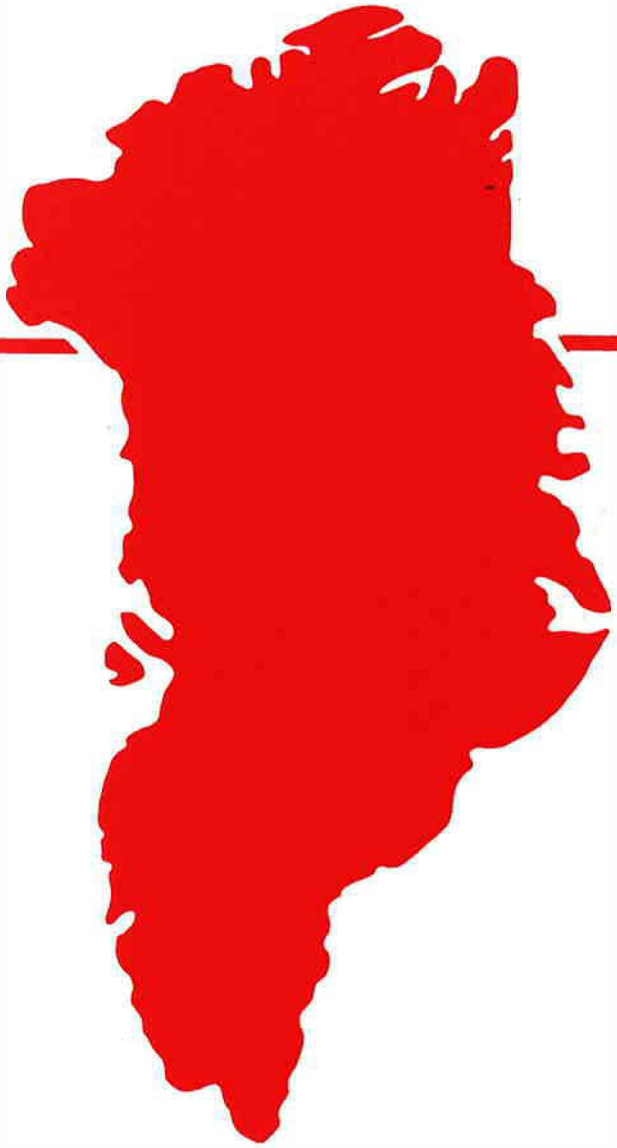
Seeps and other bitumen showings: a review of origin, nomenclature and occurrences in Greenland



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Ujarassiortut Kalaallit Nunaanni Misissuisoqarfiat
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Abstract

Studies of oil and gas seeps and solid bitumens provide important data on past and present distribution of hydrocarbons in sedimentary basins and hence have great importance in petroleum exploration.

In the present report the origin and degradation of bitumens is briefly introduced and the complicated terminology is reviewed.

Seeps and bitumens are common in most of the onshore sedimentary basins of Greenland. All known examples are listed in the present paper and examples of their geochemical composition (LECO, Rock Eval pyrolysis, GC, GC/MS) are discussed. Many of the bitumens are strongly thermally altered or severely biodegraded. In a number of cases, however, degradation is less intense and the bitumens can be geochemically correlated to known or inferred source rocks. Some of these examples are encouraging for future exploration.

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Introduction

The recognition of oil and gas seeps and solid bitumen occurrences at the surface or in the near vicinity of sedimentary basins has great importance in petroleum exploration since it may provide important data on past and present distribution of hydrocarbons within a basin.

In the early part of modern oil history, in the late 1800's and early 1900's, seepage was the most important factor for targeting drilling locations. In this period all major early oil fields were discovered near seeps and the rule-of-thumb that most prolific petroliferous basins in the world show some surface expression of hydrocarbons still holds (Link, 1952; Hunt, 1979; Macgregor, 1993). Although detailed structural analysis based on seismic data and also to some extent on well and surface structural data, is the main factor in defining prospects, hydrocarbon surface indications may be important in frontier areas. This is especially the case in basins with a complex history of folding, faulting and deep erosion, such as many of the well exposed onshore basins in Greenland.

Oil seeps and near-surface heavy hydrocarbons may have a direct economic potential. The reserves in the major tar sands in the Alberta Basin, Canada, the Orinoco Heavy Oil Belt, Venezuela, and major deposits in the USSR are enormous, almost as much as the discovered and recoverable conventional crude oil reserves in the world (e.g. Demaison, 1977). These heavy oil and tar sand deposits are particularly common in relatively young foreland basins. However, due to major technical problems, the present recovery from most tar sands is very low and not commercial with present techniques.

