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PRECAMBRIAN ORGANIC COMPOUNDS FROM THE KETILIDIAN OF SOUTH-WEST GREENLAND

PARTS I & II

BY

K. RAUNSGAARD PEDERSEN
AND
JØRGEN LAM

WITH 8 FIGURES IN THE TEXT

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CONTENTS

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.

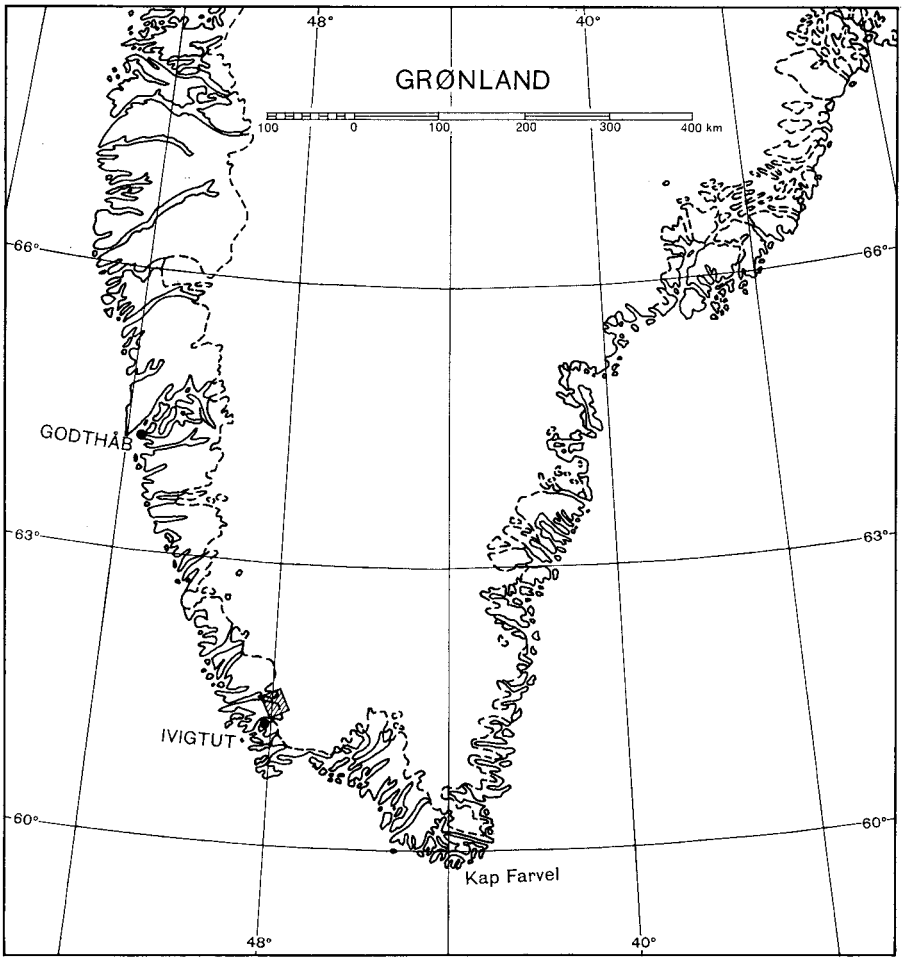

Fig. 1. Map showing the position of the Grænseland area in SW Greenland.

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.

Acknowledgments

The authors are greatly indebted to mag. scient K. ELLITSGAARD-RASMUSSEN, director of Grønlands Geologiske Undersøgelse, for permission to publish the results and for good working conditions in the field. Some of the material was collected by mag. scient. E. BONDESEN for which he is thanked.

The laboratory work was carried out in the Geological Institute and the Chemical Institute of the University of Aarhus and the chiefs of these institutes are cordially thanked.

We are grateful to professor, dr. N. A. SØRENSEN, Norges Tekniske Högskole, Trondheim, for providing pristane, and to civ. ing. O. TOLBOE, Grindstedværket, Brabrand, for the mass spectra.

The assistance of laborant, Mrs B. LARSEN and laborant H. WEILING, who undertook a part of the laboratory work, and Mrs E. BÆKGAARD, who typed the manuscript, is gratefully acknowledged.

Mr T. C. R. PULVERTAFT kindly corrected the English manuscript.

"Carlsbergfondet" and "Statens almindelige Videnskabsfond" have provided grants for instruments and laboratory assistance.

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% and the heating values (water and ash free) are from 7536 to 7671 K-cal/kg.

