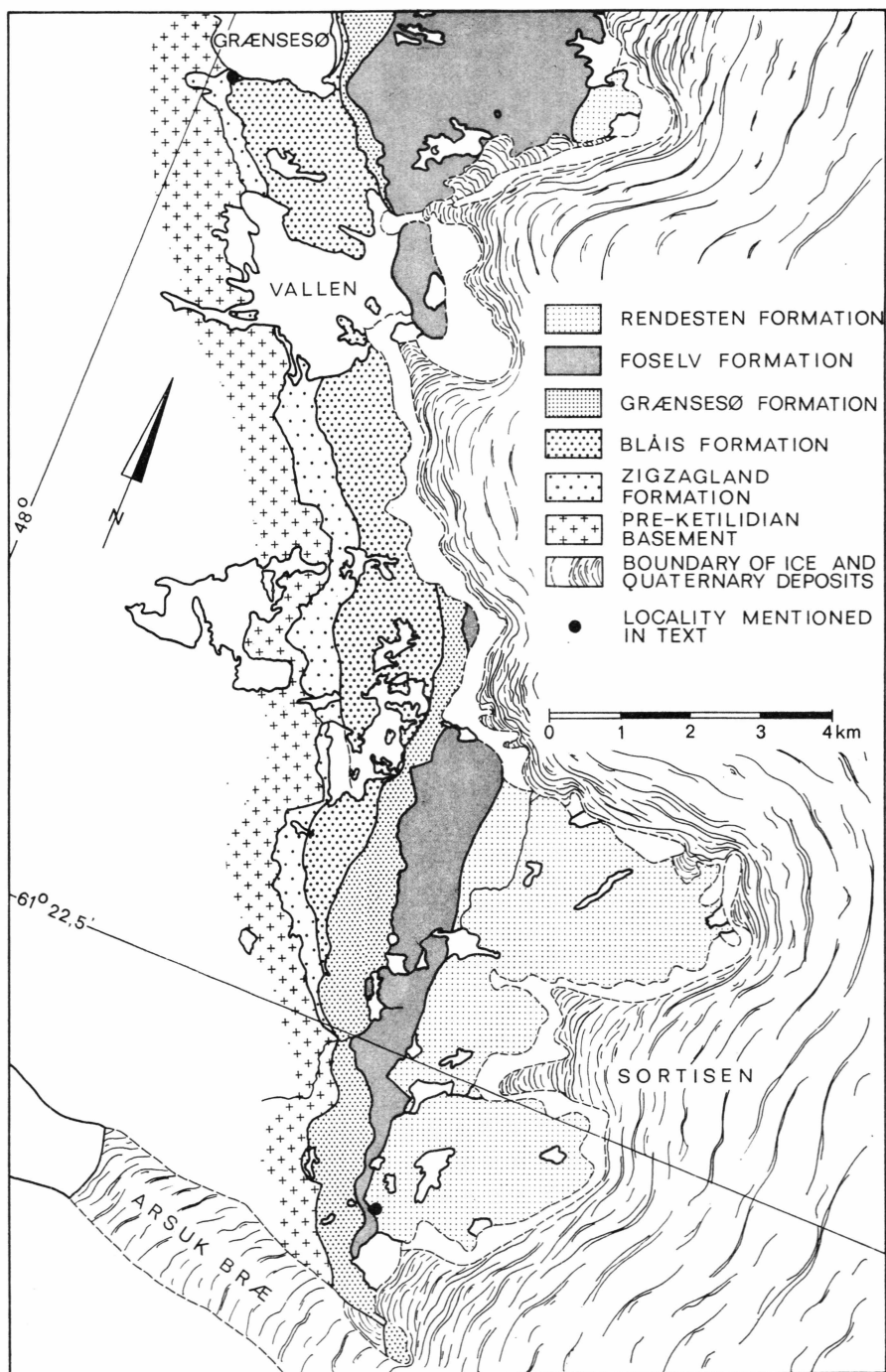
Fig. 2. Map of southern Grænseland, South-West Greenland, showing the localities of the dolomitic samples.

THE MATERIAL AND THE GEOLOGICAL SETTING

The extracted organic material treated in this paper is from three localities, two in South-West Greenland, the third from West Greenland (see map fig. 1). The rock material is dolomite of a rather dark colour and a graphite-bearing gneiss.

Table 1. *The Ketilidian succession of Grœnseland showing the formations from which organic compounds have been extracted.*

Sortis Group	Rendesten Formation	a
	Foselv Formation	c
Vallen Group	Grænsesø Formation	b
	Blåis Formation	
	Upper Zigzagland Formation	a
	Lower Zigzagland Formation	
Pre-Ketilidian Basement		

a organic compounds published in this work.
b organic compounds described in LAM & PEDERSEN, 1968.
c organic compounds described in PEDERSEN & LAM, 1970.

The material from South-West Greenland is from the low-grade (greenschist facies) metamorphic Ketilidian supracrustals of Grænseland the age of which is estimated as 1700–2000 m.y. (BRIDGWATER, 1965). The geology of the Grænseland area has been treated previously (BONDE-SEN *et al.*, 1967; RAUNSGAARD PEDERSEN & LAM, 1968, 1970; LAM & RAUNSGAARD PEDERSEN, 1968 and BONDESEN, in press).

Sample No. 70680

The sample is a dolomitic shale of a greenish grey to dark grey colour. It is from a sequence of about 140 m of dolomitic shales which forms the upper part of the Upper Zigzagland Formation of the Vallen Group (see table 1). The locality for the sample is situated on the southern shore of Grænsesø (see map fig. 2 and figs 3, 4).

Fig. 3. Dolomitic shale in Upper Zigzagland Formation, southern shore of Grænsesø.
Note the lack of vegetation.

Spheroidal microfossils of distinctive types (types 1, 2 and 3, plates
9 and 10 in BONDESEN, PEDERSEN & JØRGENSEN, 1967) have previously
been described from a black quartzite from the same part of the series as
the dolomitic shale. The dolomitic shale is finely laminated and shows
slight concentrations of small graphite grains along some of the lam-
inations (fig. 7).

Sample No. 93142

The sample is a dark grey to black dolomite from the lowermost
part of the Rendesten Formation, Sortis Group (table 1). It is from a
dolomite layer of about 5–50 m in the southern part of Grænseland
north-west of lake Mælkesø near Arsuk Bræ (see map fig. 2 and fig. 5).
The dark colour is evenly distributed in the rock sample and, as shown
by the microphotographs (fig. 8), the dolomite contains many small
grains of graphite.

These two Ketilidian samples are from the lower and the upper part
of the Ketilidian sequence of Grænseland (see table 1) and are separated

Fig. 4. Dolomitic shale in Upper Zigzagland Formation; same locality as in fig. 3.

Fig. 5. Dark dolomite (in the foreground) in the lowermost part of Rendesten Formation, Sortis Group southern Grænseland.

by about 1000–1400 m of the Blåis and Grænsesø Formations and geographically the localities are situated about 16 km from each other. The supracrustals of the Ketilidian of Grænseland have only been subjected to mild metamorphism (greenschist facies, WINDLEY et al., 1966), which was strongest to the south.
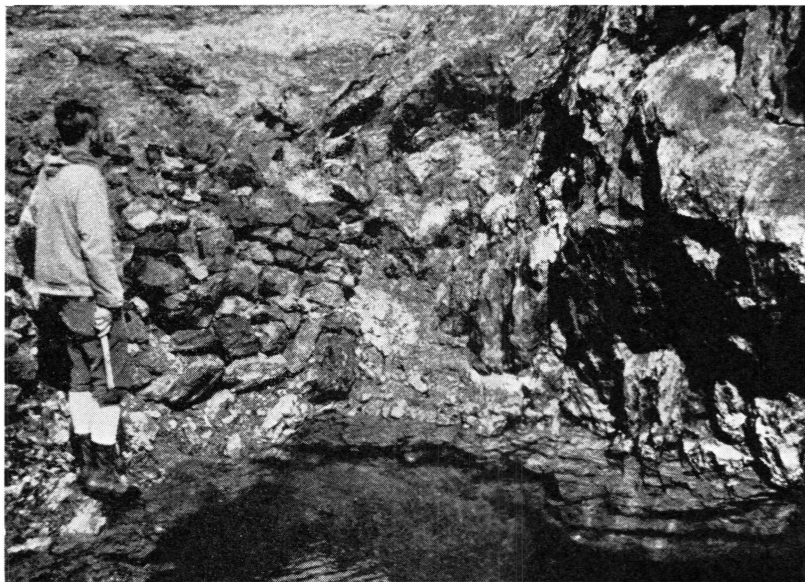
Fig. 6. Graphite layer in gneiss. Agto area. LINDEROTH photo.
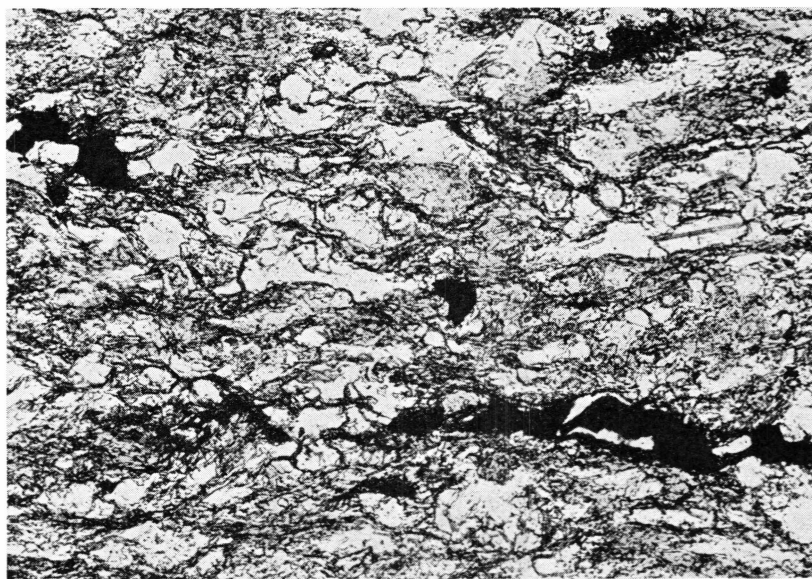
Fig. 7. Microphotograph of dark grey dolomite in Upper Zigzagland Formation.
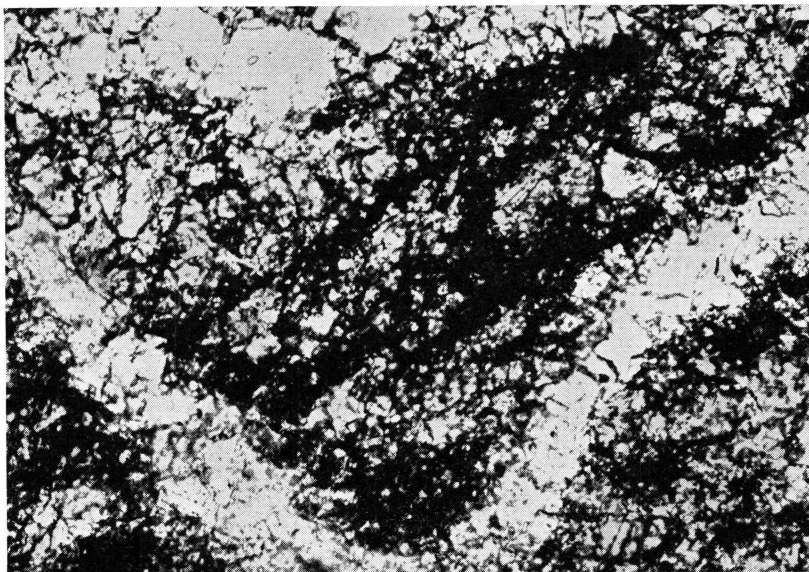GGU sample No. 70680.

