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PRECAMBRIAN ORGANIC COMPOUNDS FROM THE KETILIDIAN OF SOUTH-WEST GREENLAND

Part II

BY

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WITH 8 FIGURES IN THE TEXT

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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*.

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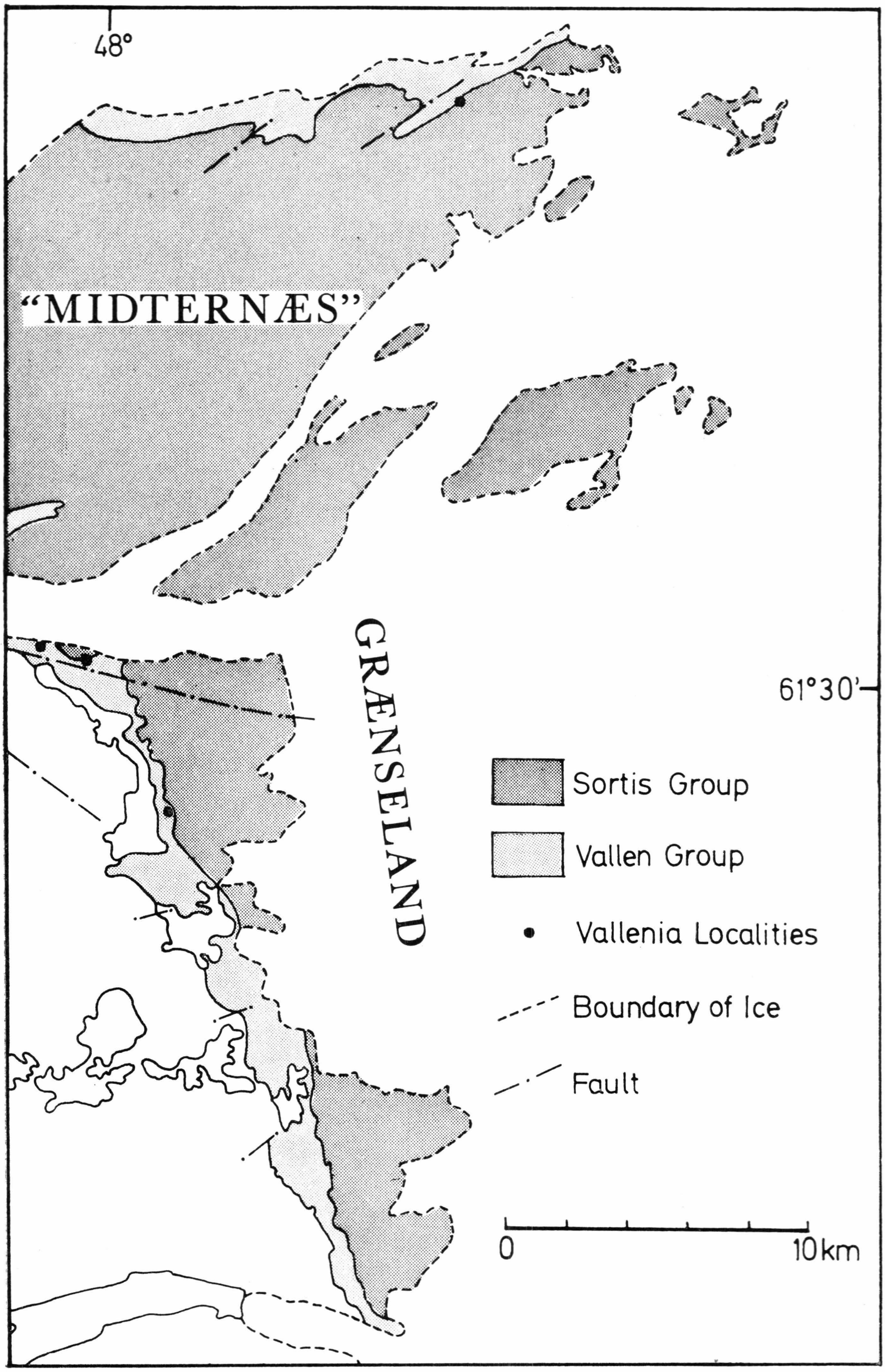

Fig. 1. Map showing the *Vallenia* localities in South-West Greenland known to date (May, 1967).

