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PRECAMBRIAN ORGANIC COMPOUNDS FROM THE KETILIDIAN OF SOUTH-WEST GREENLAND

Part I

BY

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WITH 8 FIGURES IN THE TEXT

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Abstract

Well preserved Ketilidian sedimentary rocks from South-West Greenland, about 2000 million years old and containing macroscopic and microscopic fossils, have been examined for organic material.

The results of the work on the extractions from a coal-graphite layer are presented together with a short description of the local geology around this layer.

Straight chain and branched paraffins, mono-, di-, or polycyclic aromatic hydrocarbons, borneol, camphor and other monoterpenoid compounds, fatty acids and methyl esters of fatty acids are present in samples from the coal-graphite layer, together with other organic substances as yet unidentified. Pristane, phytane and other isoprenoid hydrocarbons have been found in small amounts. The presence of these organic compounds indicates a biological origin of the coal-graphite layer.

Besides the coal-graphite other sediments (dolomites and quartzites) from the succession have yielded organic material. Further work on these samples and on the coal-graphite is in progress.

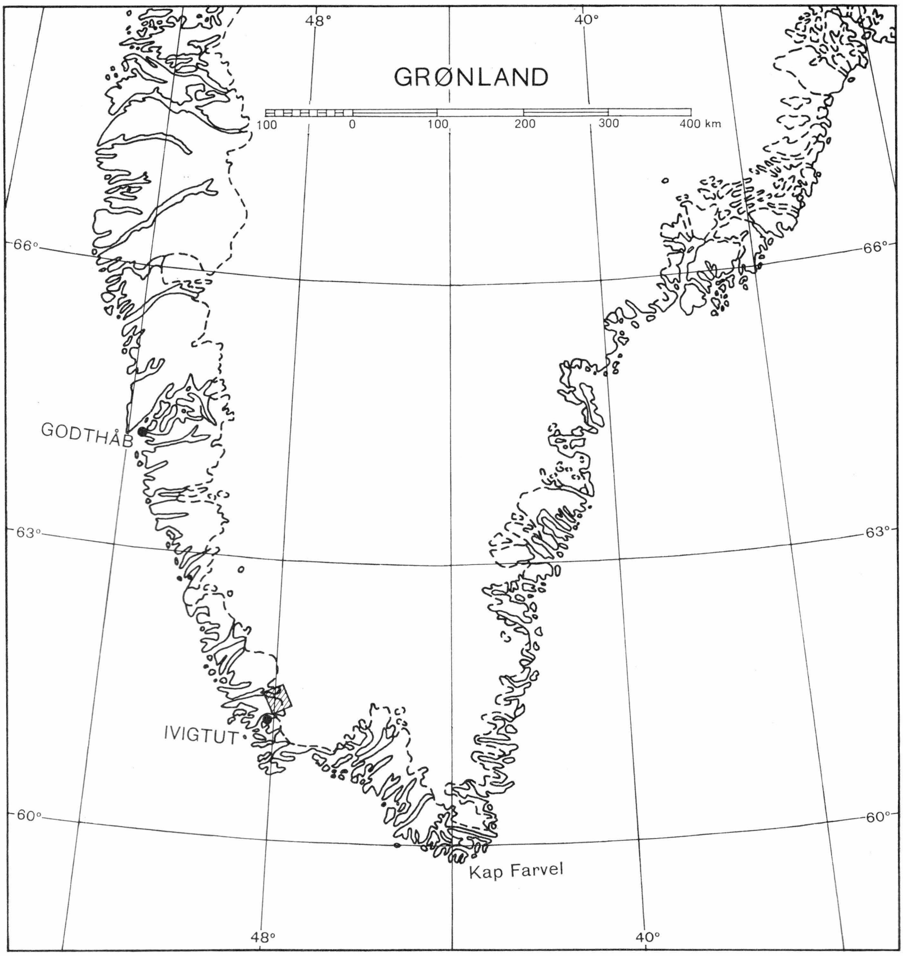

Fig. 1. Map showing the position of the Grænseland area in SW Greenland.