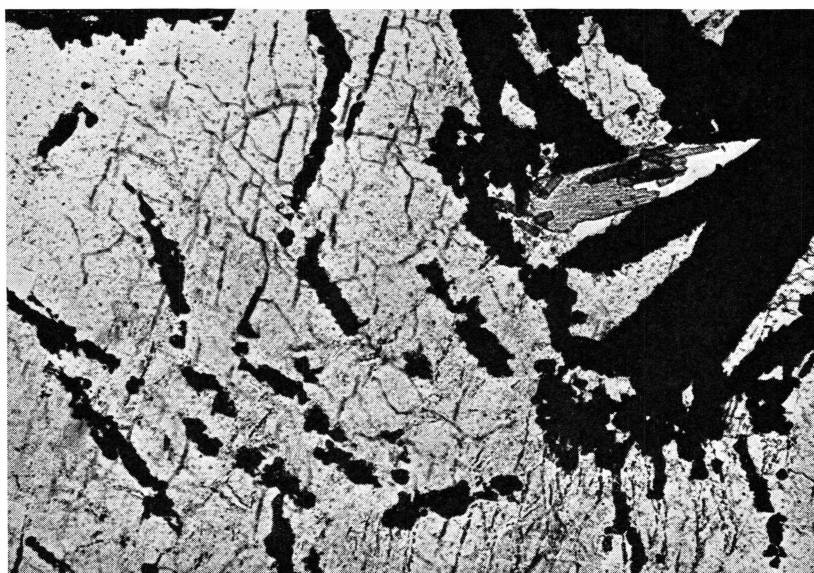Fig. 8. Microphotograph of dark dolomite. Rendesten Formation. GGU sample
No. 93142.

Fig. 9. Microphotograph of graphite from the Agto area. GGU sample No. 106449.

Sample No. 106449

This is a graphite-bearing gneiss from the Nagssugtoqidian of West Greenland. The sample is from an area with rocks of amphibolite facies. The geology of the area has been worked out by Bondesen and others (Bondesen, 1968, 1969) during the last few years. The sample is from a graphite-bearing layer about 5 m thick within a rather deformed gneiss sequence.

The sample is situated in the Agto area south-south-west of Egedesminde (see map fig. 1 and fig. 6).

The age of the Nagssugtoqidian of this area is about 1700 m.y. (Pulvertaft, 1968).

The graphite is found as close lying, folded flakes and small grains concentrated in irregular streaks (fig. 9).

The three samples are thus of about the same age, but they are of different rock types and of different metamorphic grade.

EXTRACTION AND ANALYTICAL METHODS

All the manipulations of the rock material were performed with carefully purified utensils, apparatus, and solvents redistilled in all-glass equipment in order to avoid contamination as far as possible. The surface layers of the samples were cut off, and the samples were rinsed in extraction liquid (benzene-methanol mixture 3:1 v/v). The rinsed and pulverized material of each sample was extracted and re-extracted twice according to the method described earlier by RAUNSGAARD PEDERSEN & LAM (1970). After evaporation the extracts were chromatographed on a silica column, and a series of fractions were obtained. Filter paper has been avoided because of its content of phthalates (LAM, 1967). The fractions containing saturated aliphatic hydrocarbons were separated by urea inclusion (RAUNSGAARD PEDERSEN & LAM, 1970). The most polar fractions were subjected to methyl ester conversion of fatty acids. One conversion failed, and one sample did not show detectable amounts of methyl esters after treatment. GLC-separation combined with mass spectrometry was carried out on the fractions obtained. Columns of 2 m 10 per cent. S.E. 30 on gaschrom Z were used for separation in a Perkin-Elmer 880 gas chromatograph, and the mass spectra were detected on a Hitachi-Perkin-Elmer RMU-6D mass spectrometer; ionizing voltage 70 eV; ion source temperature 250°C; gas inlet.

When these methods were applied to GGU sample No. 106449, an oily mixture was obtained which gave a series of fractions in which normal alkanes, branched alkanes, and cycloalkanes besides aromatic compounds as alkyl benzenes, alkyl naphthalenes, and fatty acids were detected. Sample No. 93142 gave fractions containing normal and branched alkanes besides cycloalkanes; also alkyl benzenes, alkyl naphthalenes, alkyl phenanthrenes, alkyl dihydronaphthalenes, and alkyl di- and tetrahydrophenanthrenes were detected, and from sample No. 70680 were mainly detected cycloalkanes, whereas normal alkanes could only be detected in trace amounts. Alkyl cycloalkanes, monoterpenoid hydrocarbons, and monoterpenols are dominating compounds in the less polar and the most polar fractions respectively; in the fractions in between alkyl benzenes and alkyl phenanthrenes were detected.
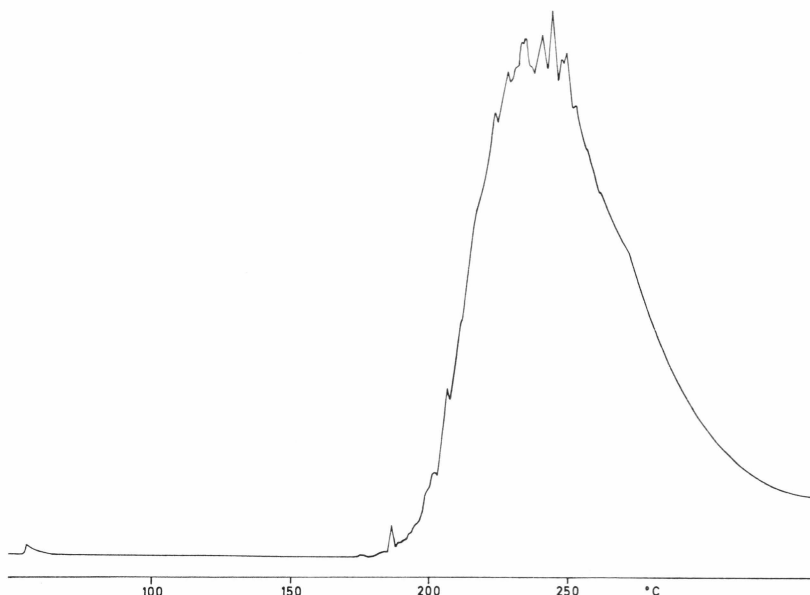
Fig. 10. GGU sample No. 70680. Gas chromatogram of alkyl benzenes homologoues. Column 10 °/₀ S.E. 30, 2 m, 6,7° C/min., 50–250° C. Helium flow 30 ml/min.

RESULTS

Sample No. 70680

The material was treated according to the method described by Raunsgaard Pedersen & Lam (1970). From 15305 g of finely milled material was obtained 250 mg of an oily mixture and about 50 mg of free sulphur. This sample differs from those previously investigated in its hydrocarbon content and also in that only trace amounts of fatty acid methyl esters are present, while some monoterpenols could be detected by means of their characteristic fragmentations. The hydrocarbon fractions do not contain normal chain hydrocarbons in more than trace amounts whereas branched chain alkanes, cycloalkanes and alkyl benzenes are the main substances. Methyl phenanthrenes and dimethyl phenanthrenes indicate fragmentation from steroids (cf. Mair, 1964); i.e. spectra of one fraction indicate the presence of carbonyl containing compounds, which is also indicated by the high intensity of the 58 m/e fragments characteristic for methyl ketones and the 71 m/e fragments from propyl ketones.

Figs 10 to 26 show a series of gas chromatograms and mass spectra obtained from the fractions extracted from sample 70680. Fig. 10 shows the presence of alkyl benzenes in a complex mixture from about C_{10}–C_6 to C_{17}–C_6 with C_{12}–C_6 (dodecylbenzene) and C_{13}–C_6 (tridecylbenzene) the most abundant alkyl benzenes present in the mixture. A C_{11}–C_6 alkyl
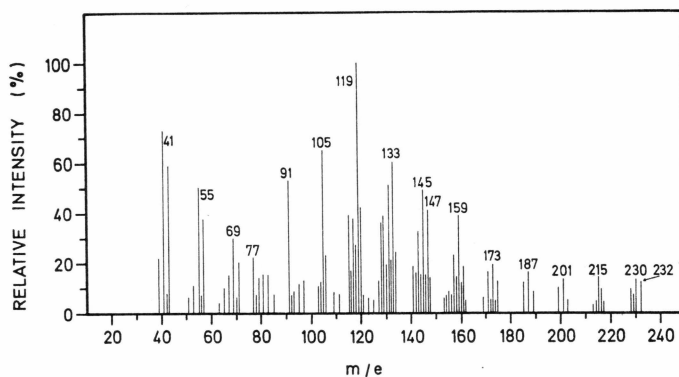
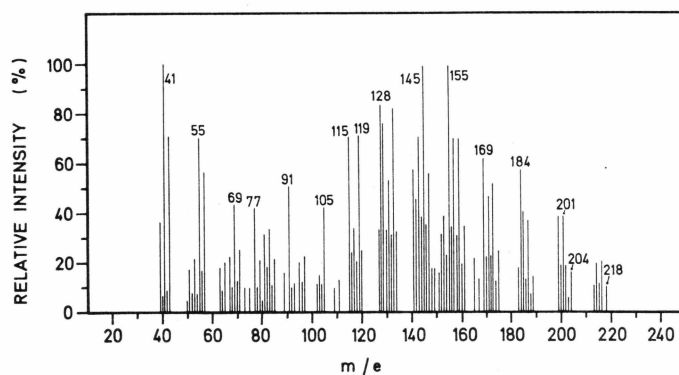Fig. 11. GGU sample No. 70680. Mass spectrum of a C_{11}–C_6 alkyl benzene.

Fig. 12. GGU sample No. 70680. Mass spectrum of a mixture of 1. alkyl benzenes
(MW 204 and MW 218), 2. alkyl naphthalene (MW 184).

benzene with the fragments m/e 77, 91, 105, 119 + $(CH_2)n$ typical for alkyl benzenes is shown in the mass spectrum (fig. 11). The mass spectrum of another fraction (fig. 12) shows a mixture of at least three compounds: (a) two alkyl benzenes with molecular weights 204 and 218 corresponding
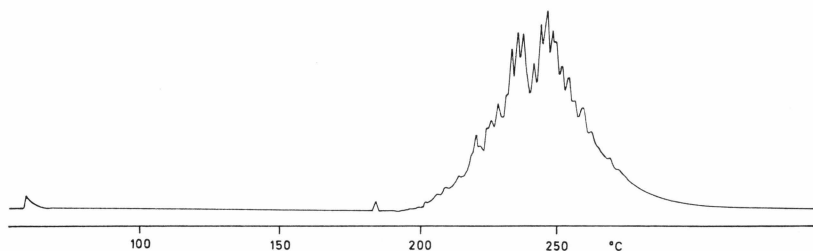

Fig. 13. GGU sample No. 70680. Gas chromatogram of an alkyl naphthalene and alkyl phenanthrene fraction besides di- and tetrahydro derivatives. Column 10 $^0/_0$ S.E. 30, 2 m, 6,7° C/min., 50–250° C. Helium flow 30 ml/min.
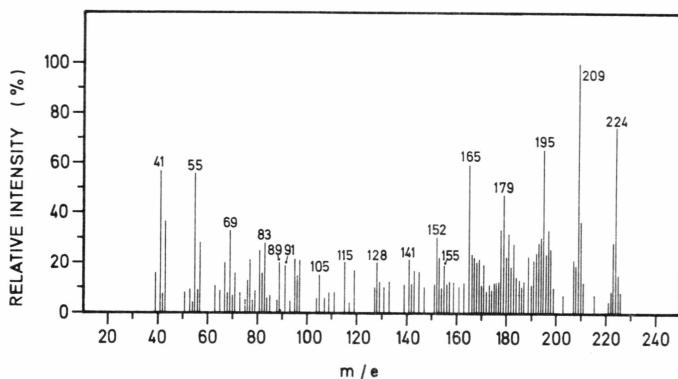
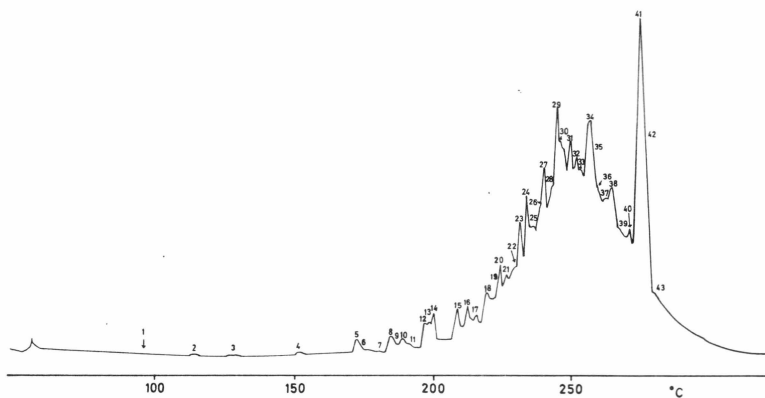Fig. 14. Mass spectrum from GGU sample No. 70680. (See text for explanation).