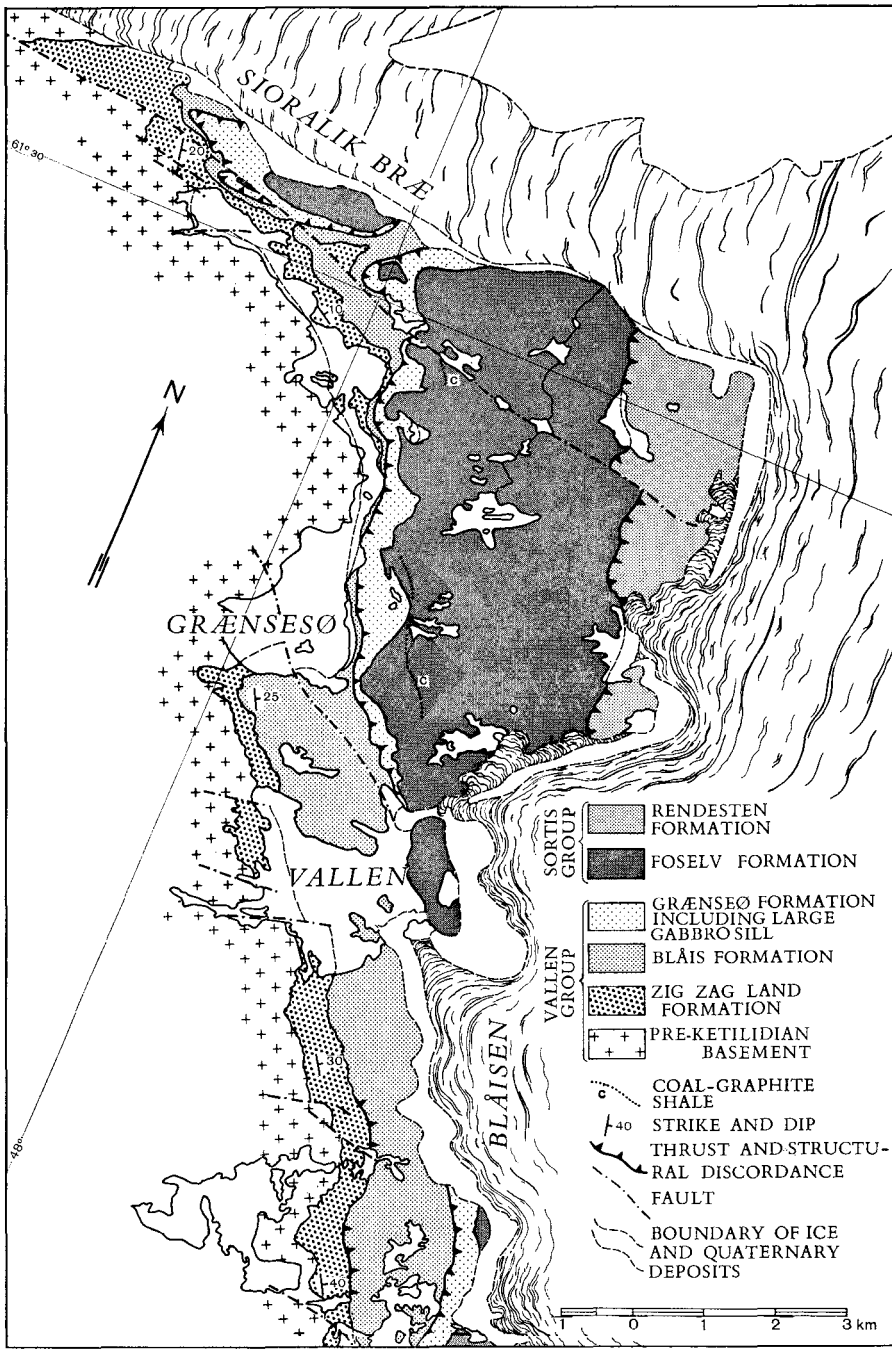

Fig. 2. Grænseland.

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.

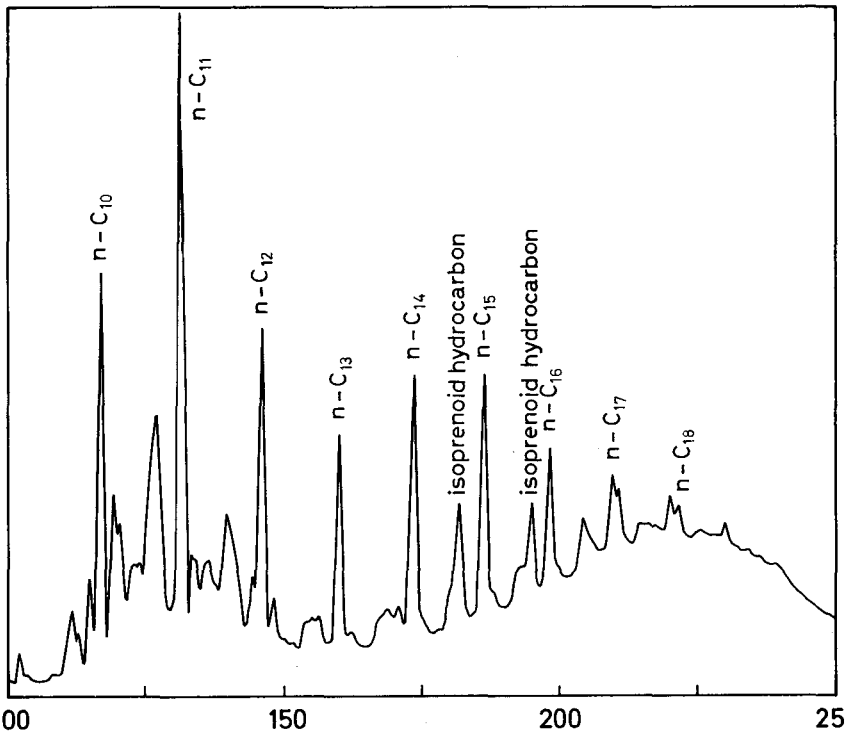

Fig. 3. Gas chromatogram of fraction I (aliphatic hydrocarbons) — 0.5 μl. Column, 10 per cent S.E. 30, 2 m. Temp. programming 5°C/min. 75–250°C. Helium flow 30 ml/min.

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).

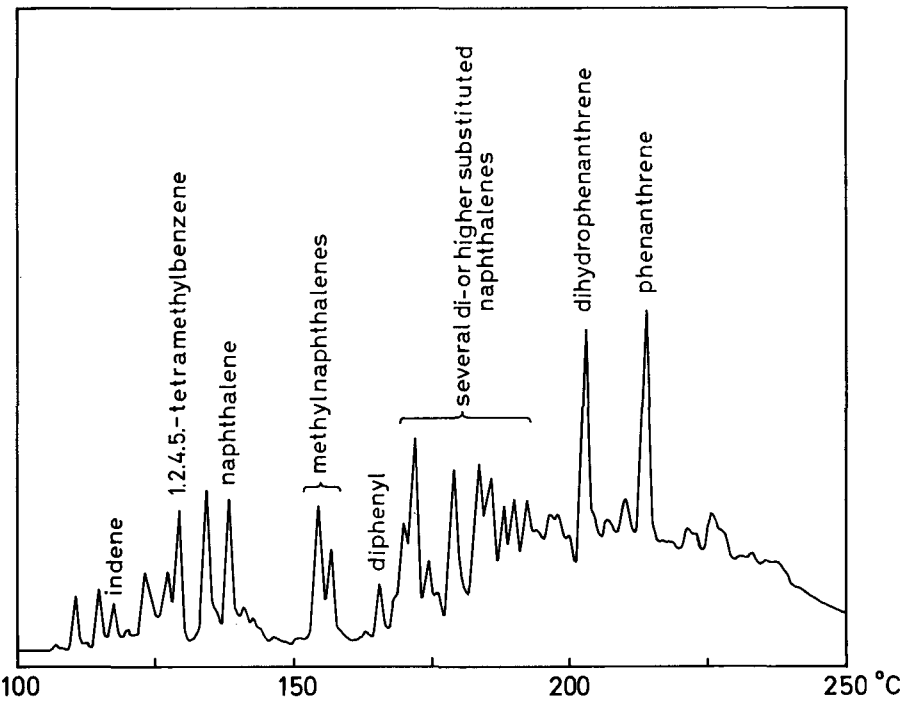

Fig. 4. Gas chromatogram of fraction II (aromatic hydrocarbons) — 1 μl. Column, 10 per cent S.E. 30, 2 m. 5°C/min. 75–250°C. Helium flow 30 ml/min.