INTRODUCTION

The examinations described in this work have been carried out in the Geological Institute, University of Aarhus, by K. RAUNSGAARD PEDERSEN and in the Chemical Institute, University of Aarhus, by JØRGEN LAM.

During the last two years a few publications have appeared which have presented information about finds of various organic compounds in Precambrian sediments of different ages (MEINSCHEIN 1965; BARGHOORN and TYLER 1965; BARGHOORN *et al.* 1965; ORÓ *et al.* 1965; EGLINTON 1966; EGLINTON *et al.* 1966; JOHNS *et al.* 1966).

The organic material described in this paper is found in rocks from the Ketilidian fold belt of South-West Greenland. Most of the Ketilidian rocks are strongly recrystallized and metamorphosed, but when the Geological Survey of Greenland (Grønlands Geologiske Undersøgelse) mapped the Ivigtut region (see fig. 1) an area with only slightly metamorphosed Ketilidian sediments and volcanics was found north-east of Ivigtut. This area, named Grænseland, is situated between Arsuk Fjord and Sermiligârssuk Fjord and borders the Indland Ice (see fig. 2). The low-metamorphic succession of Grænseland represents the geosynclinal deposits of the Ketilidian fold belt (Bondesen in prep.).

The age of the Ketilidian fold belt is estimated to be 1700–2000 m.y. (Bridgwater 1965).

In the sediments of Grænseland several types of macroscopic and microscopic fossils are found (Bondesen *et al.* 1967, Pedersen 1966 and 1967).

Samples of sediments in which fossils occur have been examined for organic matter. These and other sediments, e.g. coal-graphites, dolomites and quartzites, have yielded small amounts of organic compounds. The greatest amount of organic material has been obtained from a coal-graphite. In this paper some of the results of the work on the extracts from the coal-graphite are presented. The results of the work on organic compounds from other types of sediments will soon be published.

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GEOLOGY OF THE AREA

The geology of Grænseland has been investigated by E. BONDESEN (BONDESEN *et al.* 1967, BONDESEN in prep.). The Ketilidian metamorphic rocks are divided into a lower sedimentary group and an upper mainly volcanic group (see fig. 2).

The lower group, named the Vallen Group, is up to 1700 m thick and shows a variety of sediments. The Zig Zag Land Formation, which includes the Ketilidian basal conglomerate unconformably overlying the gneissic basement (HIGGINS and BONDESEN 1966), is characterized by quartzites and dolomitic shales. The overlying Blåis Formation begins with black pelites and is dominated by graded greywackes. The uppermost formation in the Vallen Group, the Grænsesø Formation, shows a mixed sequence of black pelites, dolomites and quartzites.

In the Vallen Group some organic structures have been found. Microscopic fossil structures are found scattered throughout the sediments, and macroscopic fossils are found in the lower part of Zig Zag Land Formation and in the uppermost part of Grænsesø Formation (PEDERSEN 1967).

Organic compounds have been shown to be present in many types of sediments from this group, especially in the sediments with fossils.

The upper group consists of volcanics and subordinate sediments. The group is more than 2500 m thick and is named the Sortis Group. The Foselv Formation, lying on the Grænsesø Formation, is made up of pillow lavas. This pillow lava formation includes a layer of coal-graphite or graphitic shale. Above the pillow lavas follows the Rendesten Formation with pyroclastics interbedded with greywackes and pelites.

The coal-graphite layer from which the organic compounds described in this paper are derived, is situated in the Foselv Formation, Sortis Group. The formation is separated into the Lower and the Upper Pillow Member by this layer of coal-graphite and graphitic shale which seems everywhere to be in the same stratigraphical position in the pillow lavas. As shown by the map (fig. 2) the layer has been traced for about 4 km in the area north of Vallen. The thickness of the coal-graphite layer varies around 1 m but locally it is about 3 m thick. In places it is disturbed by dykes and faults; against the dykes it is locally strongly graphitized.