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

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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

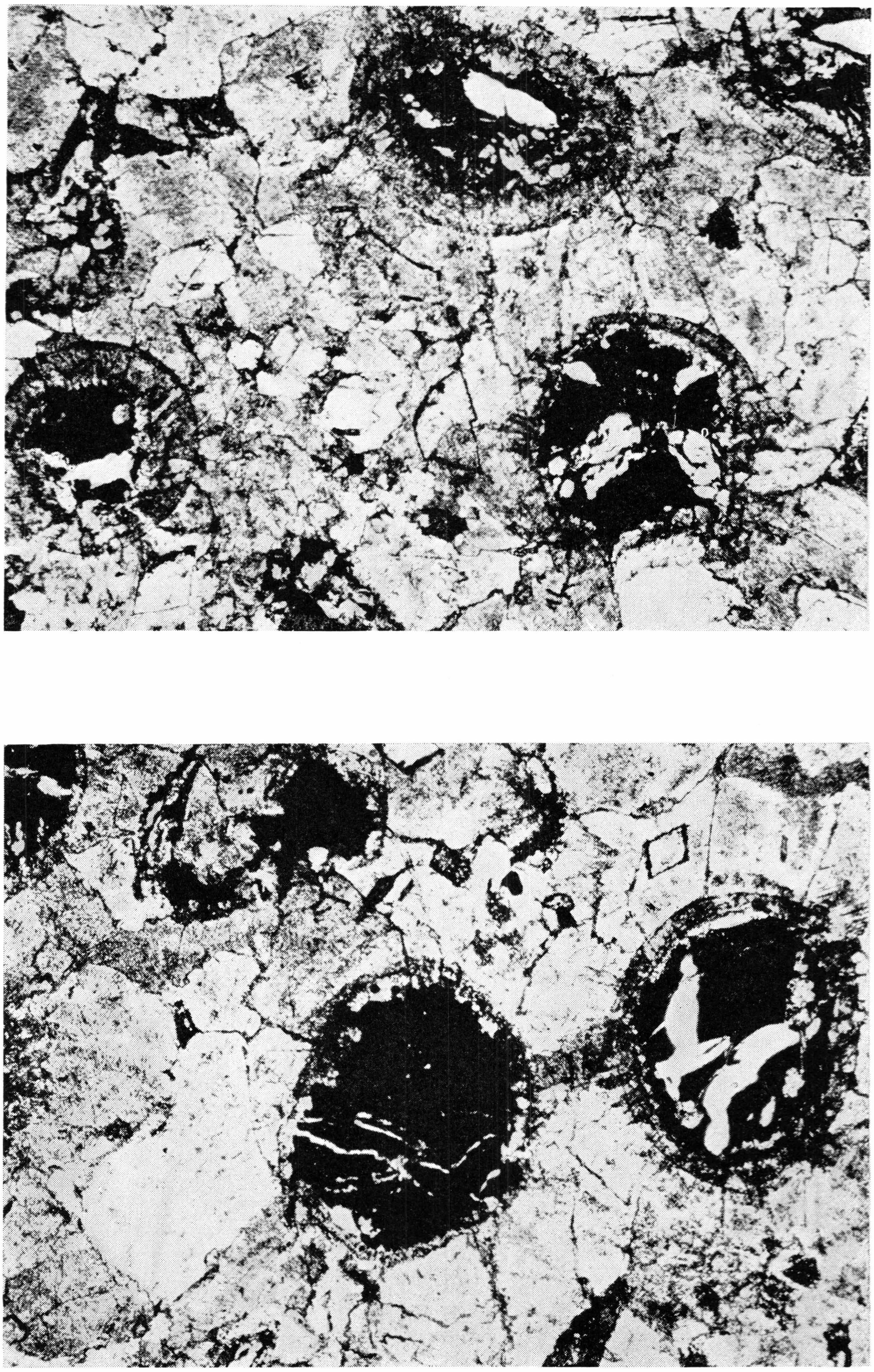

Fig. 2. Photomicrographs of thin sections of dolomite with *Vallenia erlingi* Raunsgaard Pedersen (about 40 ×).