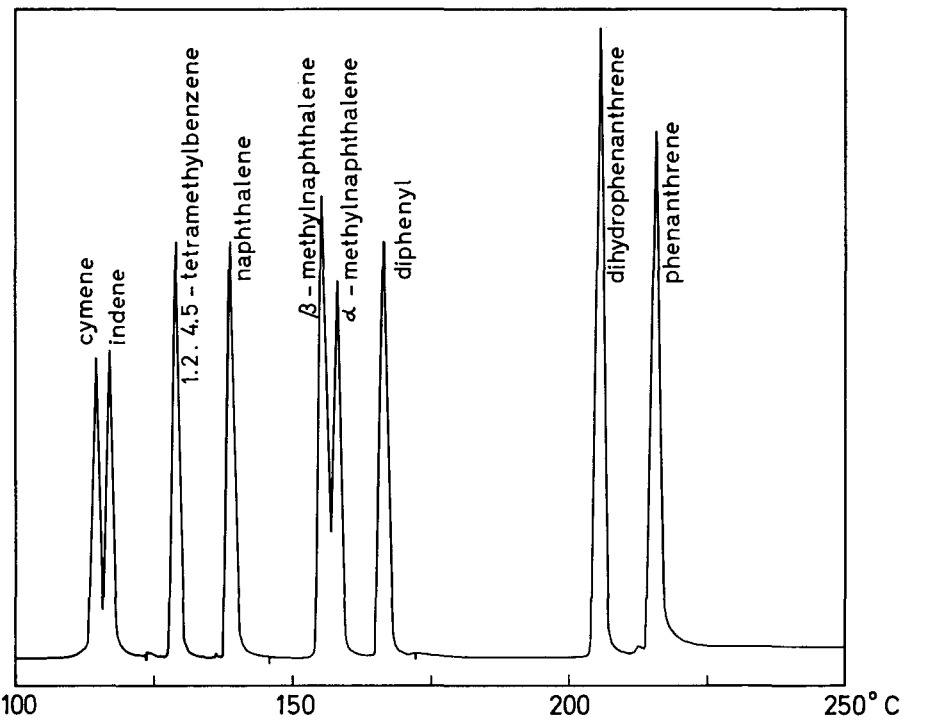

Fig. 5. Gas chromatogram of an artificial mixture of aromatic hydrocarbons (see p. 11).

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-

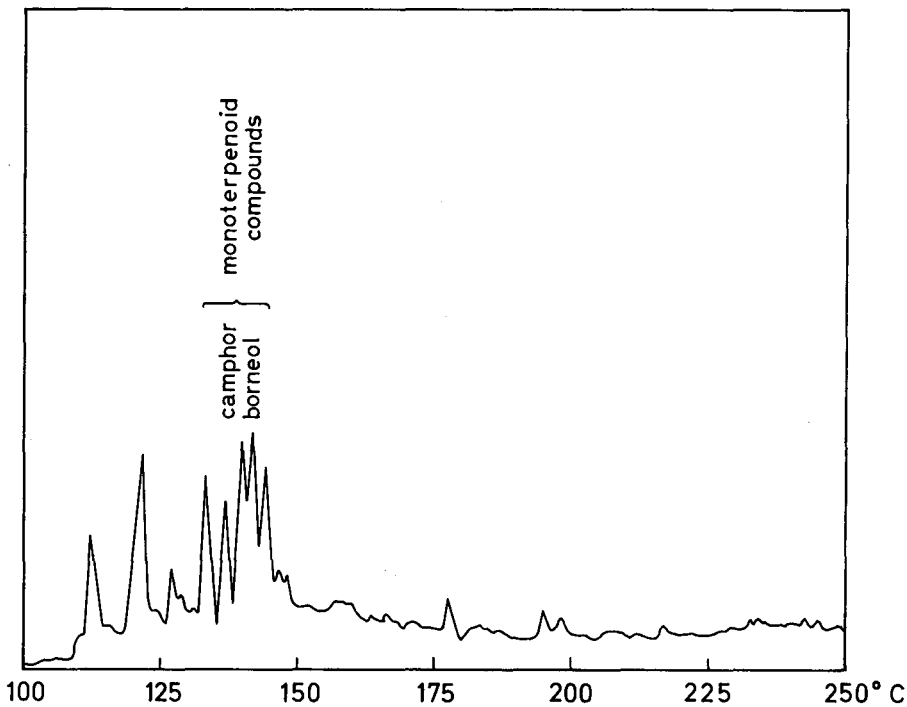

Fig. 6. Gas chromatogram of fraction III (monoterpenols etc.) — 0.5 μl. Column, 10 per cent S.E. 30, 2 m. 5°C/min. 75–250°C. Helium flow 30 ml/min.

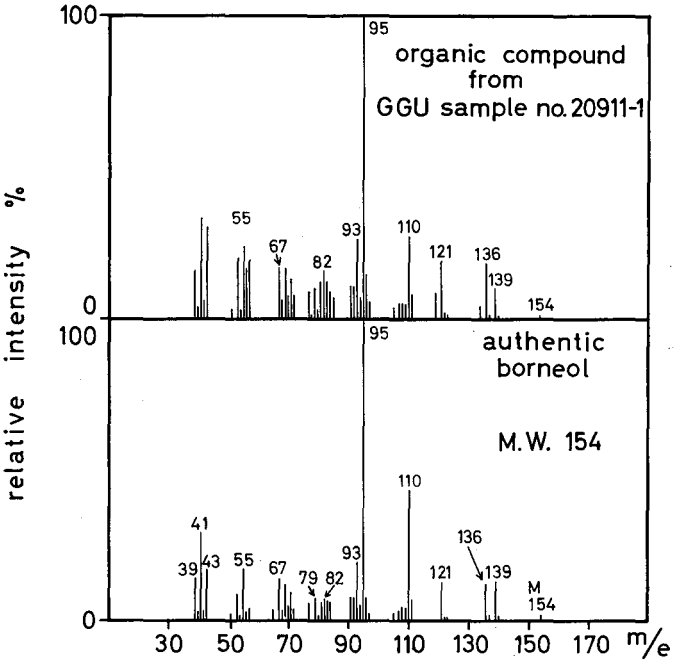

Fig. 7. Mass spectrum of organic compound from GGU sample no. 20911–1 and authentic borneol.