Analyses and heating values of the coal-graphite have been published by BONDESEN *et al.* (1967). The combustible content varies between 72.5 and 89.8$^0/_0$ and the heating values (water and ash free) are from 7536 to 7671 K-cal/kg.

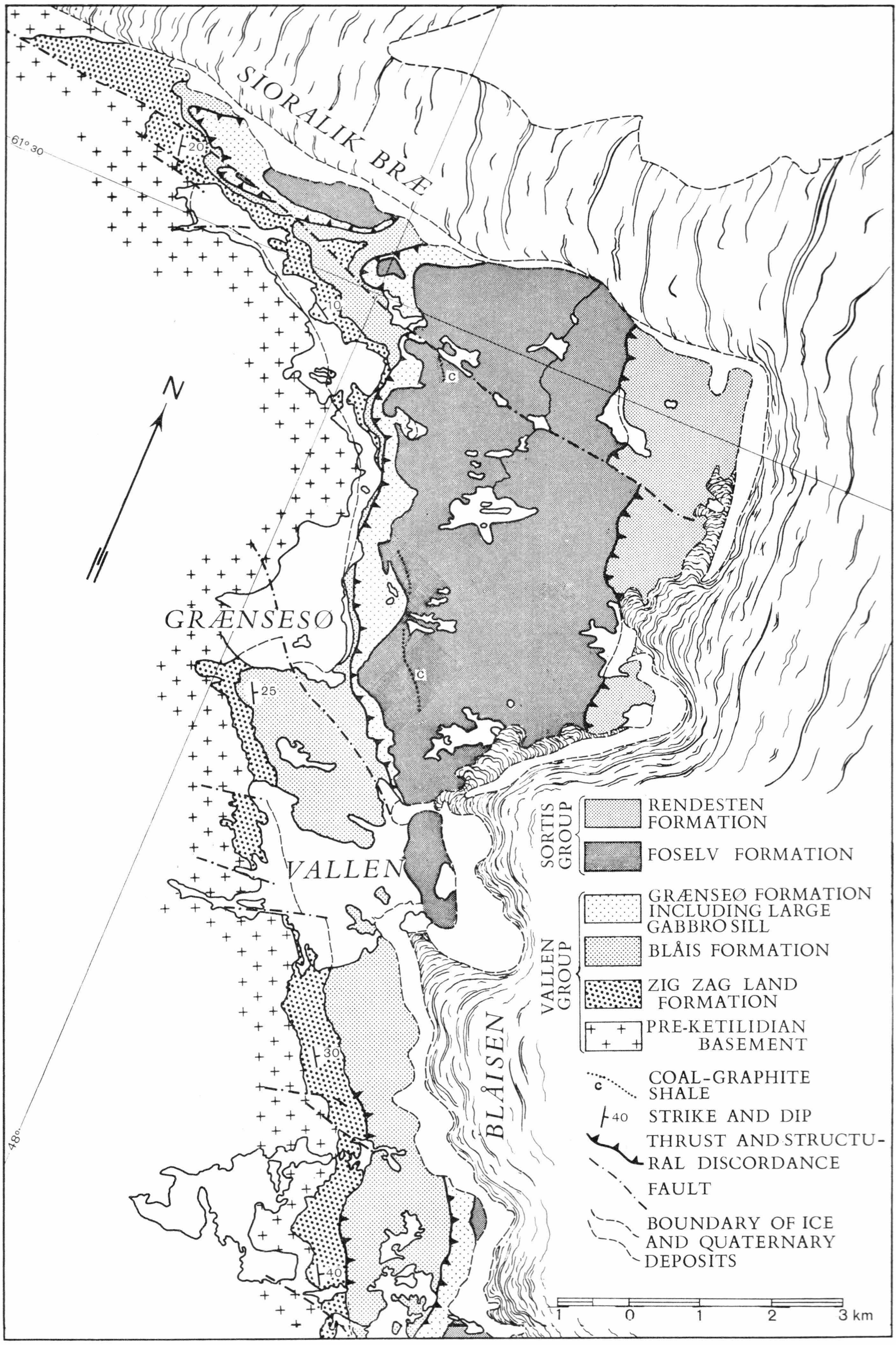

Fig. 2. Grænseland.