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-

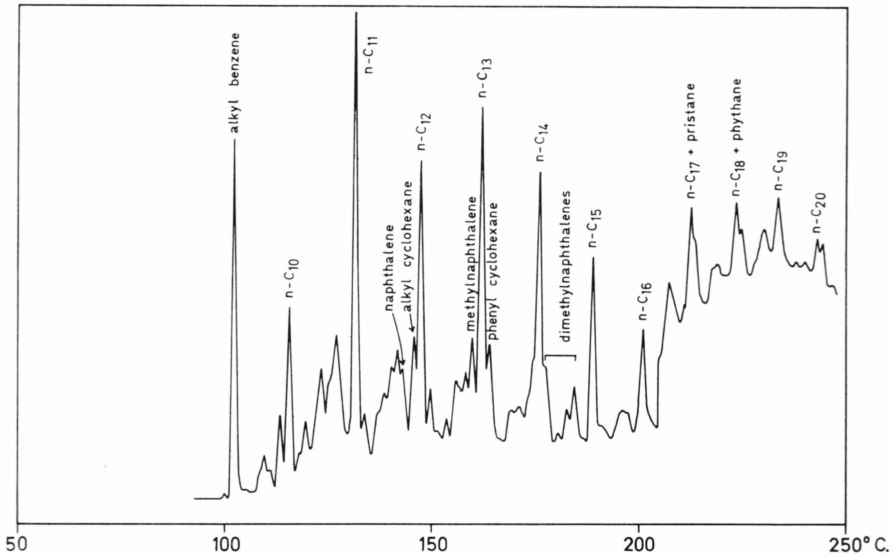

Fig. 3. Gas chromatogram of fraction I from GGU sample no. 69747–5. 1 μl injected. Column 2 m, 10 per cent S. E. 30. Temperature programming 5° C/min. 60–250°. Helium flow 30 ml/min. Chart speed 1 cm/min.

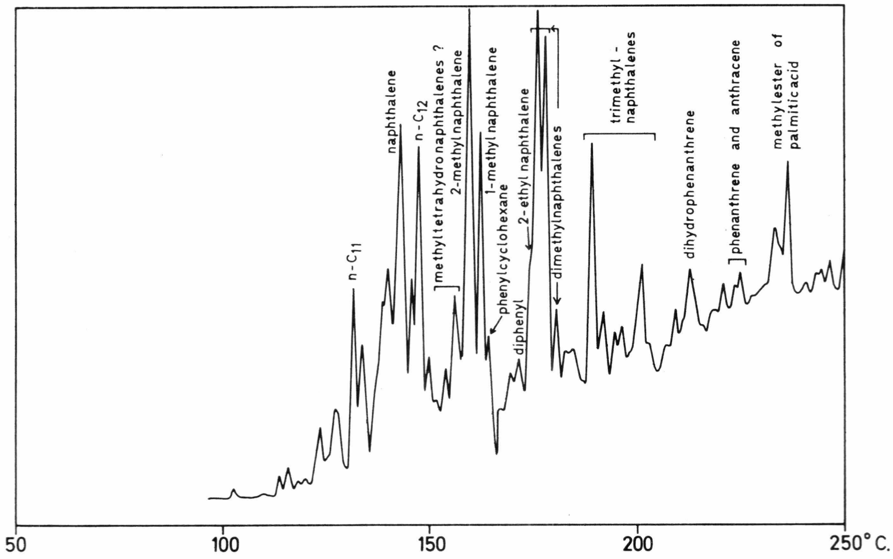

Fig. 4. Gas chromatogram of fraction II from GGU sample no. 69747–5. 1 μl injected. Column 2 m, 10 per cent S. E. 30. Temperature programming 5° C/min. 60–250° C. Helium flow 30 ml/min. Chart speed 1 cm/min.