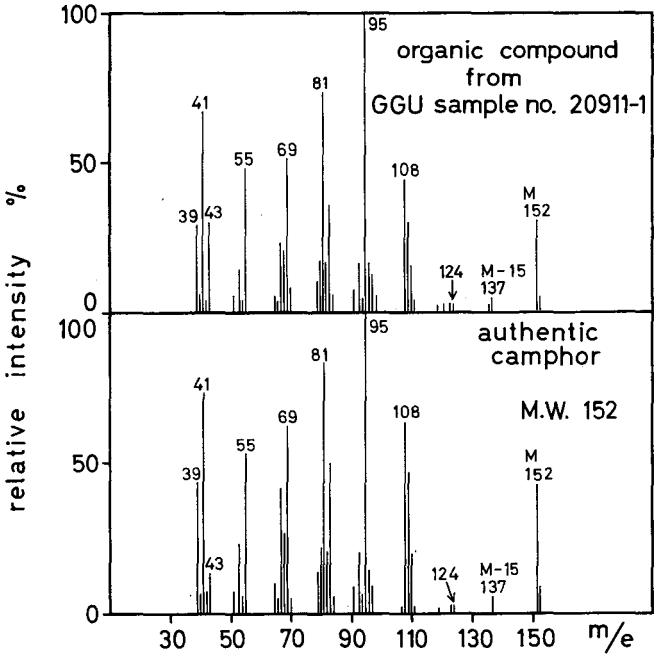

Fig. 8. Mass spectrum of organic compound from GGU sample no. 20911–1 and authentic camphor.

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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Abstract

Results of work on organic compounds extracted from well preserved Ketilidian sedimentary rocks from South-West Greenland about 2000 m.y. old are presented. The organic material was obtained from a dolomitic layer with great numbers of the globular fossil *Vallenia erlingi* RAUNSGAARD PEDERSEN.

Of the two samples examined one sample contains normal and branched alkanes with chain lengths from C_{10} to C_{20}, various aromatic hydrocarbons including benzene derivatives and naphthalenes. The other sample contains normal and branched alkanes with chain lengths from C_{10} to C_{32} and it did not show any aromaticity, but methyl esters of palmitic acid and other fatty acids are present.

The presence of these compounds provides further evidence of the organic origin of *Vallenia*.

CONTENTS

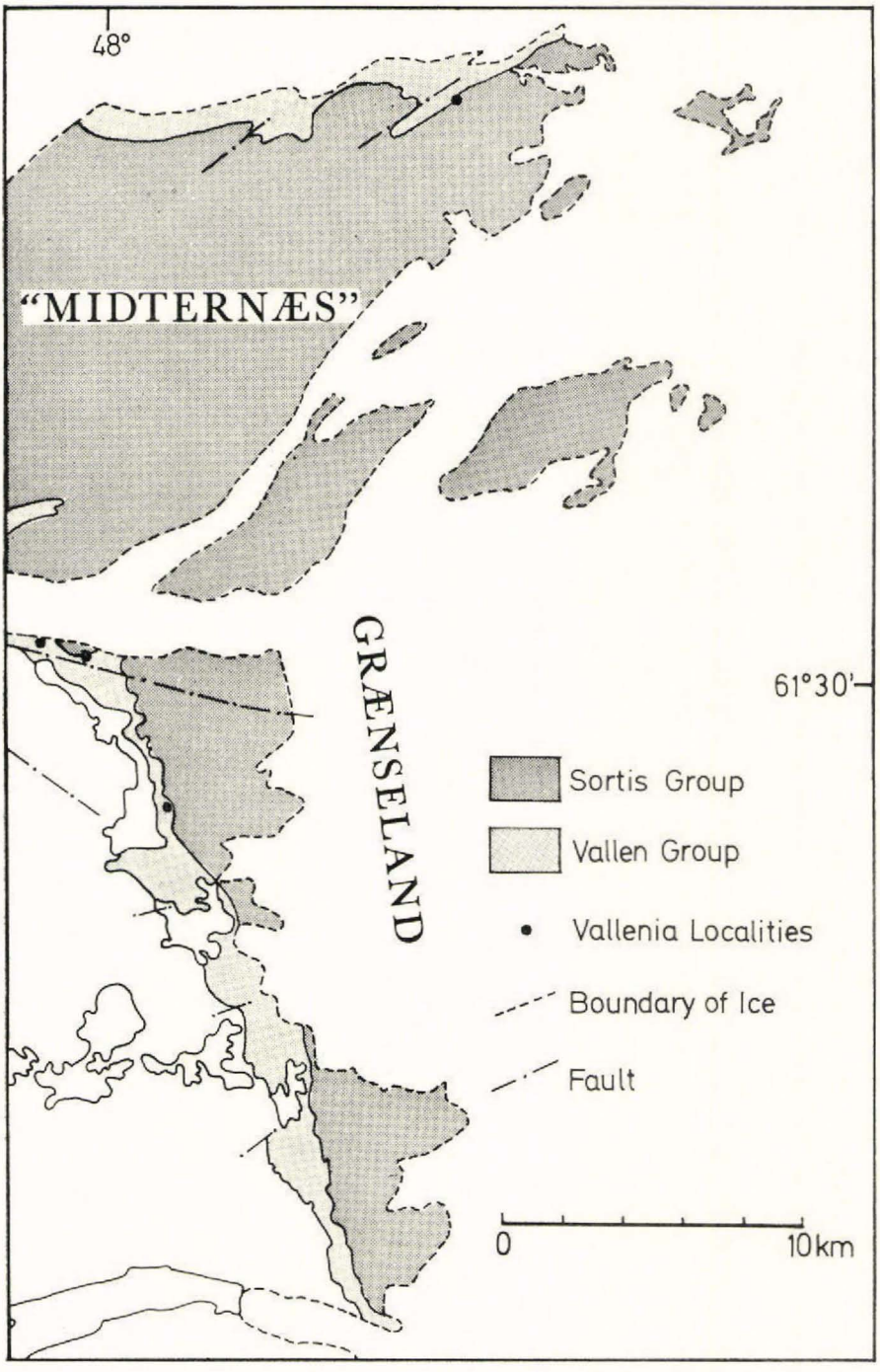

Fig. 1. Map showing the *Vallenia* localities in South-West Greenland known to date (May, 1967).

INTRODUCTION

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

The available information concerning organic compounds in Precambrian sediments has increased greatly during the last few years. The new information comes from many parts of the world and has been obtained from Precambrian rocks of various ages (EGLINTON 1966; EGLINTON, SCOTT, BELSKY, BURLINGAME, RICHTER and CALVIN 1966; JOHNS, BELSKY, MCCARTHY, BURLINGAME, HAUG, SCHNOES, RICHTER and CALVIN 1966).

In a previous paper (RAUNSGAARD PEDERSEN and LAM 1968) we have described organic matter obtained by extraction of a coal-graphite horizon from the Precambrian Ketilidian fold belt of South-West Greenland. From the coal-graphite we obtained monoterpenoid compounds, normal and branched paraffins (pristane, phytane and others) and methyl esters. As all these compounds are a result of biological activity, the metre-thick coal-graphite must represent a much thicker accumulation of organic material.