Fig. 15. GGU sample No. 70680. Gas chromatogram of an alkyl phenanthrene fraction
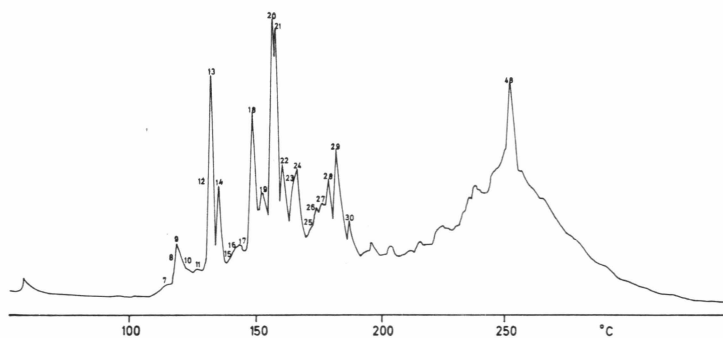Column 10 % S.E. 30, 2 m, 6,7°C/min., 50–250°C. Helium flow 30 ml/min.

Fig. 16. Gas chromatogram of the most polar fraction from sample No. 70680. Column
10 % S.E. 30, 2 m, 6,7°C/min., 50–250°C. Helium flow 30 ml/min.

to a nonylbenzene and a decylbenzene respectively and (b) an alkyl naphthalene with the molecular weight of 184 (tetramethyl naphthalene). The high intensity of the fragments of m/e 115, 128, 141, 155, 169 and 184 are characteristic for alkyl naphthalenes of this order of magnitude. A mass spectrum diagram that has not been exactly resolved is given as fig. 14. Here there are indications of trimethyl tetrahydrophenanthrene in the fragmentation pattern. Fig. 15 is a gas chromatogram of a fraction consisting mainly of methyl phenanthrene with traces of phenanthrene and the methyl ester of palmitic acid. Phenanthrene is detected from peak 20, methyl phenanthrenes from the peaks 25 and 26, dimethyl phenanthrenes from the peaks 31 to 34, and a trimethyl phenanthrene from peak 42 of the gas chromatogram by their mass spectra. Furthermore, alkyl dihydrophenanthrenes also seem to be present. The gas chromatogram of the most polar fraction of this sample is shown as fig. 16.

Figs 17 to 22 show monoterpenoid structures of which fig. 17 gives the mass spectrum of authentic borneol while fig. 18 is the mass spectrum
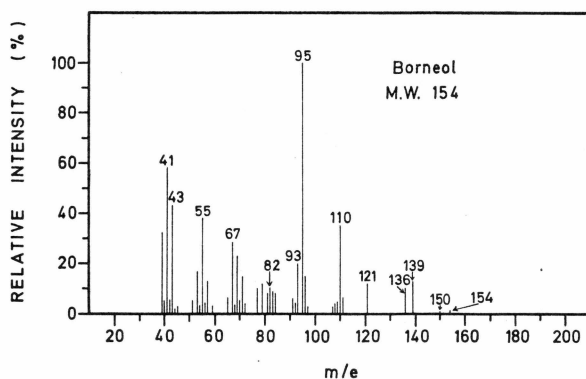

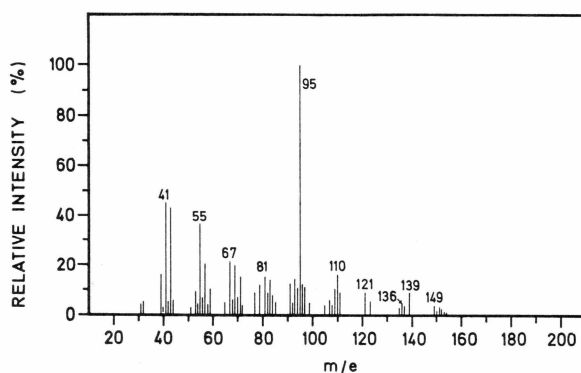Fig. 17. Mass spectrum of authentic borneol.

Fig. 18. Mass spectrum from GGU sample No. 70680, cf. borneol of fig. 17.

185   2
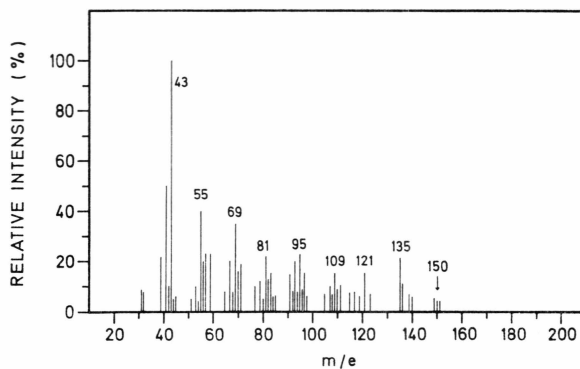
Fig. 19. Mass spectrum from sample No. 70680 with a fragmentation pattern characteristic of monoterpenoids.
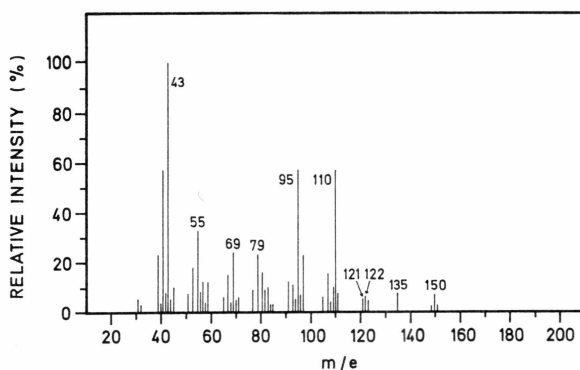

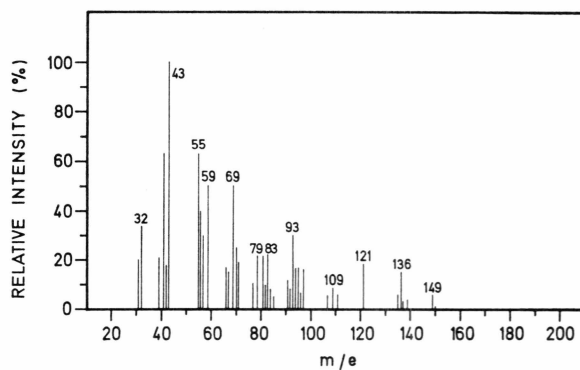Fig. 20. Mass spectrum from GGU sample No. 70680. (See text for explanation)

Fig. 21. Mass spectrum from GGU sample No. 70680. (See text for explanation).

from sample No. 70680, which is close to that of borneol. Figs 19 to 22 show mass spectra of substances present in sample No. 70680 with a fragmentation pattern characteristic of monoterpenoids (RAUNSGAARD
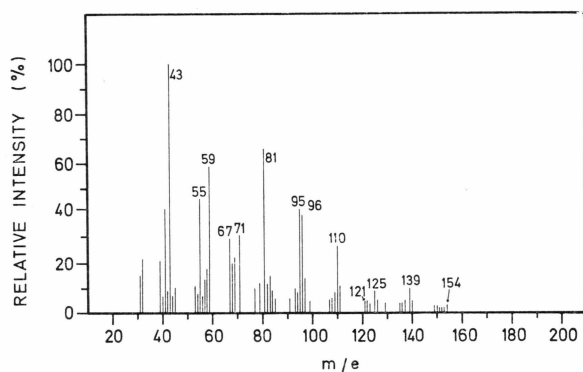
Fig. 22. Mass spectrum from GGU sample No. 70680. (See text for explanation).
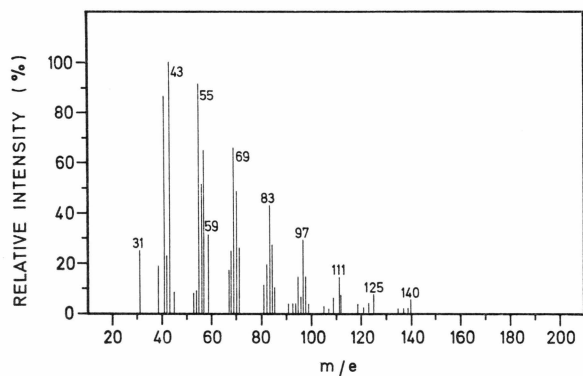

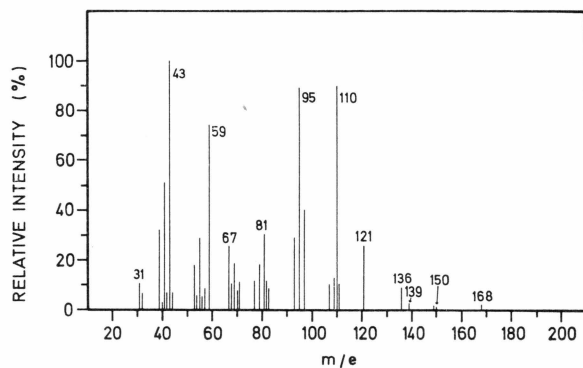Fig. 23. Mass spectrum from GGU sample No. 70680. (See text for explanation).

Fig. 24. Mass spectrum from GGU sample No. 70680, showing terpenoid fragmentation pattern.

PEDERSEN & LAM, 1970) with molecular weights of 150 and 154. For monoterpenols with a molecular weight of 150 the fragmentation pattern often shows m/e tops corresponding to M − 15 = 135 m/e, M − 29 = 121
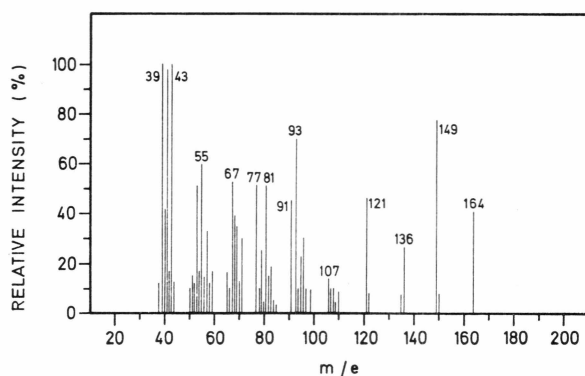
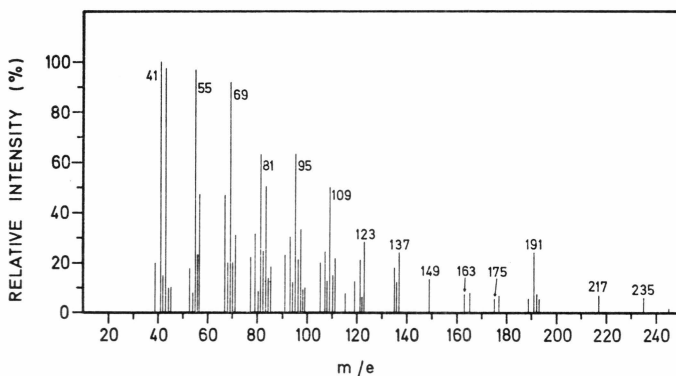Fig. 25. Mass spectrum from GGU sample No. 70680. (See text for explanation).