In the coal-graphite many types of microscopic fossil structures have been detected.

Determinations of the carbon isotope composition C^{13}/C^{12} of the coal-graphite show δ C^{13} values from –32.6 per mill. to –32.1 per mill. (BONDESEN *et al.* 1967). This value, together with the microscopic fossil structures, indicates a biological origin for the coal-graphite.

The chemical investigations, which are described in the next section, provide further evidence of advanced biological activity of the time of sedimentation.

There are no clear indications either in the coal-graphite layer or in the pillow lavas below and above, of the sedimentary conditions under which the organic material was laid down. But the variation in thickness together with the absence of the layer in some areas could be the result of deposition in small basins.

The metre-thick coal-graphite layer may represent an originally rather thick deposit and the δ C^{13} values suggest sedimentation of the organic material under extreme reducing conditions.

PRECAUTIONS AGAINST CONTAMINATION

The extraction equipment is an all-glass apparatus, and so is the evaporation equipment. Plastic and rubber tubes have been totally avoided. For extraction benzene and methanol ("Merck" analytical grade) only have been used and the residues from 500 ml of each of the solvents used have been analysed by gas-liquid chromatography and mass spectrometry for control. Small amounts (a few millilitres) of pure distilled light petroleum (b.p. below 50° C) and ether were used in order to dissolve and transfer the extracts to the column for separation. The analytically pure benzene examined contains small amounts of alkylbenzenes but not enough to be responsible for the total amount of alkylbenzenes in the carbonaceous samples. The methanol does not contain any organic material that might disturb the investigations.

EXTRACTION AND ANALYTICAL METHODS

The extracted organic compounds were obtained from a coal-graphite sample (GGU sample no. 20911–1). The outer part of the sample was cut off and discarded and the sample was then rinsed with extraction liquid (a 3:1 by volume mixture of benzene and methanol). After drying, the sample was crushed down in a mortar to pass through a 230 mesh.

132 g of the pulverized material was extracted three times with 600 ml of the above-mentioned mixture of benzene and methanol. The extraction temperature was about 40° C and the extraction time for each procedure was usually 5 days. The extracts were gathered and evaporated under mild conditions in order to reduce loss of low-boiling hydrocarbons (water-pump vacuum at a temperature of about 40° C). The residue was about 90 mg of oil.

The infrared spectrum of the complex mixture did not show very much, except indicate the presence of ester carbonyl, while the gas-liquid chromatogram reveals that many compounds are present in the mixture. When to this mixture was added a mixture of a standard solution of normal alkanes containing 10, 12, 14, 16, 18 and 20 carbon atoms respectively, it became evident from gas-liquid chromatograms that all these alkanes were also present in the sample. However there was another compound present in some abundance which showed a peak where normal undecane would be expected to be found in a gas chromatogram.

For the preliminary studies an F. & M. gas chromatograph equipped with an 0.5 m 15 per cent S.E. 30 column was used. Usually about 3 μl was injected into the instrument and programmed at 11° C per min. from 75° C to 250° C.

Most of the sample (70 mg) was dissolved in one millilitre of light petroleum and transferred to a small silica gel column. The column was about 2 cm high and had a diameter of 0.55 cm; in the bottom was placed a glasswool stopper rinsed with light petroleum. The elution was carried out by adding a further ml of light petroleum (fraction I). Fraction II was prepared by elution with 1 ml of a mixture containing 10 per cent of ether in light petroleum. The column was then eluted with 4 ml of ether (fraction III). After evaporation fraction I gave 28 mg of a colourless oil. Fraction II (3 mg) was also colourless and smelt like naphthalene, and fraction III gave 20 mg of a yellow "oil", which partly solidified. From the gas-liquid chromatograms of the three fractions it was evident that many compounds were present in various amounts in each of the fractions.