Further indications of the presence of life during Ketilidian sedimentation have been found and include several types of micro- and macrofossils (RAUNSGAARD PEDERSEN 1966; BONDESEN, RAUNSGAARD PEDERSEN and JØRGENSEN 1967; RAUNSGAARD PEDERSEN 1967).

The organic material described in this paper is also from the Ketilidian of South-West Greenland. The rock samples were obtained in this case from the Grænseland and Midternæs areas (see map, fig. 1) north-east of Ivigtut where the Ketilidian sediments and volcanics are only slightly metamorphosed in contrast to the greater part of the Ketilidian fold belt.

In the rock samples hitherto investigated most organic material was obtained by the extraction of the coal-graphite where until now only microfossils have been found.

The organic matter treated here is from a dolomitic rock rich in small macrofossils of a single species together with microfossils of several different types. The amount of organic material in the dolomite is much smaller than in the coal-graphite.

The organic compounds from other samples of Ketilidian sediments are under examination and the results will soon be ready for publication.

Acknowledgments

The director of Grønlands Geologiske Undersøgelse, mag. scient. K. ELLITSGAARD-RASMUSSEN is gratefully acknowledged for making the field work possible and for permission to publish these results.

The work in the laboratory was carried out in the Chemical Institute and the Geological Institute of the University of Aarhus and the chiefs of these institutes are cordially thanked.

We are grateful to civilingeniør O. TOLBOE and civilingeniør P. E. BRANDT, Grindstedværket, Brabrand, for the mass spectra and to Dr. A. K. HIGGINS for collecting some of the material.

The assistance of Miss H. WEILING and Mrs. B. LARSEN, who undertook some of the laboratory work, and Miss H. JACOBSEN, who typed the manuscript, is gratefully acknowledged.

Mr. T. C. R. PULVERTAFT kindly corrected the English manuscript.

"Statens Almindelige Videnskabsfond" has provided grants for instruments and "Carlsbergfondet" has provided grants for laboratory assistance and the mass spectra.

GEOLOGICAL SETTING

The geology of the Grænseland area has been outlined in two previous papers (BONDESEN, RAUNSGAARD PEDERSEN and JØRGENSEN 1967; RAUNSGAARD PEDERSEN and LAM 1968).

The Ketilidian succession has been sub-divided as follows:

Sortis Group	Rendesten Formation
	Foselv Formation
Vallen Group	Grænsesø Formation
	Blåis Formation
	Zig Zag Land Formation

The lower group is a varied sedimentary group and the upper consists mainly of volcanic rocks. From a coal-graphite layer in the pillow lavas of the Foselv Formation finds of distinct organic compounds have already been published (RAUNSGAARD PEDERSEN and LAM 1968).

The organic material described in this paper is derived from the uppermost part of the sedimentary group, from the upper part of the Grænsesø Formation. In a dolomitic layer in this formation a great number of globular fossils have been found. These fossils are described

under the name *Vallenia erlingi* RAUNSGAARD PEDERSEN (BONDESEN, RAUNSGAARD PEDERSEN and JØRGENSEN 1967). *Vallenia* specimens are from about 0.5 to 1.5 mm in diameter; they have a carbonaceous core and around this core two thin outer layers. Besides *Vallenia* microscopic carbonaceous fragments with cellular structures and microscopic globules have been found in the dolomitic layer.

The *Vallenia*-bearing dolomite has been found at four localities in the Grænseland and Midternæs areas (map, fig. 1). The distance between the outermost two localities is 25 km. In all four localities *Vallenia* is found in the same stratigraphic position in the sequence. The Grænsesø Formation has many other dolomitic layers but in spite of exhaustive searching *Vallenia* has only been found in this uppermost dolomitic layer.

The *Vallenia*-bearing dolomitic rock has a homogranoblastic saccharoidal texture and consists of twinned carbonate minerals with a grain size of about 1 mm, scattered small quartz grains, colourless mica flakes, and pyrite grains. Individual carbonate crystals often continue through the outer spherical layers of *Vallenia*. The single specimens of *Vallenia* are separated usually by only a few millimetres but are not normally in contact with each other. As seen from the photomicrograph fig. 2, *Vallenia* is one of the dominant constituents in the dolomite.

The organic material described here was extracted from two samples of the *Vallenia* dolomite. One of the samples (GGU sample no 52970) is from the southernmost locality, 600 m east of the south-east corner of Grænsesø (locality 1 in BONDESEN, RAUNSGAARD PEDERSEN and JØRGENSEN 1967); the other (GGU sample no. 69747–5) is from the northern locality in the Midternæs area (locality 3 in BONDESEN, RAUNSGAARD PEDERSEN and JØRGENSEN 1967).

The age of the Ketilidian succession of Grænseland is not known exactly but has been estimated as 1700 to 2000 m.y. from dating in nearby areas (BRIDGWATER 1965). An attempt is being made to date the time of sedimentation.

EXTRACTION AND ANALYTICAL METHODS

1878 g of a dolomitic sample from the Midternæs locality (GGU sample no. 69747–5) was extracted in the manner already described by the writers (RAUNSGAARD PEDERSEN and LAM 1968) after removal of surface contamination and pulverization of the pure sample. The experimental methods and precautions against contamination have also been described.