Fig. 26. Mass spectrum from GGU sample No. 70680. (See text for explanation).

m/e, M − 43 = 107 m/e, M − 18 = 132 m/e, M − 17 = 133 m/e, M − 15 − 18 = 117 m/e, but also other prominent peaks may be abundant. For monoterpenols with a molecular weight of 154 the corresponding M − 15 = 139 m/e, M − 18 = 136 m/e, M − 15 − 18 = 121 m/e, M − 43 = 111 m/e and M − 18 − 43 = 93 m/e may be of a relatively high intensity (see von Sydow, 1963). Figs 21 and 22 show m/e 59 fragments of a high intensity indicating tertiary alcohol function. Fig. 23 may be due to an alkyl substituted cyclohexane like for instance:
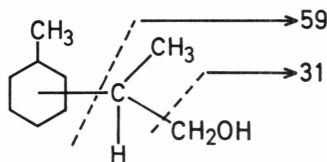
where oxygen may be lost and with fragments of fairly high intensity of m/e 31 and 59. Fig. 24 and fig. 25 are mass spectra showing terpenoid fragmentation pattern, but the substances have higher molecular weights

than are normal for monoterpenoids. In fig. 24 a 'monoterpenol' with two alcohol groups may be a possibility; fig. 25 may represent a compound with one methyl group more than is usual in monoterpenols. Fig. 26 shows the mass spectrum of one of several examples of fragmentations indicating steroid origin (m/e 109, 123, 137, 149, 163, 175, 191, and 217 peaks with especially high intensity of the 191 fragment) (cf. ANDER-SON *et al.*, 1969).

The mass spectra of figs 17 to 26 correspond to the most polar substances from sample No. 70680. It is therefore most likely that the compounds are alcohols, while monoterpenoid material detected in less polar fractions corresponds to hydrocarbons and maybe also ketones.
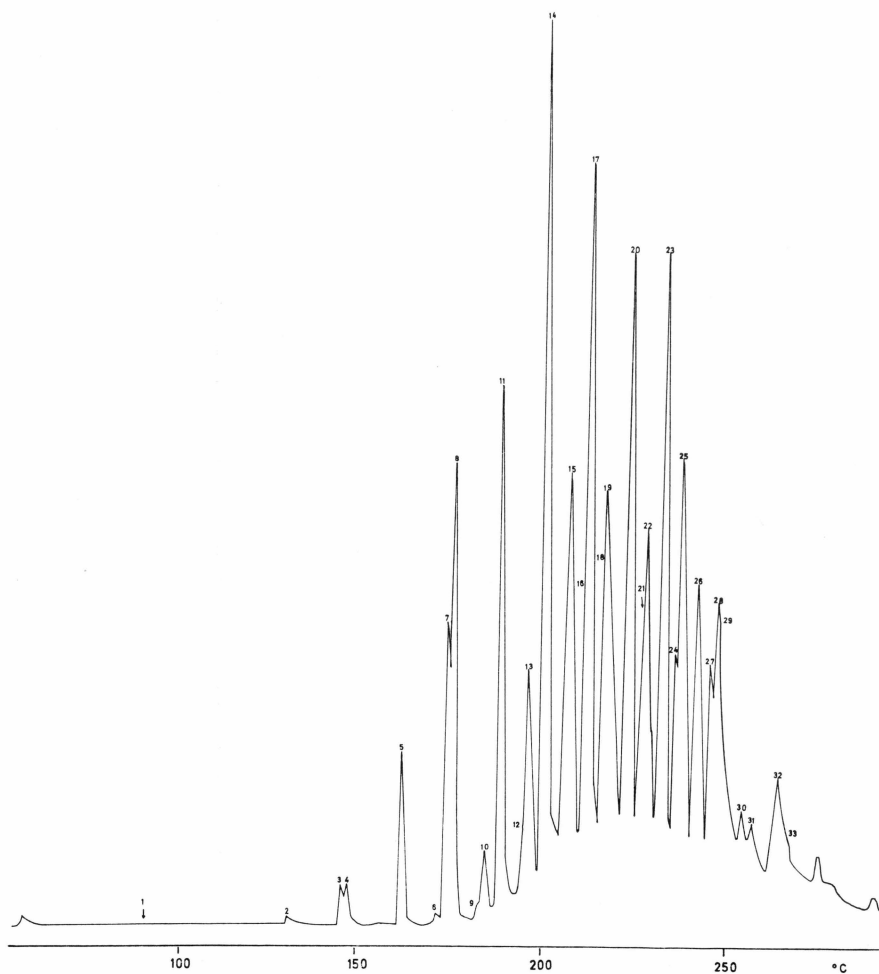

Fig. 27. GGU sample No. 93142. Gas chromatogram of the urea inclusion separated hydrocarbon fraction, showing normal alkanes and branched (iso- and anteiso-) alkanes. Column 10 % S.E. 30, 2 m, 5°C/min., 50–250°C. Helium flow 30 ml/min.
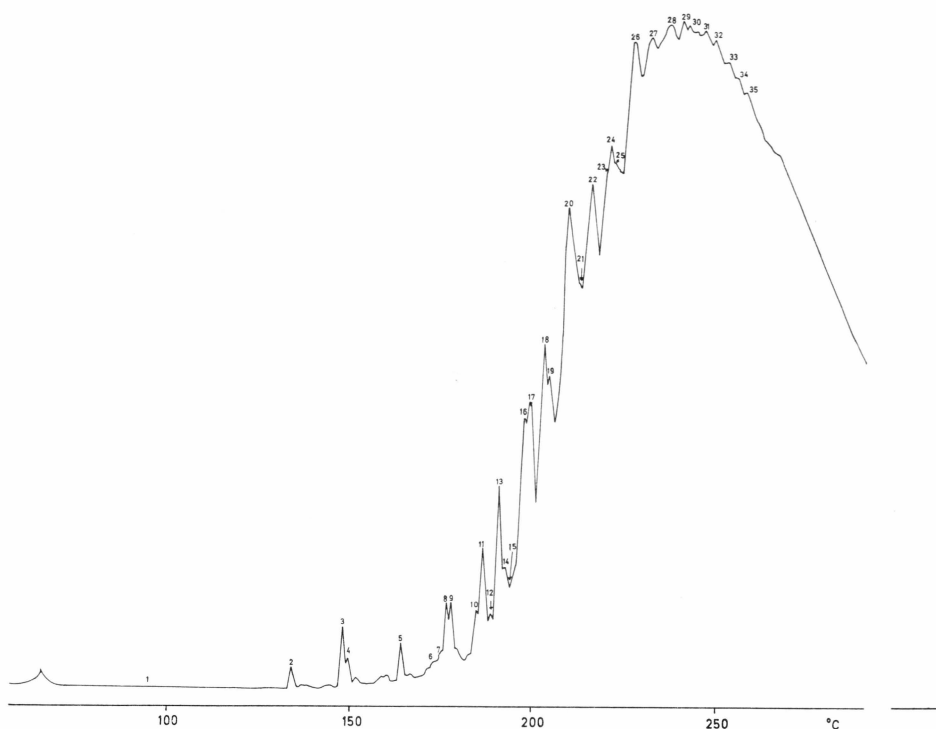
Fig. 28. GGU sample No. 93142. Gas chromatogram of cycloalkane fraction from urea inclusion separation. Column 10 % S.E. 30, 2 m, 5°C/min., 50–250°C. Helium flow 30 ml/min.

Sample No. 93142

The result of the extraction of 7519 g of material was 126 mg of an oily extract.

Normal alkanes from C_{11} to C_{20} with C_{15}, C_{16} and C_{17} most abundant in the mixture are determined in the fraction obtained from urea inclusion, while a fraction of non-included material showed mainly alkyl cycloalkanes and branched (isoprenoid) aliphatic hydrocarbons. The included material is less than one fourth of the total amount of saturated hydrocarbons. Alkyl cycloalkanes present in the mixture are in the range C_{10} to C_{21}. Furthermore, homologous series of alkyl benzenes and alkyl substituted naphthalenes with a number of carbon atoms corresponding to methyl naphthalenes up to hexamethyl naphthalenes are detected. In the fractions containing naphthalenes there are also indications of dihydronaphthalene derivatives. Diphenyl, phenanthrene, methyl phenanthrene, dimethylphenanthrene and more or less saturated phenanthrenic structures are also present indicating residues from steroids which may have been dehydrogenated in the presence of free sulphur under increased pressure and temperature. Fragmentation to various
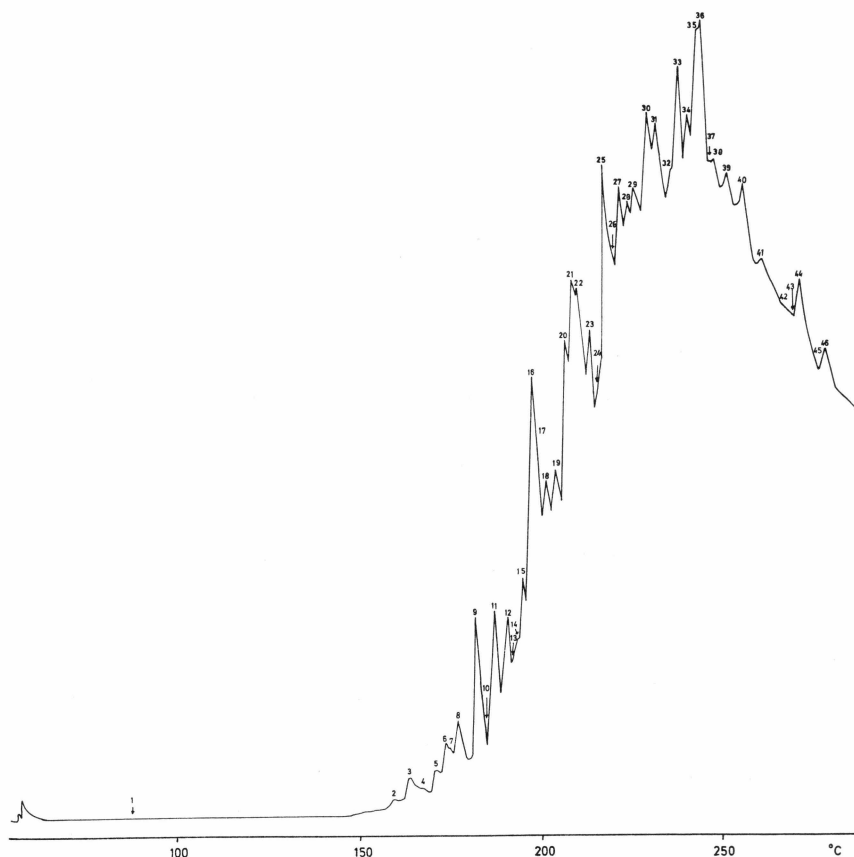
Fig. 29. GGU sample No. 93142. Gas chromatogram of a fraction of a complex mixture mainly containing alkyl naphthalenes, alkyl phenanthrenes and partly hydrogenated alkyl derivatives. Methyl esters of fatty acids were also detected. Column 10 $^0/_0$ S.E. 30, 2 m, 5°C. Helium flow 30 ml/min.

steps yielding phenanthrenes, naphthalenes and other cyclic compounds may have resulted during the time passed since the Precambrium.