Exploitation of seep material has been common since earliest historical time and asphalt has been used as a building material, for sculptures and ornaments, as embalming, and for ship construction since several thousand years B.C. (Abraham, 1960; Nissenbaum, 1978; Hunt, 1979; Connan, 1988). The early sources were mainly deposits situated in Mesopotamia (present-day Iraq), Palestine (along the Dead Sea), Greece and Albania. The early Spanish explorers in America used asphalt from Trinidad, Peru, Cuba, Venezuela, and later California (Abraham, 1960; Moore, 1984). More recent exploitation, contemporaneous with modern oil production, is known from the wurtzilite and gilsonite deposits of Utah and the grahamite deposits of Oklahoma (Abraham, 1960).

Geological setting

Oil seeps and other bitumens occur in a wide variety of geological settings, but in far the most cases in association with several kilometres thick sedimentary successions. Oily material may occur on the surface or in Recent sediments (asphalt lakes, tar pits and springs), and in or at the surface of the marine water column overlying a sedimentary basin (multicoloured slicks) and as tar on nearby beaches (Landes, 1973).

In deeply eroded basins seepage is particularly common along faults, thrusts and unconformities, at the surface of dipping porous beds, in eroded antiforms, and in association with magmatic intrusions, mud volcanoes and piercement salt domes (Link, 1952; Hunt, 1979; Clarke & Cleverly, 1991; Macgregor, 1993). Solid bitumen is also found in uplifted palaeo-reservoirs, in palaeo-migration conduits, in cracks and porous beds in the vicinity of previously generating source rocks, in hydrothermal veins (see later under Greenland examples), and very often in association with sulphide mineralizations (e.g. Macqueen & Powell, 1983; Parnell, 1988a; several papers in Simoneit (ed.) 1990) or uraniferous mineralizations (e.g. Curiale *et al.*, 1983; Parnell, 1988b).

In exploration and production wells reservoir bitumens or tar mats close to the oil/water contact have often been reported (Rogers *et al.*, 1974; Milner *et al.*, 1977; Moore, 1984; Dahl & Spears, 1986).

It is important to classify observations into 1) active or 'live' seeps, which may be gas, light oil, heavy oil or asphalt, and 2) inactive or 'dead' seeps, which generally are solid bitumens of the asphaltite or pyrobitumen family (see later) (Hunt, 1979). The application of this distinction is, however, often quite difficult in Greenland because of the cold temperature (limited viscosity) and remoteness of the occurrences; due to logistic problems many bitumen localities reported in Greenland have never been revisited.

Processes of degradation

Seeping material and solid bitumen in particular have undergone a complex history of degradation since they originally formed as oil within a source rock. The various processes of degradation of accumulated crude oil is illustrated schematically in Fig. 1. Most of these processes may also have been active during degradation of bitumens that have never been trapped (e.g. hydrothermally or contact metamorphic generated hydrocarbons found near source rocks).

Bitumen collected at the surface may have been altered by several processes, either contemporaneously or in different order depending on basin history. The processes of alteration change the chemical composition and physical properties (see e.g. typical effects of biodegradation in Table 1) of the bitumen and with knowledge of the initial composition, the history and intensity of alteration may be interpreted. The processes of alteration are briefly reviewed below; for a detailed discussion on this chemically complicated and economically important subject the reader is referred to the important contributions by Evans *et al.* (1971), Bailey *et al.* (1973a,b), Milner *et al.* (1977), Price (1980), Connan (1984), Connan & Restle (1984), Tissot & Welte (1984).

Thermal alteration

Thermal alteration or "cracking" of crude oil takes place during deep subsidence of the reservoir or during local heating due to circulating hydrothermal fluids or to igneous intrusions. During this heating the hydrocarbons are cracked to shorter molecules and the process eventually leads to the formation of methane and a carbonaceous residue. Most of the gas leaks out of the reservoir whereas the residue is retained as dark pore fillings which are often observed in palaeo-reservoirs. Products of intermediate steps are light oils, condensates and wet gases, all typically associated with solid bitumens. Some of the changes in composition and properties of both the increasingly more mature hydrocarbons and the residue are shown in Table 1. Under natural long-term conditions thermal cracking of crude oil starts at about 125°C and continues to about 180°C when all hydrocarbons have been transformed into methane. During short-term heating by intrusions or hydrothermal solutions the hydrocarbons may survive considerably higher temperatures.