In order to do further analytical investigation 0.5 μl of the fractions were injected into a Perkin-Elmer 880 gas chromatograph equipped with a 2 m 10 per cent S.E. 30-Gaschrom Z column (helium flow) and connected with a Hitachi-Perkin-Elmer RMU–6 D mass spectrometer; mass range 600; ionizing voltage 70 eV; ion source temperature 250° C; gas inlet.

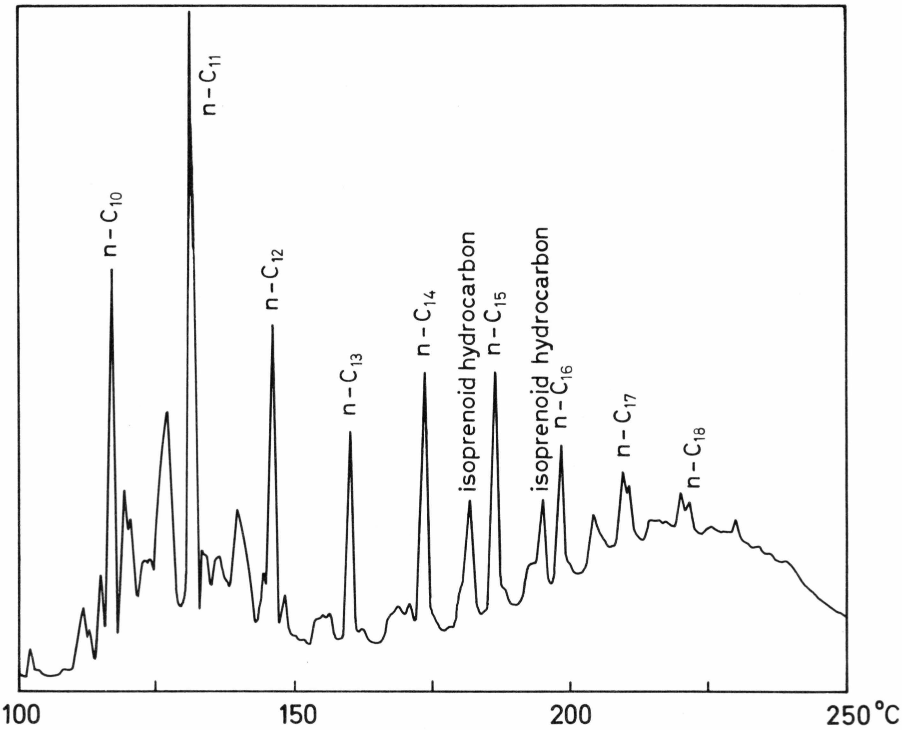

Fig. 3. Gas chromatogram of fraction I (aliphatic hydrocarbons) — 0.5 μl. Column, 10 per cent S.E. 30, 2 m. Temp. programming 5°C/min. 75–250°C. Helium flow 30 ml/min.

RESULTS

Fraction I consists mainly of normal and branched hydrocarbons with from 10 to 20 carbon atoms (even and odd numbered) besides some alkyl-benzenes. The normal alkanes in this range are easily determined by gas chromatograms and the corresponding mass spectra. The normal undecane is especially abundant in the gas chromatogram (see fig. 3).

Fraction II contains alkyl-benzenes with from two to four substituents, indene, diphenyl, napthalene, monoalkyl naphthalenes α-methyl-, β-methyl-, ethyl- and di- or higher substituted naphthalenes as well as phenanthrene (see fig. 4). An artificial mixture of cymene, indene, 1, 2, 4, 5,—tetramethylbenzene, naphthalene, α-methylnaphthalene, β-methylnaphthalene, diphenyl, dihydrophenanthrene and phenenthrene was examined by means of gas chromatography and mass spectrometry and the agreement with the extracted organic material is very good (compare figs. 4 and 5).