Figs 27 to 35 show the gas chromatograms and mass spectra resulting from the fractions in this sample. Fig. 27 is the gas chromatogram of alkanes separated from cyclic and the major part of the branched alkanes. Peaks 2, 4, 5, 8, 11, 14, 17, 20, 23 and 26 in the gas chromatogram correspond to the normal alkanes with C_{11}-, C_{12}-, C_{13}-, C_{14}-, C_{15}-, C_{16}-, C_{17}-, C_{18}-, C_{19}- and C_{20}-chains. Peaks 3 and 7 indicate alkylcyclohexanes, whereas all the peaks in between the normal alkanes from C_{14} to C_{20} correspond to iso- and anteisoalkanes. Fig. 28 is a gas chromatogram of the cycloalkane fraction from urea inclusion separation. Minor amounts of normal alkanes are still present in this fraction, peaks 2, 4, 5, 9, 13 and 18 correspond to normal alkanes from C_{11} to C_{16}. Alkyl

cyclohexanes are detected from most of the peaks of this gas chromatogram. Fig. 29 shows the gas chromatogram of a complex mixture of aromatic or partly hydrogenated aromatic compounds of naphthalenic and phenanthrenic structures and alkyl derivatives thereof. This mixture was subjected to further TLC-separation on silica impregnated with caffeine (BERG & LAM, 1964; LAM & BERG, 1965). An interaction between caffeine and the π-electron-rich aromatic systems results in separation of hydrocarbons depending on the number of π-electrons so that π-electron-rich substances are absorbed stronger by the thin-layer material than the substances with the partly hydrogenated structure. Fractions were isolated from two zones of a thin-layer plate which after further in-
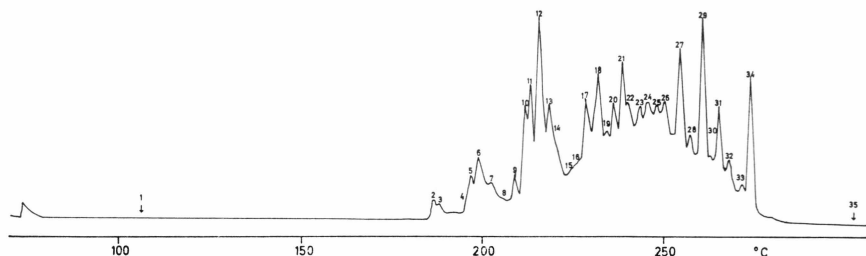

Fig. 30. GGU sample No. 93142. Gas chromatogram of a subfraction from a fraction containing naphthalenes and phenanthrenes (cf. fig. 29) showing mainly substituted naphthalenes and hydronaphthalenes. Column 10 % S.E. 30, 2 m, 5°C/min., 50–250°C. Helium flow 30 ml/min.
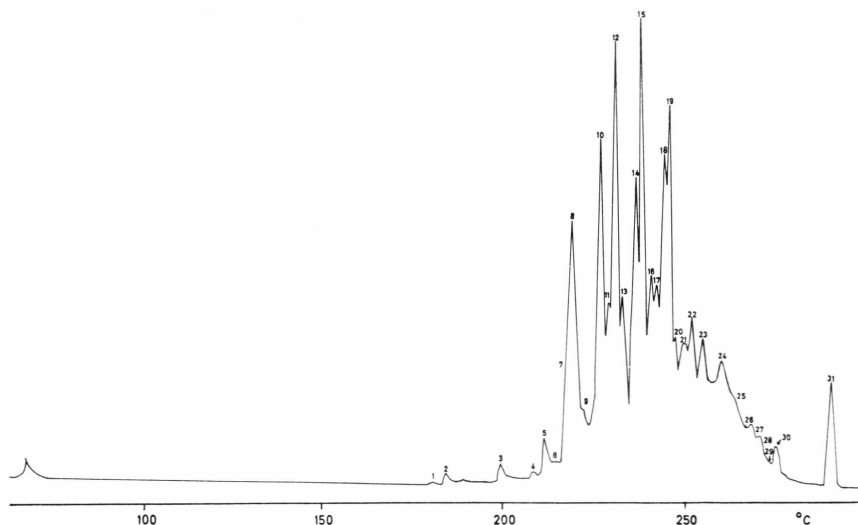

Fig. 31. GGU sample No. 93142. Gas chromatogram of a subfraction of the fraction containing naphthalenes and phenanthrenes (cf. fig. 29); mainly phenanthrenes and alkyl phenanthrenes.
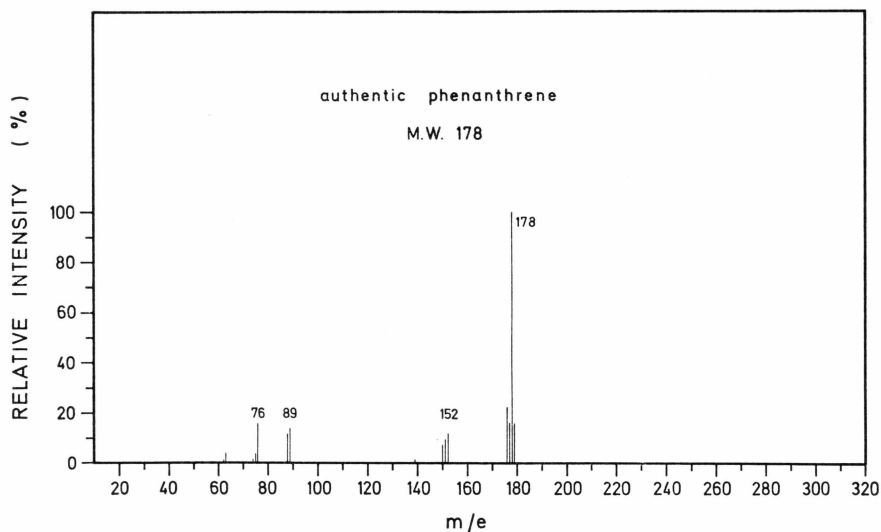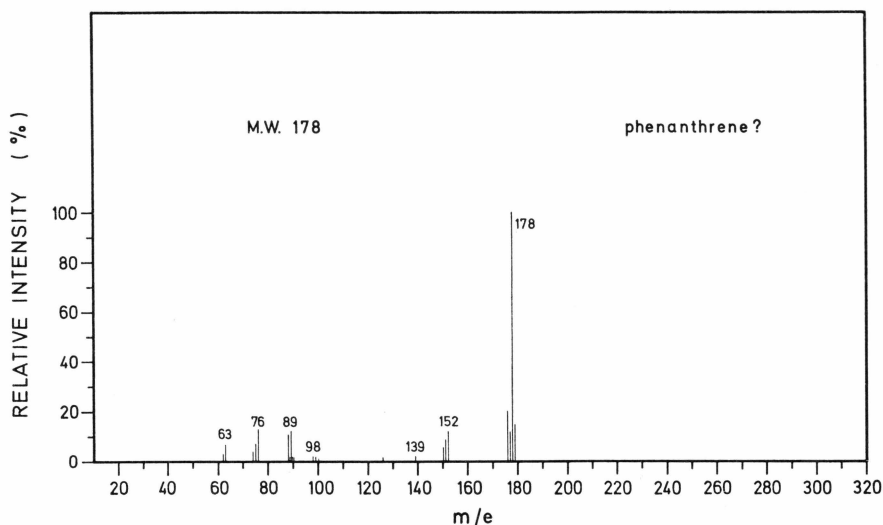
Fig. 32. Mass spectrum of authentic phenanthrene.

Fig. 33. Mass spectrum from sample No. 93142. Phenanthrene.

vestigation by means of combined gas chromatography—mass spectro-
metry revealed a large number of alkyl substituted naphthalenes and
more or less hydrogenated naphthalene and phenanthrene structures (cf.
fig. 30 showing the gas chromatogram), and a series of products mainly
representing phenanthrene, mono-, di- and trimethyl phenanthrenes. Fig.
31 is the gas chromatogram of this fraction. Fig. 32 is the mass spectrum
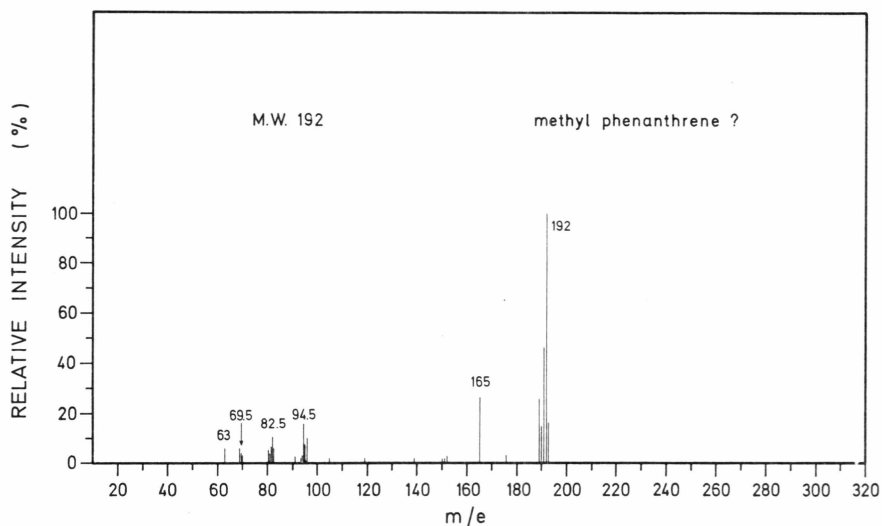of authentic phenanthrene while fig. 33 shows the mass spectrum of peak

Fig. 34. Mass spectrum from GGU sample No. 93142. An alkyl phenanthrene.
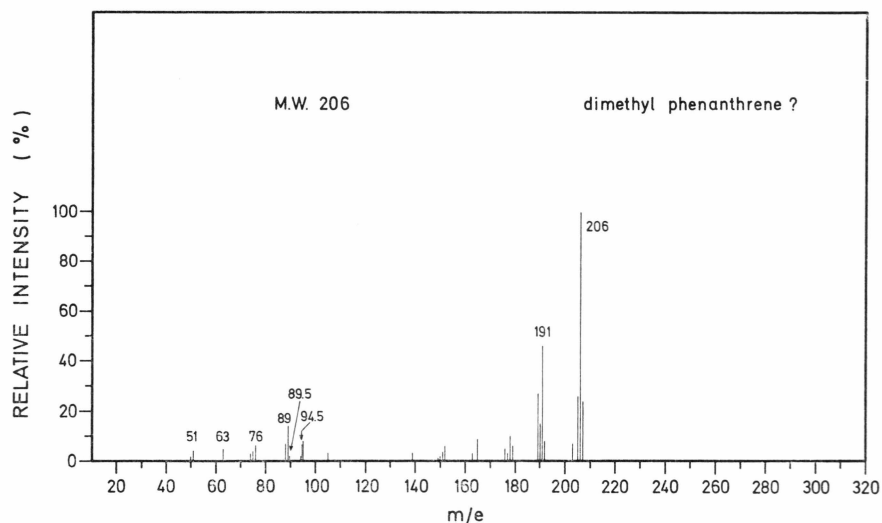
Fig. 35. Mass spectrum from GGU sample No. 93142. A dimethylphenanthrene.