Generally this interval of thermal alteration corresponds to a vitrinite reflectance from 1.3% to 2.0 %, but hydrocarbons have been reported in rocks with much higher values (e.g. Price, 1993).

Deasphalting

The process of deasphalting takes place when the relative amount of light oil, gas or CO_2 in a reservoir is increased by *in-situ* thermal cracking or by migration from external sources. The process includes destabilisation of the crude oil with precipitation of asphaltenes and 'gravity segregation' at the base of the oil pool, and is one of the possible mechanisms for formation at tar mats near the oil-water contact (Dahl & Speers, 1986). An additional factor for the deasphalting may be a pressure decline due to uplift.

Water washing

Alteration by water washing takes place in the reservoir or in the migration conduit when the oil is in contact with meteoric water or circulating basinal brines. During this process light hydrocarbons are washed or flushed away in amounts which are roughly proportional to their solubility in the actual formation water. Generally solubility increases with decreasing carbon number, ring formation, branching and unsaturation (Lafargue & Barker, 1988). A water-washed crude therefore has a relatively low gasoline-range content, a low content of aromatics, an intermediate content of naphthanes, a high content of *n*-alkanes and asphaltenes, and a high gravity. The ultimate product of water washing may be an asphaltene-rich bitumen, e.g. at the bottom of the oil pool near the present or palaeo oil-water contact (tar mats).

Biodegradation

Biodegradation of petroleum is a widespread phenomenon in nature and takes place at or near the surface and also in deeper reservoirs with a gradually decreasing effect down to temperatures of about 60°C. The maximum temperature of biodegradation that has been detected is about 80°C. The microorganisms that grow on hydrocarbon substrates include both aerobic and anaerobic bacteria, fungi and yeast, with the bacteria being the most effective. The microorganisms are brought into contact with the oil through surface (meteoric) water that also carries dissolved oxygen and additional nutrients (N, P).

During biodegradation compounds are selectively attacked, during the first stages simple *n*-alkanes are removed, later branched saturates and aromatics are removed. During strong biodegradation polycyclic hydrocarbons like steranes and hopanes are altered, and the residual material consists mainly of asphaltenes. This selective removal of compounds may be used to establish a detailed ranking of biodegradation as suggested by for example Seifert & Moldowan (1979), Connan (1984), Volkman *et al.* (1984) and is shown in a simplified version for the Greenland samples in Table 3. The changes in bulk chemical composition and physical properties are shown in Table 1.

Inspissation

This process includes drying and thickening of bitumen by surface evaporation, first of gasses and then of progressively heavier compounds. Inspissation is of little importance in surface material compared to other processes, especially in cold climates like Greenland.

Oxidation

In addition to oxidation by biological processes abiogenic oxidation may occur. The processes involved are little understood and probably of limited importance since crude oils occurring at surface conditions are usually strongly degraded by other processes.

Terminology

Due to the long history of exploitation of bitumen and studies related to petroleum exploration a complex variety of terms has developed, many of which have only been used locally.

Many attempts of classification systems have been published. The traditional schemes are purely generic and based on parameters like solubility, fusibility and H/C ratios (Fig. 2) (see Hunt *et al.*, 1954; Abraham, 1960; Rogers *et al.*, 1974; Hunt, 1979). A classification system, much inspired by the German tradition of coal petrography and using reflectance and fluorescence values of polished samples, has been developed by Jacob (1967, 1983) (Table 3). More recent genetic classifications have been suggested using sophisticated geochemical methods like GC/MS (Curiale, 1986) (Fig. 3).

Bitumen should first be distinguished from crude oil (light to intermediate, heavy, extra heavy) on the criteria viscosity and gravity (Table 2, see details in Cornelius (1984)). Further subdivision into bitumen families and species may be carried out on the basis of physical properties and geochemistry (Table 3). Two bitumen families are recognized, the asphaltite family and the pyrobitumen family. The asphaltite family consists, in order to increase degradation, of asphalt, gilsonite, glance pitch, grahamite, and with strong thermal degradation also of epi-impsonite, meso-impsonite and cata-impsonite (Table 3). These are all suggested to be derived from asphaltite-rich oil and correspond to the 'post-oil bitumen' of Curiale (1986) (Fig. 3). The pyrobitumen family consists of ozocerite (+elaterite), würzilite and albertite and with strong thermal alteration also of the impsonites (Table 3). The name pyrobitumen is rather misleading and this family is suggested to have been derived directly from paraffinic-rich source rocks (oil-shales). It compares to the 'pre-oil bitumens' of Curiale (1986) (Fig. 3) or to the general term mineral waxes (Abraham, 1960).