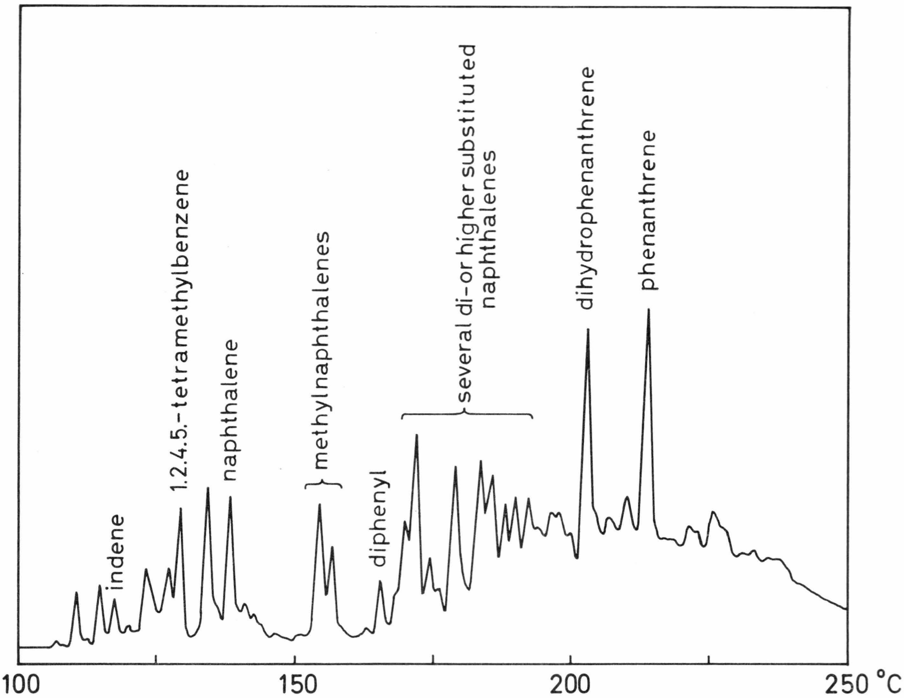

Fig. 4. Gas chromatogram of fraction II (aromatic hydrocarbons) — 1 μl. Column, 10 per cent S.E. 30, 2 m. 5°C/min. 75–250°C. Helium flow 30 ml/min.

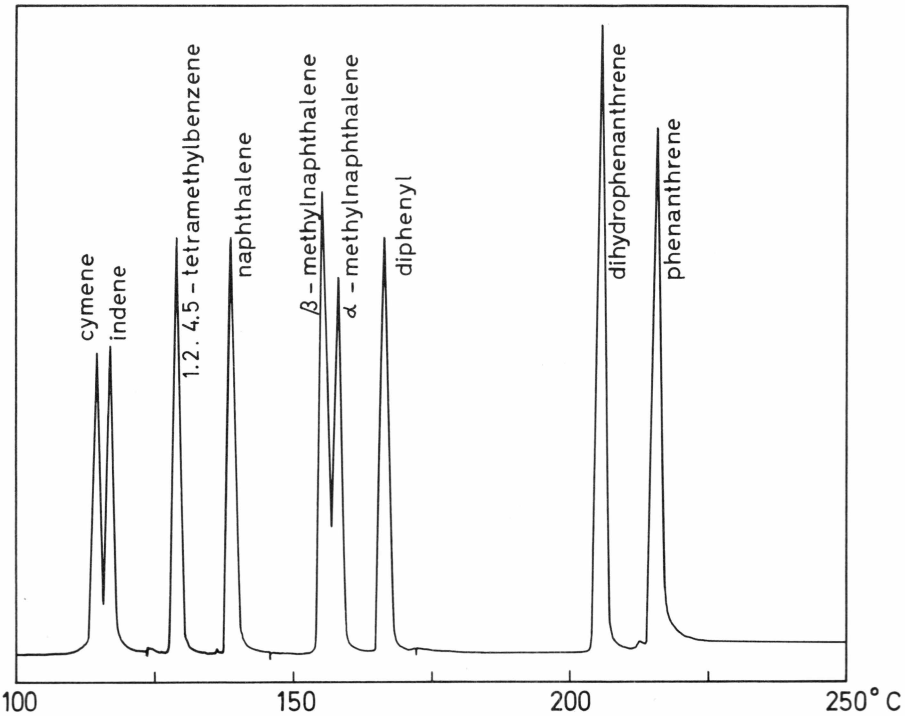

Fig. 5. Gas chromatogram of an artificial mixture of aromatic hydrocarbons (see p. 11).