8 from the gas chromatogram of fig. 31 which closely corresponds to phenanthrene, and figs 34 and 35 show mass spectra of substances which are probably identical with mono- and dimethyl phenanthrenes, in agreement with the molar peaks and fragmentation pattern for these substances. The peaks of the gas chromatogram of fig. 31 (Nos 12, 18, 19, and 22 to 24) correspond to methyl phenanthrene, two dimethyl phenanthrenes and to at least three trimethyl phenanthrenes respectively.

The investigation of the most polar fraction (the fatty acid fraction) failed, but it is believed that free fatty acids are present in this sample as there are indications of methyl esters in minor amounts, especially methyl palmitate in the aromatic hydrocarbon mixture.

Sample No. 106449

The material (8500 g) was treated in the same way as the two previous samples. The yield of an oily extract was 183 mg, and an additional 700 mg of free sulphur was isolated.

Separation on a silica column gave fractions containing normal and branched alkanes besides cycloalkanes, which could be further fractionated by the urea inclusion method. Further development on the silica column showed the presence of alkyl benzenes, alkyl naphthalenes,
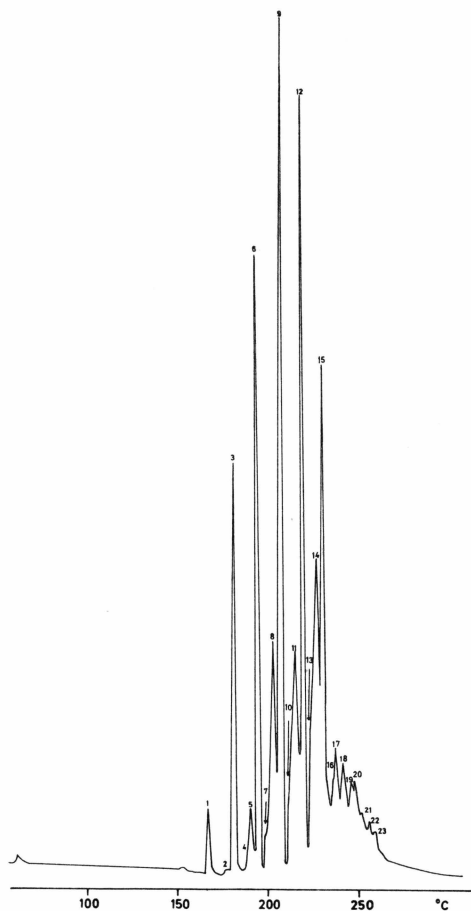

Fig. 36. GGU sample No. 106449. Gas chromatogram of fraction obtained by urea inclusion separation. Straight-chain, iso- and anteisoalkanes. Column 10 % S.E. 30, 2 m, 10°C/min., 50–250°C. Helium flow 30 ml/min.
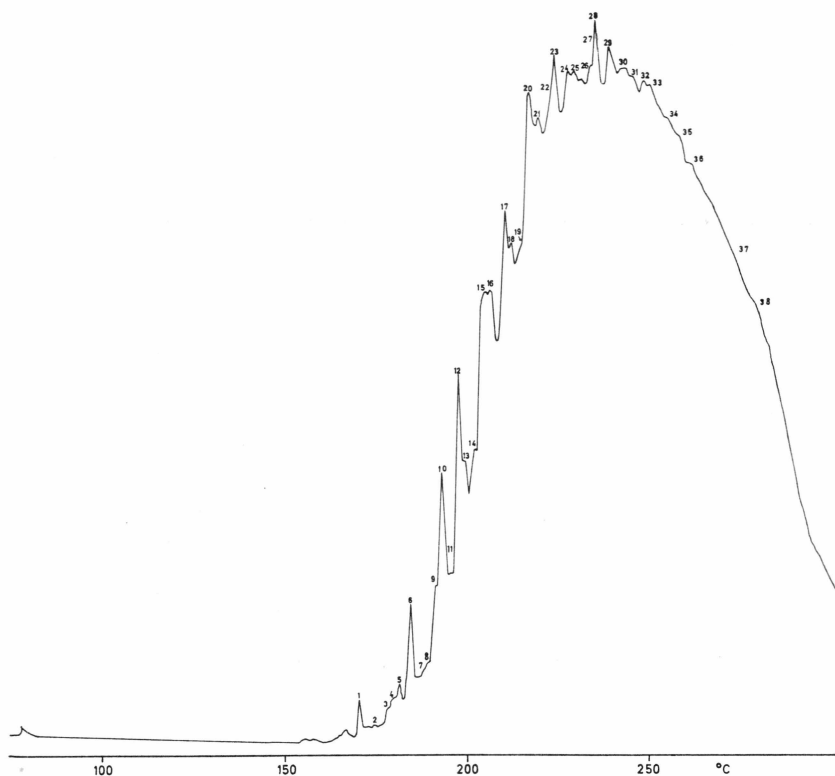
Fig. 37. GGU sample No. 106449. Gas chromatogram of fraction separated from the normal alkanes by urea inclusion. Branched and cyclic alkanes. Column 10 % S.E. 30, 2 m, 5°C/min., 50–250°C. Helium flow 30 ml/min.

methyl esters of palmitic and stearic acids, and of an α-methyl substituted acid (showing a m/e top of 88 of high intensity).

Fig. 36 shows the gas chromatogram of a fraction obtained from urea inclusion separation. Peaks 3, 6, 9, 12 and 15 correspond to the normal alkanes with 14, 15, 16, 17 and 18 C-atoms respectively. The less intense peaks in between these peaks represent iso- and anteisoalkanes which were not entirely separated from the normal alkanes. Fig. 37 is the gas chromatogram of the mixture separated from the normal alkanes included in urea. Peaks 10 and 12 contain branched and normal C_{15}-alkanes respectively; peak No. 17 contains normal C_{16}-alkane. The mass spectra of the various peaks reveal that alkyl cycloalkanes are generally present (prominently alkyl cyclohexanes with mass fragments of m/e 83, 97 + $(CH_2)n$). The gas chromatogram of the fraction shown in fig. 38 is dominated by various alkyl benzenes in a complex mixture. The most abundant alkyl benzenes present in the mixture are a group of hydrocarbons with 12 C-atoms in the side chains. In the mass spectra (fig. 39)
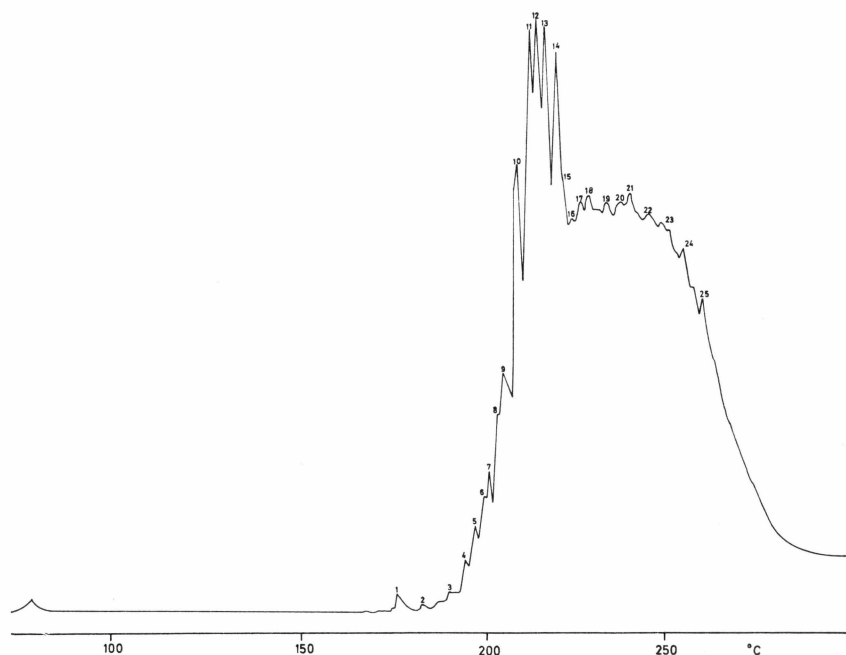
Fig. 38. GGU sample No. 106449. Gas chromatogram of alkyl benzene peaks. Nos 11–14 represent isomers with a total of 12 C-atoms in the side-chains. Column 10 %/₀ S.E. 30, 2 m, 5°C/min., 50–250°C. Helium flow 30 ml/min.
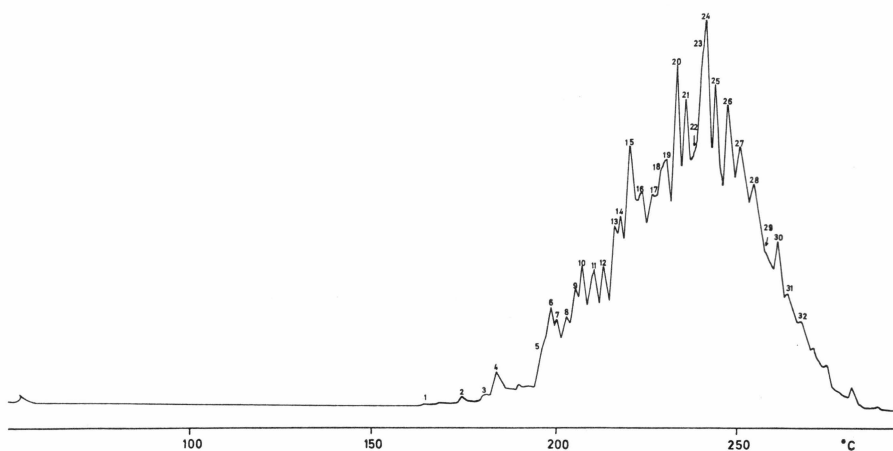

Fig. 39. GGU sample No. 106499. Gas chromatogram of a mixture containing alkyl naphthalenes, alkyl phenanthrenes and methyl esters of fatty acids. Column 10 %/₀ S.E. 30, 2 m, 5°C/min., 50–250°C. Helium flow 30 ml/min.
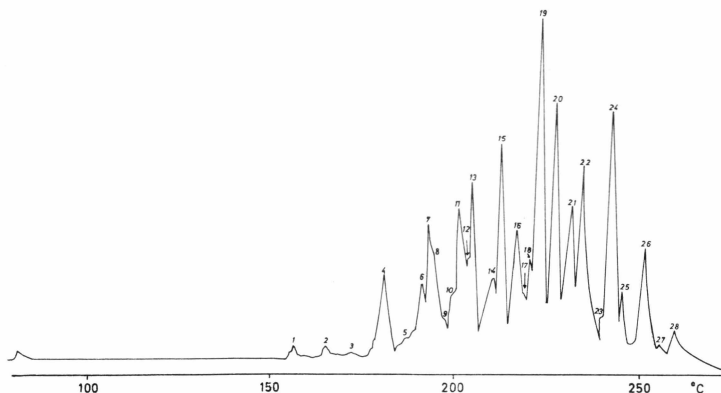
Fig. 40. GGU sample No. 106449. Gas chromatogram of free fatty acids converted to the corresponding methyl ester. Column 10 $\%$ S.E. 30, 2 m, 5°C/min. Helium flow 30 ml/min.

corresponding to the peaks of this gas chromatogram the presence of alkyl naphthalenes, alkyl phenanthrenes, alkyl di- or tetrahydro-napthalenes, and methyl esters of fatty acids has been detected. From peak 4 in the gas chromatogram a dimethyl naphthalene was detected, peak 25 contains the methyl ester of palmitic acid and a methyl phenanthrene, 27 a methyl ester of an α-methyl substituted C_{16} fatty acid and peak 30 shows traces of the methyl ester of stearic acid. Fig. 40 shows the gas chromatogram of the most polar fraction from separation on silica after conversion of the fatty acid material to the corresponding methyl ester. From peaks 4, 8, 13, 16, 20, 22 and 25 of the gas chromatogram the methyl esters of the normal fatty acids C_{12} to C_{18} were detected and from peaks 6, 11, 15, 21 and 23 methyl esters of branched C_{13}-, C_{14}-, C_{15}-, C_{17}- and C_{18}-acids were detected by means of the mass spectral data and the relative retention values. Furthermore, monounsaturated acids with 15, 16, 17, 18, and 19 C-atoms were detected by means of their fragmentation pattern in good agreement with that of methyl oleate published by HALLGREN, RYHAGE & STENHAGEN (1959). The monounsaturated methyl esters correspond to peaks 14, 19, 22, 24 and 26 respectively. Figs 41 and 42 show the mass spectra of the methyl esters of normal C_{12}- and normal C_{16}-fatty acids respectively. Fig. 43 is the mass spectrum of authentic normal C_{16}-fatty acid methyl ester (methyl palmitate) while figs 44, 45, 46, 47 and 48 show the mass spectra of methyl esters of monounsaturated C_{15}-, C_{16}-, C_{17}-, C_{18}- and C_{19}-acids. (See table 2). Fig. 49 represents the mass spectrum of authentic oleate for comparison.