The extract was reduced in a vacuum evaporator and the residue

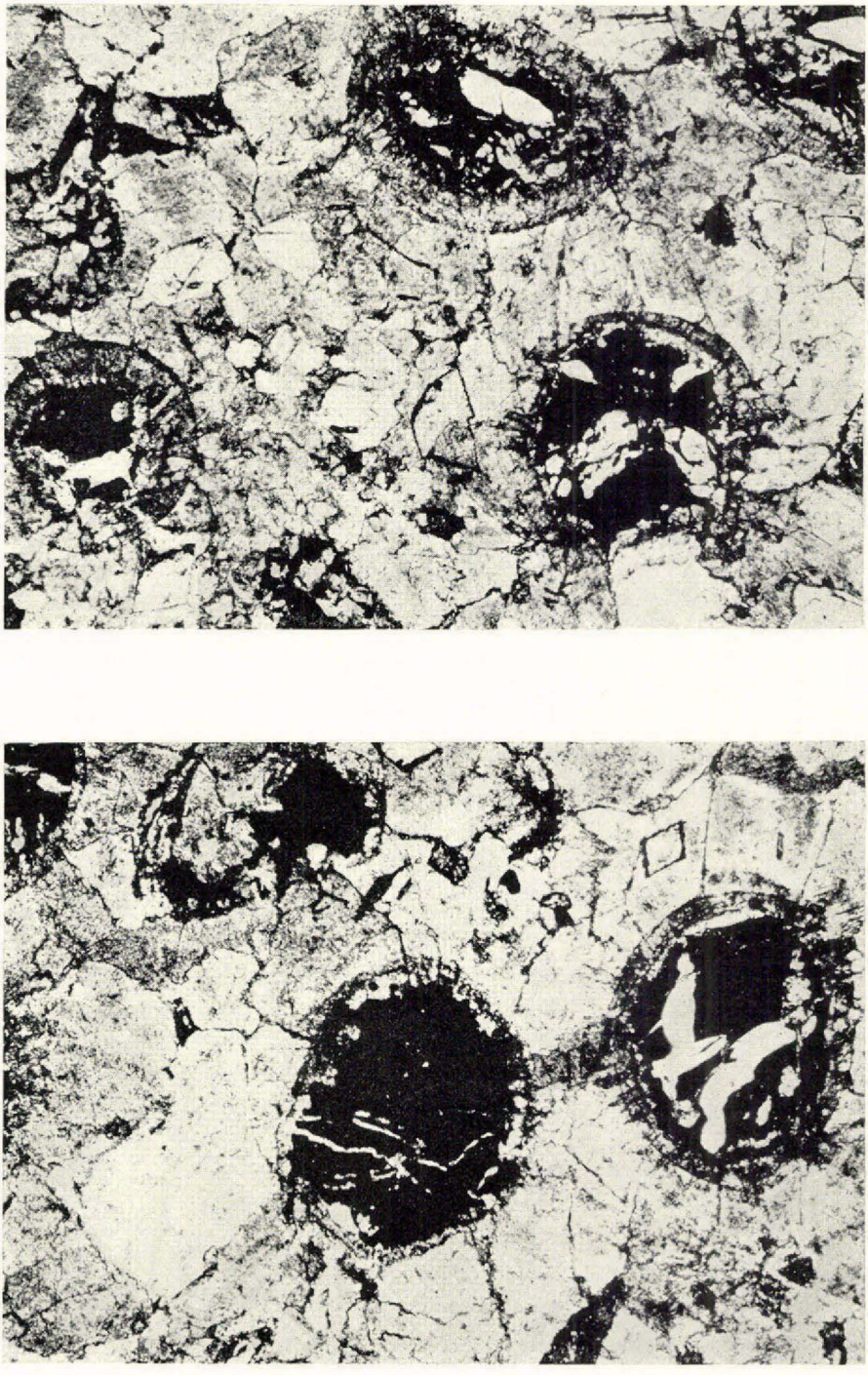

Fig. 2. Photomicrographs of thin sections of dolomite with *Vallenia erlingi* RAUNSGAARD PEDERSEN (about 40×).

was extracted with light petroleum and with ether, using 5 ml of each solvent. After repeated evaporation 28 mg of an oil was obtained.

Preliminary studies of the mixture when examined in a gas chromatograph (0.5 m column, 10 per cent S. E. 30) revealed the presence of normal alkanes from C_{10} to C_{20} with a maximum at C_{13}. The crude material (24 mg) was dissolved in 1 ml of light petroleum and two-thirds of the solution (containing 16 mg of the sample extract) was poured into a column of silicagel (2 cm high and 0.5 cm in diameter); after elution with 1.5 ml of light petroleum a fraction of 8 mg was obtained (fraction I). Further elution with ether gave another 5–6 mg (fraction II). After preliminary gas chromatography it was evident that many normal alkanes were present in fraction I when compared to a standard solution.

The fractions I and II were then subjected to an examination by gas-liquid chromatography and mass spectrometry after injection into a Perkin-Elmer 880 gas chromatograph equipped with a 2 m 10 per cent S. E. 30 Gaschrom Z column (helium flow) combined with a Hitachi-Perkin-Elmer RMU-6D mass spectrometer; mass range 600; ionizing voltage 70 eV; ion source temperature 250°C; gas inlet.

1998 g of a dolomitic sample with *Vallenia* from the southernmost Grænseland locality (GGU sample no. 52970) was extracted in the same way as the first sample. After separation in a silicagel column two fractions were obtained. They were examined by infrared and mass spectrometry.

RESULTS

Sample no. 69747-5

In fraction I (fig. 3) the dominant compounds were n-alkanes from C_{10} to C_{20} which were determined on the basis of their retention times compared to those of a standard mixture of normal alkanes. The other compounds determined were isoprenoid alkanes, such as pristane and phytane, and other aliphatic hydrocarbons (cyclohexane derivatives). Phenylcyclohexane and other benzene derivatives, and small amounts of naphthalene, methylnaphthalenes and dimethylnaphthalenes may partly originate from the benzene ("Merck") used, as a re-examination of the benzene did in fact reveal small amounts of aromatics (especially naphthalene derivatives).

Aromatic hydrocarbons have been reported from other investigations of old sediments (Barghoorn and Tyler 1965; Blumer 1965). As the proportions of aromatic hydrocarbons differ between the benzene methanol solvent and the sample examined, we believe that small amounts of polycyclic hydrocarbons may be present in the sample in-

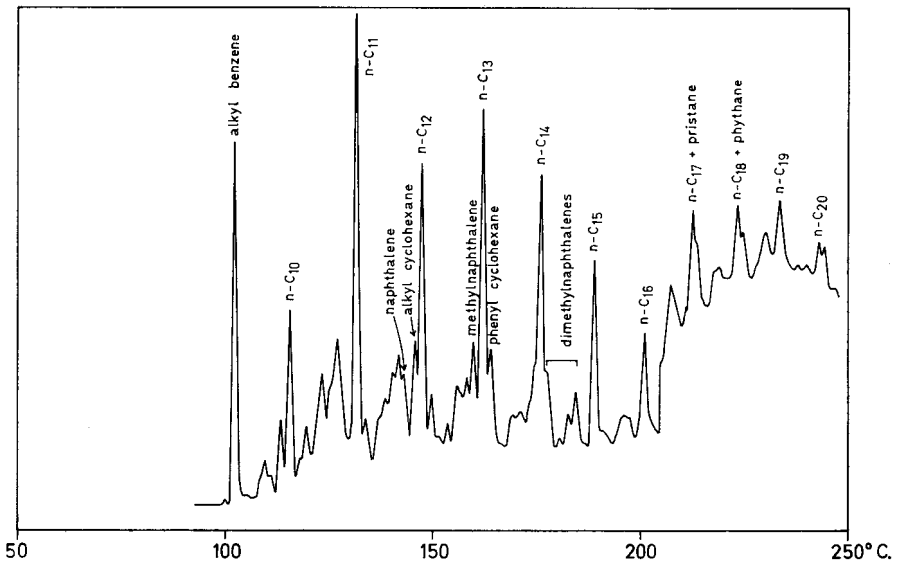

Fig. 3. Gas chromatogram of fraction I from GGU sample no. 69747–5. 1 μl injected. Column 2 m, 10 per cent S. E. 30. Temperature programming 5°C/min. 60–250°. Helium flow 30 ml/min. Chart speed 1 cm/min.