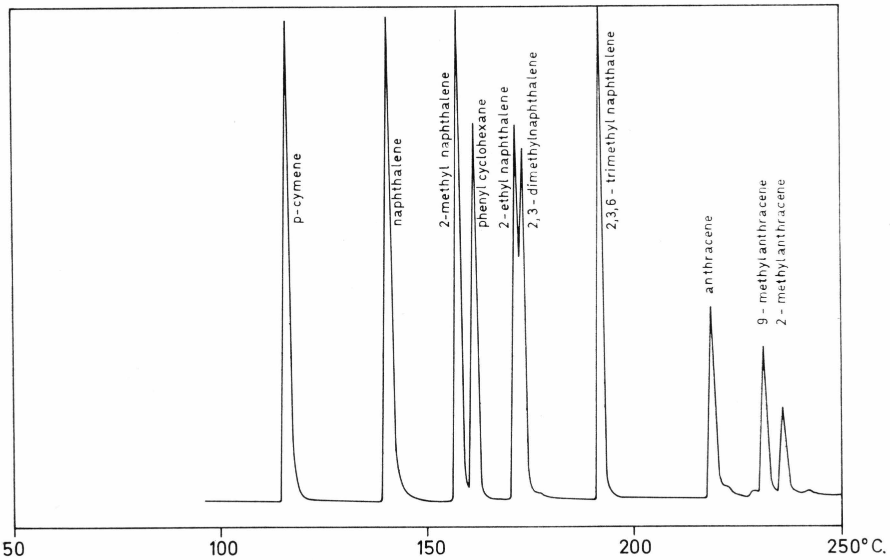

Fig. 5. Gas chromatogram of a synthetic mixture. 0.5 μl injected. Column 2 m, 10 per cent S. E. 30. Temperature programming 5°C/min. 60–250°C. Helium flow 30 ml/min. Chart speed 1 cm/min.

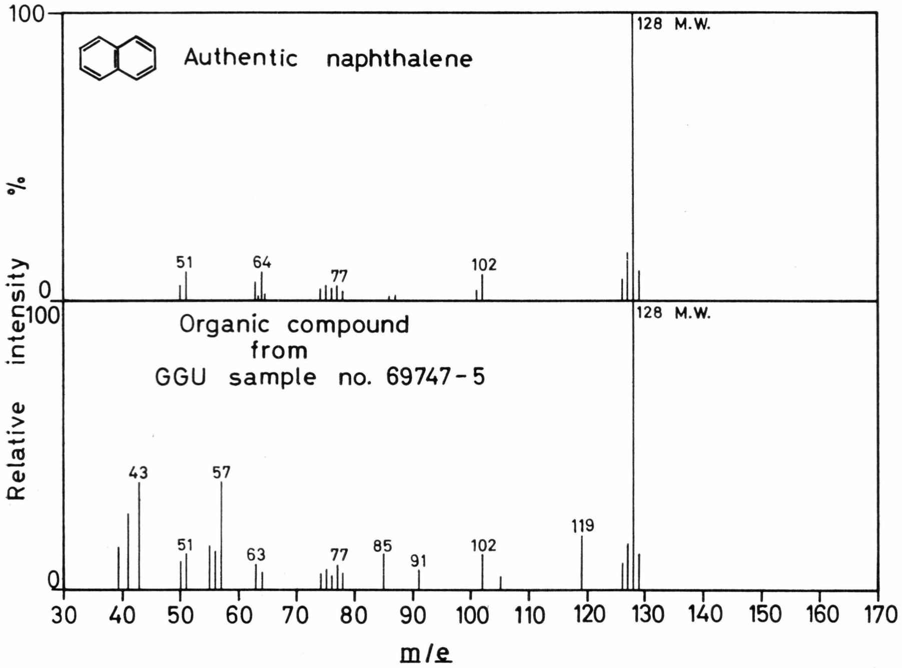

Fig. 6. Mass spectra of organic compound from GGU sample no. 69747–5 and of authentic naphthalene.