Table 2. *Methyl esters of fatty acids isolated as free fatty acids and converted to the methyl esters.*

		GLC peak No.			GLC peak No.
C_{12}	(n)	4	C_{16}	(=)	19
C_{13}	(br)	6	C_{16}	(n)	20
C_{13}	(n)	8	C_{17}	(=)	22
C_{14}	(br)	11	C_{17}	(n)	22
C_{14}	(n)	13	C_{18}	(=)	24
C_{15}	(=)	14	C_{18}	(n)	25
C_{15}	(br)	15	C_{19}	(=)	26
C_{15}	(n)	16			

(n): normal
(br): branched
(=): monounsaturated

The composition of the fatty acid fraction from this sample is fairly similar to those from the Green River Shale sample of Eocene age published by LEO & PARKER (1966), who also emphasize that a relatively large representation of branched chain acids indicates a bacterial origin. Monounsaturated acids from C_{15} to C_{19} together with normal fatty acids from C_{12} to C_{18} (odd and even) yield the main pattern of the most polar fraction from the extract.

Fig. 41. Mass spectrum from GGU sample No. 106449. (See text for explanation).

3*

Fig. 42. Mass spectrum from GGU sample No. 106449. (See text for explanation).

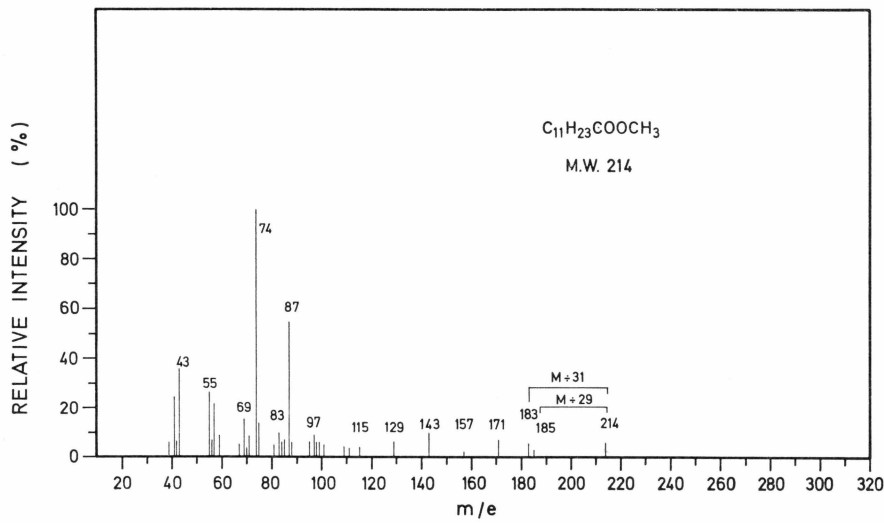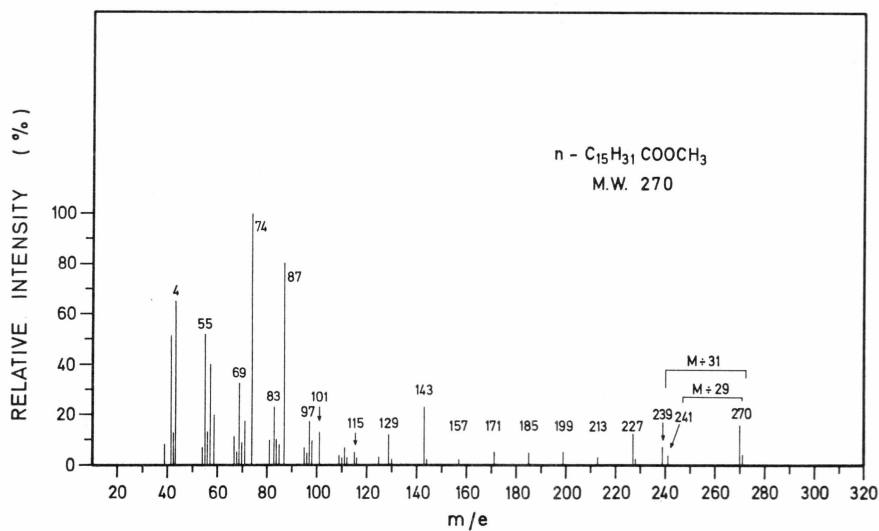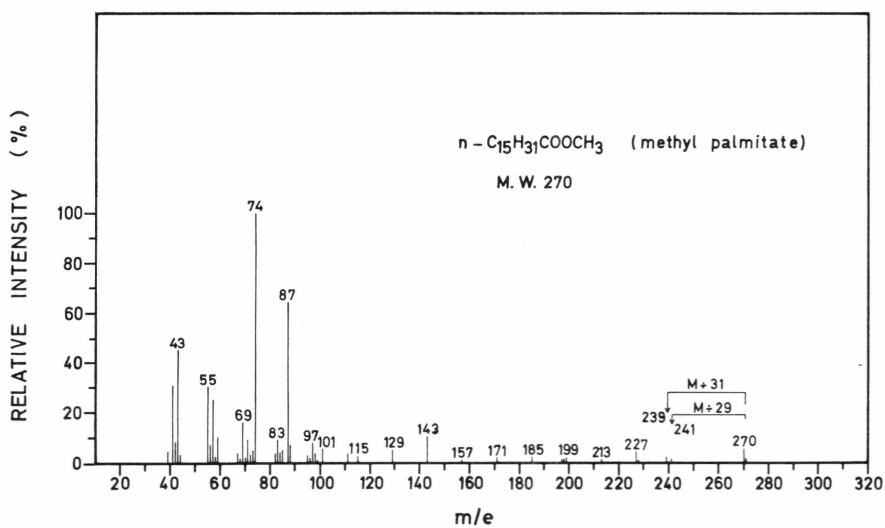Fig. 43. Mass spectrum from authentic methyl palmitate.

Fig. 44. Mass spectrum from GGU sample No. 106449. (See text for explanation).
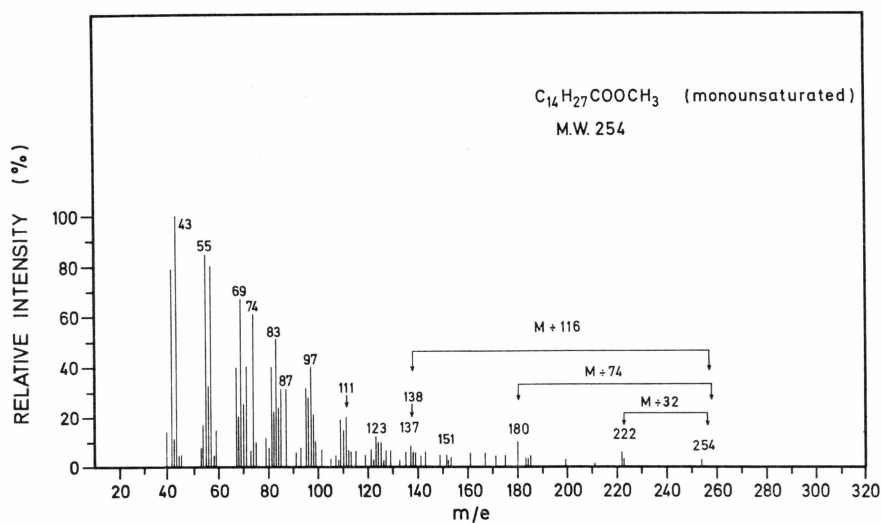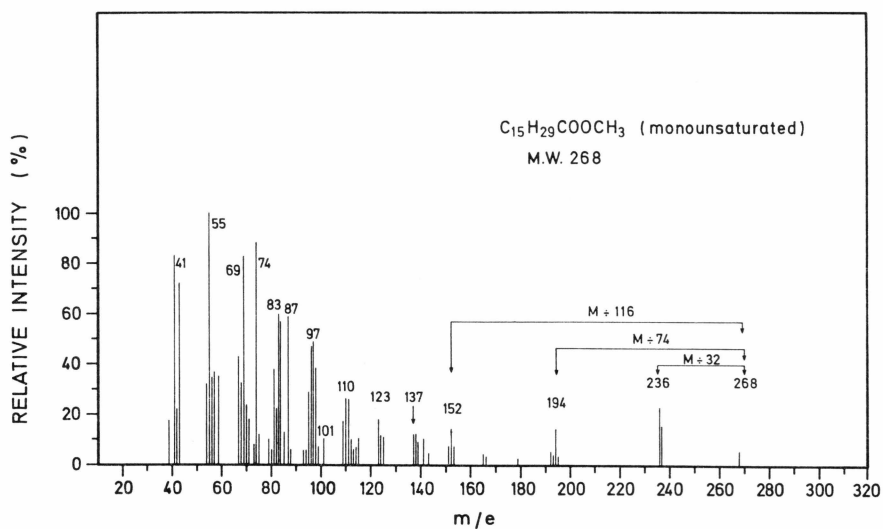

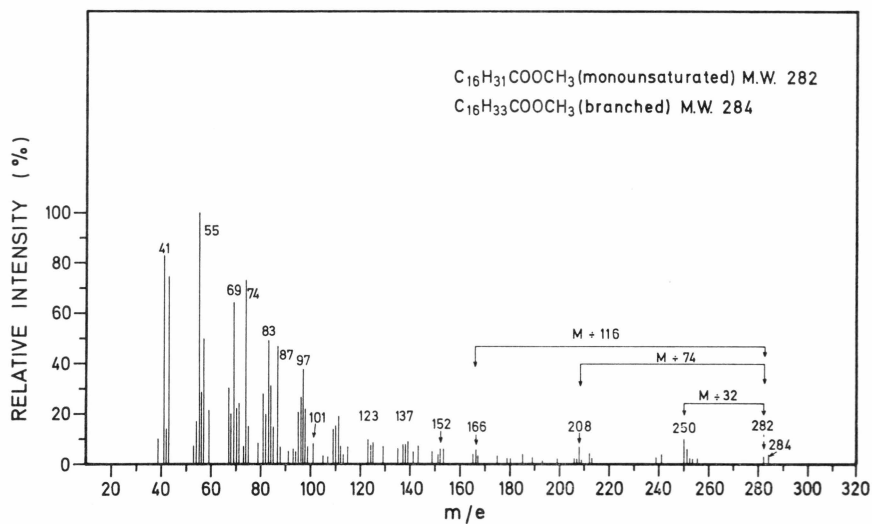Fig. 45. Mass spectrum from GGU sample No. 106449. (See text for explanation).