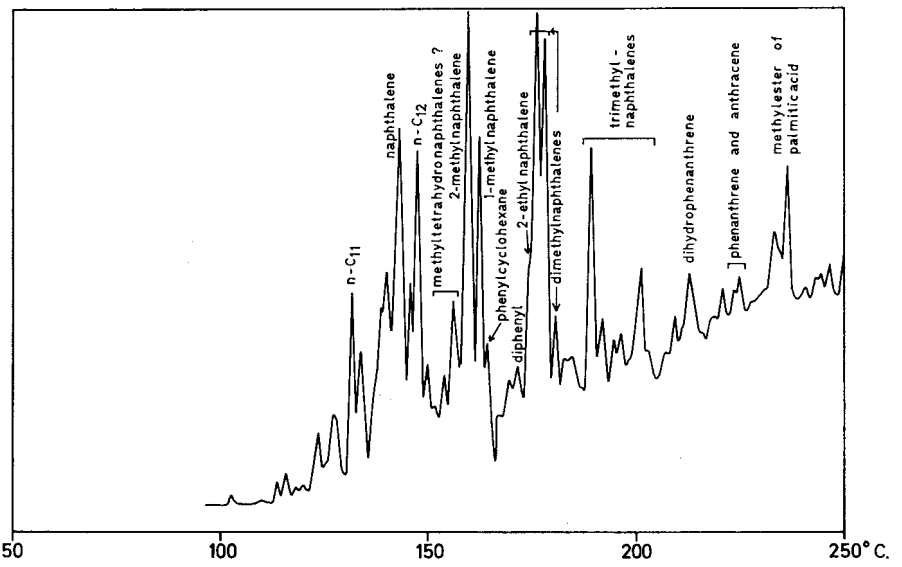

Fig. 4. Gas chromatogram of fraction II from GGU sample no. 69747–5. 1 μl injected. Column 2 m, 10 per cent S. E. 30. Temperature programming 5°C/min. 60–250°C. Helium flow 30 ml/min. Chart speed 1 cm/min.

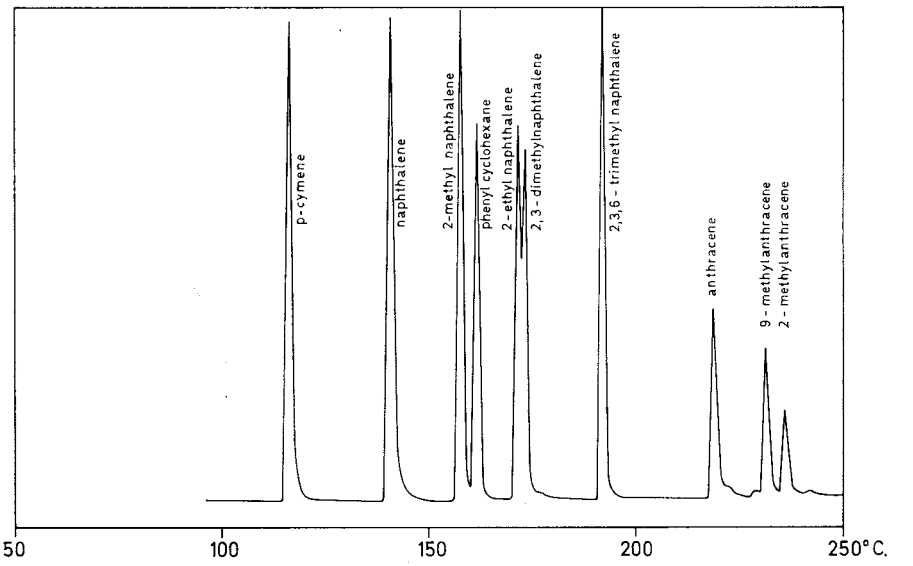

Fig. 5. Gas chromatogram of a synthetic mixture. 0.5 μl injected. Column 2 m, 10 per cent S. E. 30. Temperature programming 5°C/min. 60–250°C. Helium flow 30 ml/min. Chart speed 1 cm/min.

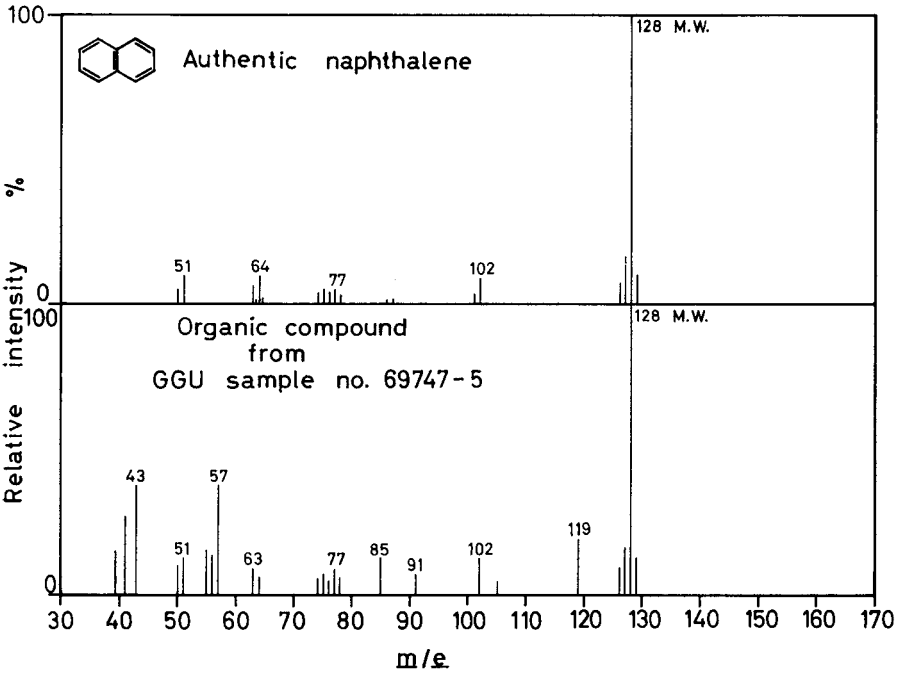

Fig. 6. Mass spectra of organic compound from GGU sample no. 69747–5 and of authentic naphthalene.