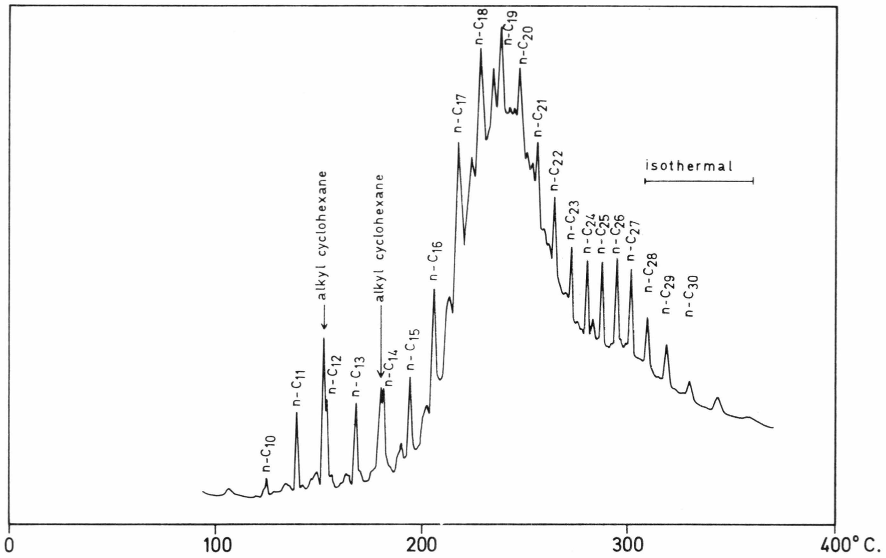

Fig. 7. Gas chromatogram of fraction I from GGU sample no. 52970. 1.5 μl injected. Column 2 m, 10 per cent S. E. 30. Temperature programming 10° C/min. 80–300° C. Helium flow 30 ml/min. Chart speed 1 cm/min.

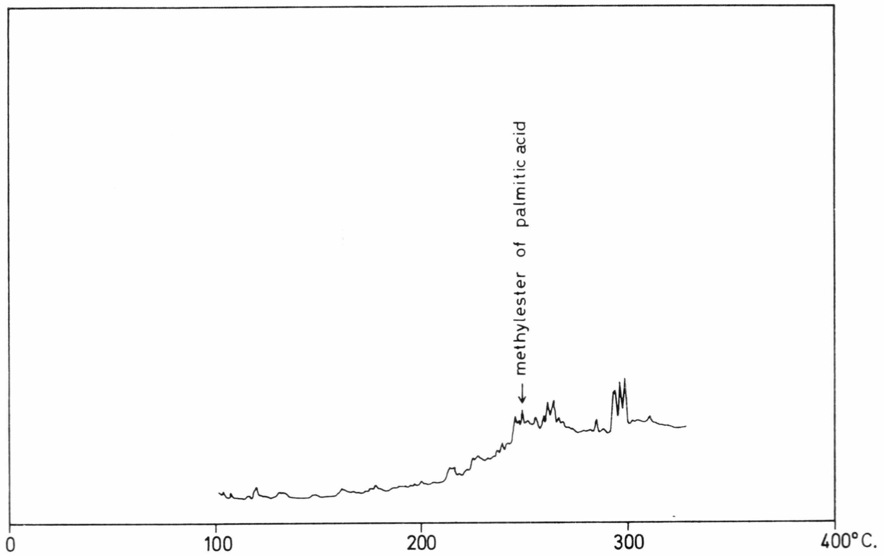

Fig. 8. Gas chromatogram of fraction II from GGU sample no. 52970. 1.5 μl injected. Column 2 m, 10 per cent S. E. 30. Temperature programming 10° C/min. 80–300° C. Helium flow 30 ml/min. Chart speed 1 cm/min.

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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