Fig. 46. Mass spectrum from GGU sample No. 106449. (See text for explanation).
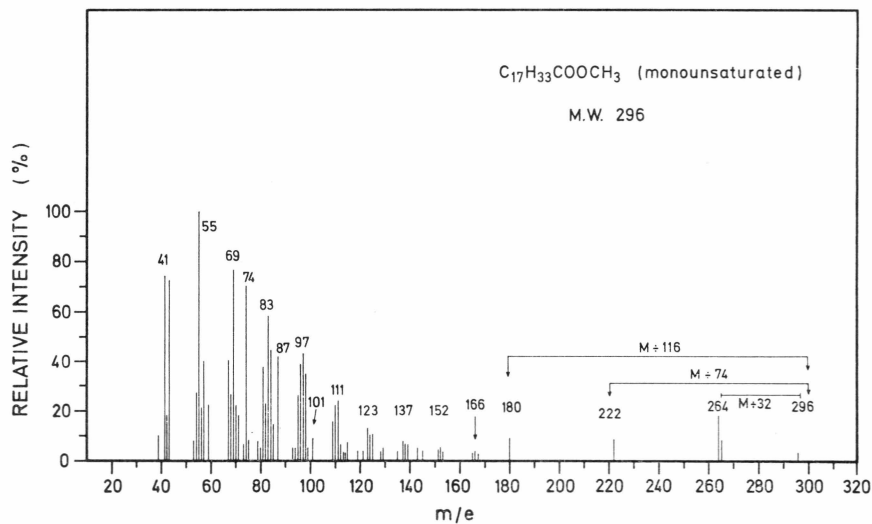

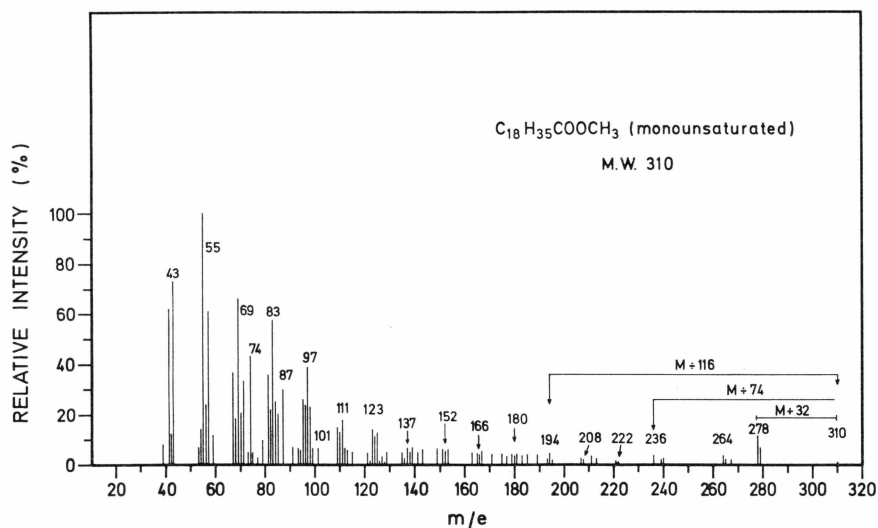Fig. 47. Mass spectrum from GGU sample No. 106449. (See text for explanation).

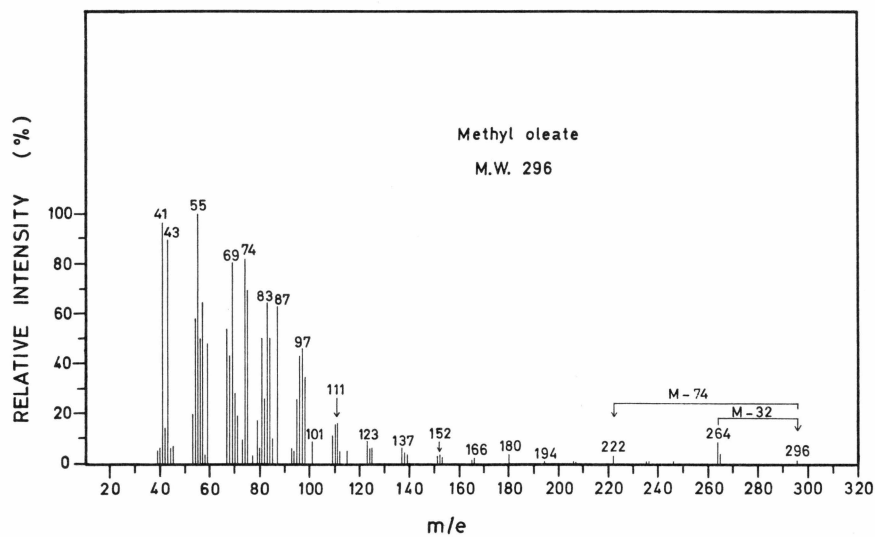Fig. 48. Mass spectrum from GGU sample No. 106449. (See text for explanation).

Fig. 49. Mass spectrum from authentic methyloleate.

COMPARISONS

Most of the samples so far examined are from various parts of the 4000 m thick series of supracrustal rocks of the Ketilidian of Grænseland (see table 1). Their relative age is as shown in table 3 which summarizes all the results so far obtained. A rock series of about 2000 m separates the oldest and the youngest sample, but no data are available relating to the real age difference. The graphite sample listed in table 3 is from the Agto area in West Greenland with metamorphic rocks of amphibolite facies.

From table 3 it is seen that the dolomitic samples yield almost the same total amount of extracts (15 to 17 mg per 1000 g) and that the slightly metamorphosed coal–graphite samples yield about three times as much extract (42 to 48 mg per 1000 g) whereas the strongly metamorphosed graphite sample gave only 22 mg of extract per 1000 g.

The aliphatic material is similar from all the samples with the normal C_{14}–C_{18} hydrocarbons most abundant except in the dolomitic sample No. 70680. The branched hydrocarbons are represented by iso- and anteisoalkanes and probably the isoprenoid hydrocarbons pristane and phytane are also present, although these hydrocarbons, frequently reported in geological material, do not form any great part of the aliphatic hydrocarbon content. Cyclic hydrocarbons with alkyl side chains are present in all the samples examined.

Aromatic hydrocarbons as alkyl benzenes, alkyl naphthalenes, and alkyl phenanthrenes were found in all the samples, but the dolomite with *Vallenia* (No. 52970), which was one of the primarily investigated samples, was the one where the analytical technique may have failed.

The two slightly metamorphosed coal–graphite samples 70634–3 and 70634–5, and a series of other coal–graphite samples examined (unpublished data), reveal the presence of monoterpenoid substances as camphor, borneol, and various other monoterpenols, whereas only one examined dolomite sample (No. 70680) shows the presence of mono-terpenols (and monoterpene hydrocarbons) of which one seems to be borneol, but camphor could not be detected in this sample.

Table 3. *Organic compounds from extracts of various rocks from the Precambrian of Greenland.*

rock type	GGU sample No.		dolo-mitic	car-bon con-tent	meta-morphic facies	extracted material mg per kg	Predominating homologous series of organic substances			
							alkanes	aromatic hydro-carbons	monoter-penoids	fatty acids
Dolomite, grey	70680	Rendesten Formation	×	1	greenschist	16	b c d	e f g	h	
Coal–graphite	70634–3	Foselv Formation		3	greenschist	48	a b c	e f g	h	i j
Coal–graphite	70634–5	Foselv Formation		3	greenschist	42	a b c	e f g	h	i j
Coal–graphite	20911–1	Foselv Formation		3	greenschist	k	a b c	e f g	h	i j
Dolomite with *Vallenia* .	69747–5	Grænsesø Formation	×	2	greenschist	15	a b c			i (traces)
Dolomite with *Vallenia* .	52970	Grænsesø Formation	×	2	greenschist	k	a¹ b c	e f g		i
Dolomite, black	93142	Zigzagland Formation	×	1	greenschist	17	a b c	e f g		
Graphite.............	106449			3	amphibolite	22	a² b c	e f g		i j

Sample No. 20911–1 (PEDERSEN & LAM, 1968)
Sample Nos 69747–5 and 52970 (LAM & PEDERSEN, 1968)
Sample Nos 70634–3 and 70634–5 (PEDERSEN & LAM, 1970)
Sample Nos 70680, 93142, and 106449 (this report).

Carbon content:
  1 no visible macroscopic carbonaceous material.
  2 with smaller grains of carbonaceous material.
  3 with greater amount of carbonaceous material.

a normal alkanes C_{11}–C_{20}
a¹ normal alkanes C_{10}–C_{32}
a² normal alkanes C_{14}–C_{18}
b branched alkanes (including iso-and anteisoalkanes)
c alkyl cycloalkanes
d monoterpene hydrocarbons
e alkyl benzenes
f alkyl naphthalenes

g alkyl phenanthrenes
h monoterpenoids (oxygen containing compounds)
i fatty acids or methyl esters of fatty acids
j unsaturated fatty acids
k recording of amounts omitted because of phthalate contamination.

Methyl esters of fatty acids and free fatty acids have been detected by their polarity and by their spectra after conversion to the corresponding methyl esters.

Monounsaturated fatty acids have been detected in the coal–graphite and graphite samples, whereas fatty acids with more than one double bond have not been revealed. The fatty acid chain lengths are of the order of magnitude from C_{12} to C_{18} with the C_{16} acids predominant. Branched acids and acids with an odd number of carbon atoms are also present. The monounsaturated acids are also within this size range and the C_{16} and C_{18} acids dominate this group.

The various samples show compounds which have not been sufficiently well determined for precise identification although there are indications of dibenzothiophenes, aliphatic alcohols and ketones other than those with a monoterpenoid structure. In the primarily examined samples di-alkyl phthalates (especially di-n-butyl phthalate) caused a good deal of trouble. Since contamination has been carefully avoided only trace amounts of phthalates have been seen.

CONCLUSION

Organic compounds from the Ketilidian have been found in graphitic and dolomitic rocks of different types (dark dolomites, dolomite with *Vallenia* and dolomitic shale). These sediments were deposited under different conditions and the conditions for biological activity must have been rather variable.

The presence of monoterpenoid structures detected preferentially in coal–graphite samples, and the detection of phenanthrene, naphthalene and their alkyl derivatives in all the samples indicate a biological origin. Furthermore, there are indications of more or less saturated phenanthrenic and naphthalenic structures which, besides alkyl cyclohexanes, alkyl benzenes, iso- and anteisoalkanes point to the same conclusion. The high sulphur contents often present in the samples may be responsible for the dehydrogenation of products derived from higher terpenoid structures (e.g. triterpenes and diterpenes).

The fatty acids present in various samples are mainly identical with the fatty acids present in recent plant material although the relative amounts of odd numbered acids seem to be more abundant in the old material than it is at the present day.

Monounsaturated acids are often seen, but neither aliphatic acids nor esters containing more than one double bond have ever been identified. Esters of fatty acids with an intensive fragmentation peak at 88 m/e indicate an α-methyl substitution; this again may be an indication of a biological formation.

The graphitic samples are characteristic in their relatively high yield of organic material, mostly saturated hydrocarbons. The mono-terpenoid compounds detected in polar fractions are oxygen-containing substances such as borneol and camphor. In the strongly metamorphosed graphite No. 106449 there were no signs of monoterpenoids, whereas the grey dolomite No. 70680 contains monoterpenoids. Camphor could not be detected in this material, and it differs in its lack of normal alkanes, while aliphatic branched-cyclic alkanes are dominant. It should be emphasized that the dolomite No. 70680 differs both geologically and

chemically from the other dolomites investigated, and may have formed under different conditions.

The different types of sediments from which organic compounds and fossils have been described seem to show that about 2000 m.y. ago in West Greenland there were variations in the accumulation of organic material perhaps depending on the rate of production of organic material and/or depositional conditions. There was possibly also a difference in the biological activities, perhaps with different types of organisms, depending upon the local external conditions.

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