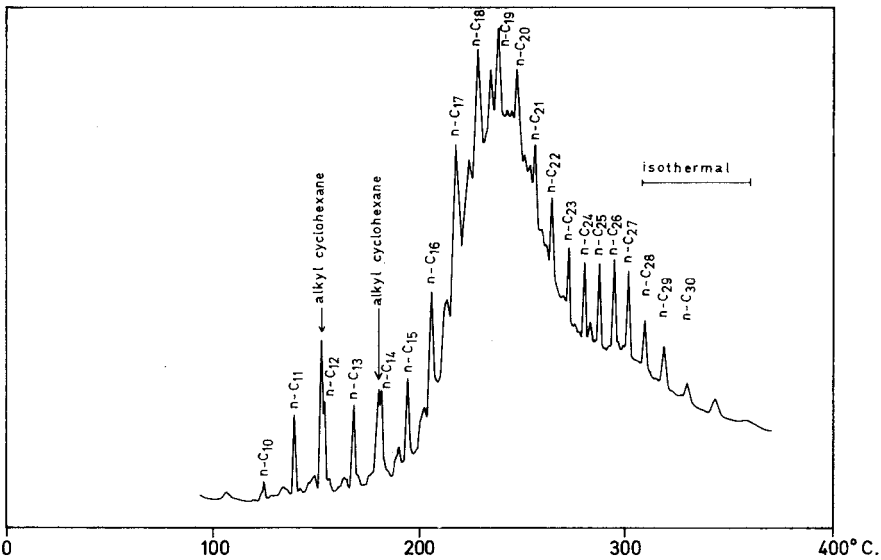

Fig. 7. Gas chromatogram of fraction I from GGU sample no. 52970. 1.5 μl injected. Column 2 m, 10 per cent S. E. 30. Temperature programming 10° C/min. 80–300° C. Helium flow 30 ml/min. Chart speed 1 cm/min.

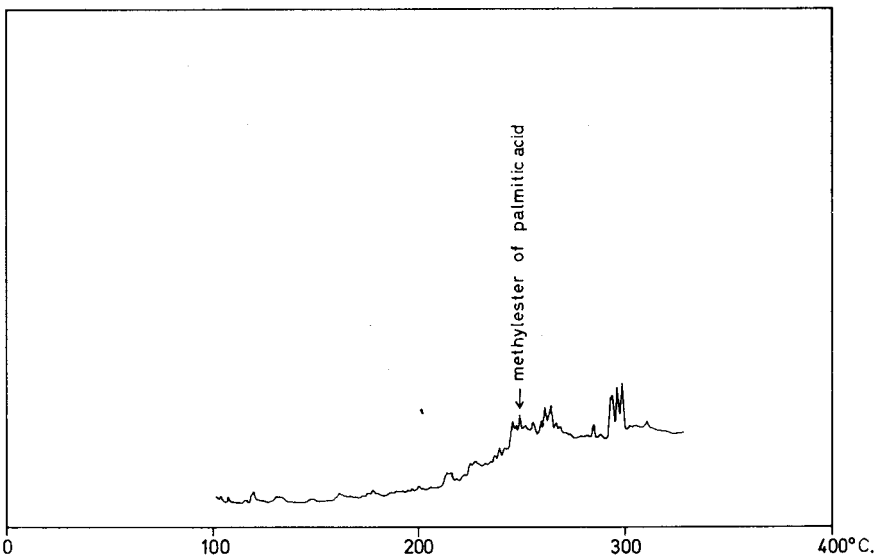

Fig. 8. Gas chromatogram of fraction II from GGU sample no. 52970. 1.5 μl injected. Column 2 m, 10 per cent S. E. 30. Temperature programming 10° C/min. 80–300° C. Helium flow 30 ml/min. Chart speed 1 cm/min.

vestigated and in samples earlier investigated (RAUNSGAARD PEDERSEN and LAM 1968).

Fraction II (fig. 4) contained lesser amounts of normal alkanes while aromatic hydrocarbons were much more dominant in this fraction than in fraction I. Naphthalene, 1-methyl-, 2-methyl-, 1-ethyl- and 2-ethylnaphthalene, and various di- and trimethylnaphthalenes appeared to be present. Phenylcyclohexane, biphenyl, phenanthrene and/or anthracene, and also alkylanthracenes were determined. There was evidence of the presence of the methyl ester of palmitic acid.

A synthetic mixture of cymene, naphthalene, 2-methylnaphthalene, phenylcyclohexane, 2-ethylnaphthalene, 2,3-dimethylnaphthalene, 2,3,6-trimethylnaphthalene, anthracene, 9-methylanthracene and 2-methylanthracene was prepared, and comparison of the retention times of fractions of the sample with those of the synthetic mixture (fig. 5) showed good agreement when carried out under equal conditions. Mass spectra of compounds which have corresponding retention times in the gas chromatograms were compared (see for example fig. 6).

The mass spectra often show some discrepancies, especially within the lower fragment pattern, which are due to alkyl-impurities; the gas chromatographic fractions cannot be expected to be quite pure because of the complexity of the mixture. The single and double charged ions accord well with those of the authentic material.

Sample no. 52970

One fraction (20 mg) eluted with light petroleum was found to contain mainly normal alkanes from C_{10} to C_{32} and with a maximum at C_{18} to C_{20} (fig. 7). Furthermore alkyl cyclohexanes (83, 97, 111, 125 ... fragment peaks are predominant in some of the mass spectra) and branched hydrocarbons (isoprenoid) such as pristane and phytane seem to be present in respectively the n-C_{17} and n-C_{18} peaks of the gas chromatogram (the predominant fragment peaks are 169 and 183 m/e in the mass spectra).

In an ether-eluted fraction (a few mg) from the silicagel column, methyl esters of palmitic acid and probably also myristic and stearic acids (74 and 87 m/e peaks of the mass spectra) appear to be present; this is revealed in separation by gas chromatography. The retention times of the components in the fraction fit well with those of the synthetic equivalents of the compounds believed to be present.

CONCLUSION

The examinations of the organic compounds extracted from a dolomitic layer with a great number of the c. 2000 m.y. old Precambrian fossil *Vallenia erlingi* RAUNSGAARD PEDERSEN show the presence of normal and branched alkanes with chain lengths from C_{10} up to C_{32}, various aromatic hydrocarbons and methyl esters of palmitic acid and other fatty acids.

The organic compounds present further evidence of the organic origin of *Vallenia*.

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