The most interesting substances from fraction III are the monoterpenols of which at least borneol and four others are present (see fig. 6).

The mass spectrum of the borneol was checked against the spectrum for authentic borneol (see figs. 6 and 7). Camphor was also detected and its spectrum was found to be consistent with that of the authentic compound (see figs. 6 and 8). Mass spectral data for borneol and camphor, based on an examination of recent plant material, have been published by von Sydow (1963, 1964). Mass spectra corresponding to various peaks in the gas-liquid chromatogram show high peaks at 60 m/e, 74 m/e and 87 m/e indicating the presence of fatty acids and methyl esters of fatty acids.

The mass spectra of pristane and phytane were developed in order to inspect the normal heptadecane peak and the normal octadecane peak of the gas chromatogram (fig. 3) for the presence of the branched hydrocarbons in question. Pristane and phytane are present but they are no more dominant than other branched (terpenoid) alkanes. The synthetic phytane was prepared according to a method developed by N. A. Sørensen (Sørensen and Sørensen 1949).

Two other carbonaceous samples reveal great amounts of sulphur but only small amounts of oily matter. A preliminary study of two non-

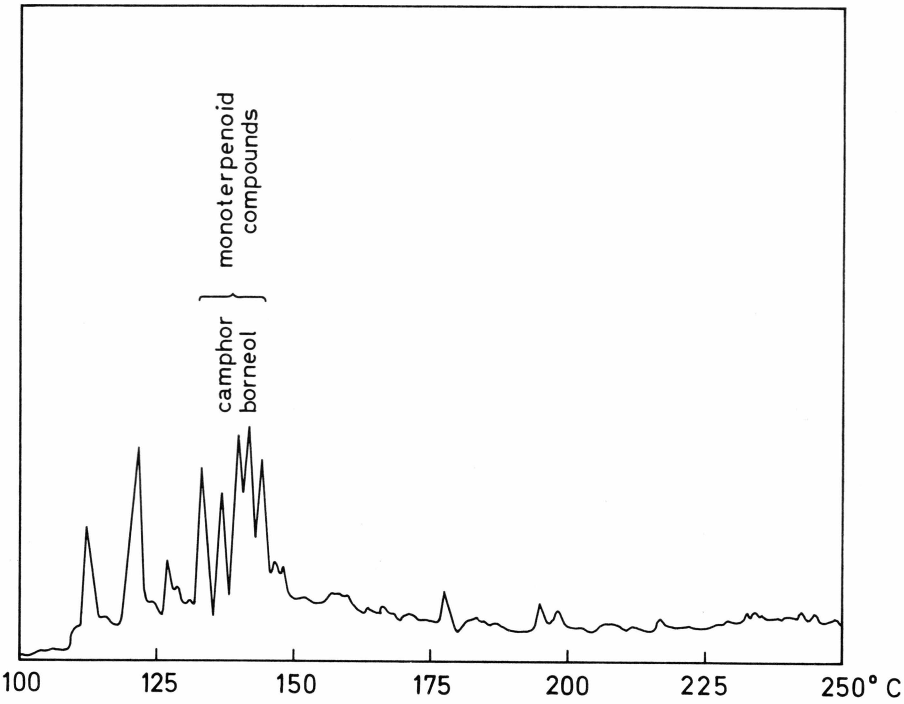

Fig. 6. Gas chromatogram of fraction III (monoterpenols etc.) — 0.5 μl. Column, 10 per cent S.E. 30, 2 m. 5°C/min. 75–250°C. Helium flow 30 ml/min.

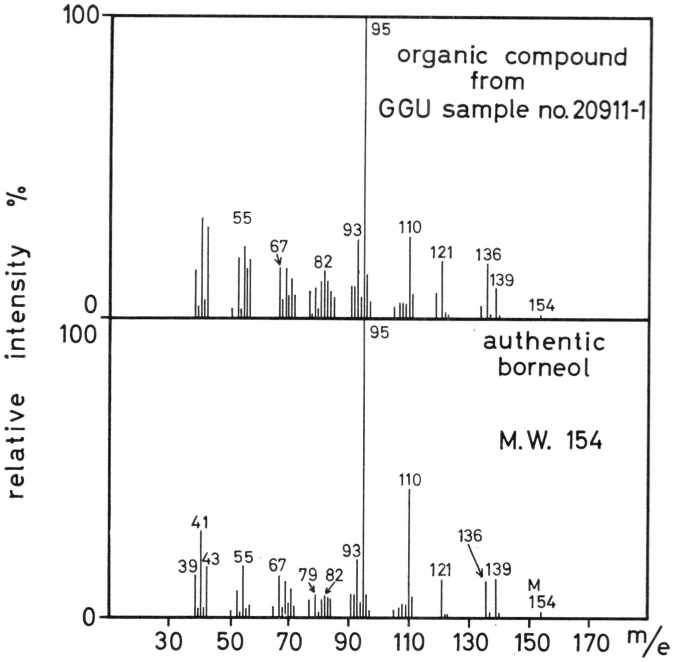

Fig. 7. Mass spectrum of organic compound from GGU sample no. 20911–1 and authentic borneol.

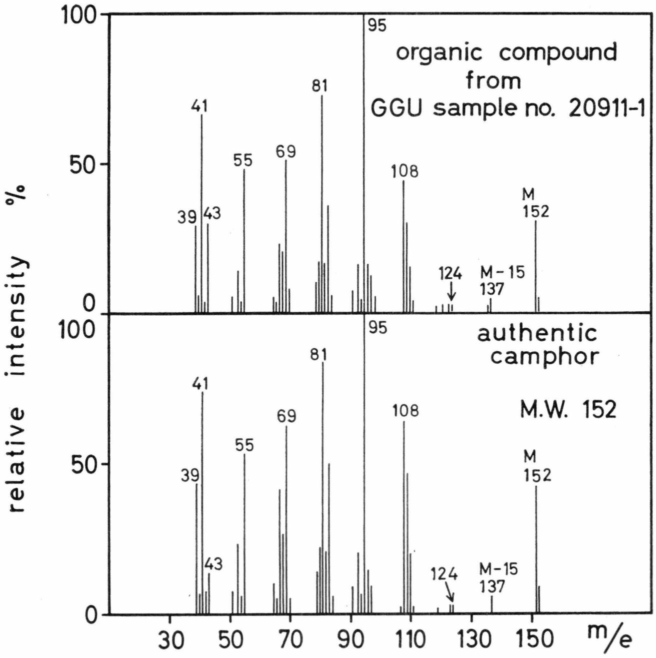

Fig. 8. Mass spectrum of organic compound from GGU sample no. 20911–1 and authentic camphor.

carbonaceous dolomitic samples has been carried out. It should be emphasized that the number of C-atoms in the alkanes which could be detected in the carbonaceous material investigated is not more than 18–20, whereas in the non-carbonaceous samples alkanes with 18–20 carbon atoms are the most abundant and some with up to 32 carbon atoms are present. In both cases even and odd numbered n-alkanes show a smooth distribution, a fact observed by many authors (e.g. EGLINTON 1966 and BLUMER 1965). Besides the n-alkanes various amounts of branched alkanes were detected by the mass spectra. Many of the substances from all three fractions determined by the mass spectra have been verified in the gas chromatogram by means of comparison with reference compounds.

CONCLUSION

The chemical examination of the coal-graphite has shown that monoterpenoid compounds, normal paraffins and branched paraffins (e.g. pristane, phytane) and methyl esters are present. All these compounds indicate an advanced biological activity and the metre-thick coal-graphite layer in the Ketilidian sediments must be the result of a large scale accumulation of organic material 1800–2000 m.y. ago.

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