A large number of other terms exist in the older or local literature (see review by Abraham, 1960). Montan wax, hatchetite, scheererite, liverite ("liquid wurtzilite"), ingramite, retinite, and ionite should all be classified within the pyrobitumen family, whereas Bermudez pitch, tabbyite, and argulite should be classified within the asphaltite family. Thucholite is a uraniferous bitumen, whereas antraxolite and shungite are coaly materials that resemble bitumen. Jet is black lignite (coal) of gemstone quality and is especially well known from the Yorkshire coast of north-east England.

In the previous studies of Greenland samples, the general term bitumen has been used for all products of once-liquid oil, more or less biodegraded and/or thermally altered, which was generated and migrated from a source rock (see Christiansen *et al.*, 1989). No previous attempts have been made to classify into bitumen species and instead the degree of biodegradation and thermal alteration has been interpreted directly from the analytical data (especially GC and GC/MS).

Examples from Greenland

Bitumen occurrences have been reported from most of the onshore sedimentary basins in Greenland (Fig. 4). They have typically been found during regional mapping campaigns, during detailed sedimentological analysis or during specific studies of hydrocarbon source and reservoir rocks including shallow core drilling. Systematic surface geochemical programmes (sniffing techniques or soil sampling with subsequent light gas analyses (see Philp & Crisp, 1982 for reviews) or metal and magnetic analysis magnetic analysis (e.g. Saunders *et al.*, 1991) have not yet been carried out in Greenland. However, a similar programme with Eh, Ph, light gas and metal analysis of near surface sediments from the shot holes used for a dynamite seismic survey has been tested by ARCO in parts of Jameson Land (confidential data).

Previous bitumen studies have concentrated on the description of geological relations; structure, reservoir and source rocks, diagenetic history etc. The analytical work which is described in the preceding section has mainly been LECO and Rock Eval pyrolysis followed by gas chromatography (GC). In a number of cases gas chromatography/mass spectrometry (GC/MS), carbon and sulphur isotope analysis, pyrolysis-GC; reflectance, and fluorescence measurements have also been applied. Bulk data such as Ni and V content, viscosity, pour point and API gravity have not yet been measured.

Selected field data, interpretation of thermal and biodegradation, Rock Eval, GC and reflectance data of samples from the various parts of Greenland are listed in Table 4. Rock Eval parameters are shown in Figs 5 and 6, extraction data in Fig. 7, selected GC data in Fig. 8, and selected GC/MS data in Fig. 9.

North Greenland

Most of the previously reported bitumen occurrences are from the Early Palaeozoic Franklinian basin in North Greenland which due to a typical foreland setting in its late history and considerable uplift is an expected site for solid bitumens. The solid bitumens and seep material have been described in some detail by Christiansen *et al.* (1989) and considered further by Jakobsen & Omoto (1993). The bitumens occur in close association with either Cambrian or Silurian source rocks or as a result of long-distance migration in Cambrian strata in the southern part of the basin. Most of the bitumens found near the source rocks have a relatively high thermal maturity similar to that of the nearby source rocks. The bitumen mainly occurs as solid black material which fills vugs in carbonates or as fine-grained residue in limestones and sandstones.

The long-distance migrated bitumens in the southern part of the region have not been thermally altered and biomarker data suggest peak generation conditions. They are recognized in dark oil-stained sandstones or limestones, as dark vug-filling material in limestones or dolomites, and in one case as black asphalt seeping from a vein.

Bitumens and seeps have not yet been reported from sediments in the Late Palaeozoic to Mesozoic Wandel Sea basin.

North-East Greenland

Bitumens and seeps have been reported a number of places in North-East Greenland, either in uplifted and eroded sediments from the Late Palaeozoic to Mesozoic rift basins, in Tertiary basalts, or in fault zones in the basement (Fig. 4, Table 4).

During the summer of 1990 an oil seep was discovered in a mineralized breccia in Germania Land. The geochemistry of this seep using TOC, Rock Eval pyrolysis, GC, py-GC and GC/MS is described in detail by Christiansen *et al.* (1991).

Black solid bitumens occur in carbonate-filled veins in both Middle and Upper Devonian sandstones in Gauss Halvø. These bitumens have been generated from nearby saline (Middle Devonian) and freshwater (Upper Devonian) lacustrine source rocks (Christiansen *et al.*, 1990a, unpublished GC/MS data).

The Upper Permian carbonates on Gauss Halvø contain solid black bitumen and Triassic sandstones from the same area are impregnated with oil; in both cases unpublished GC/MS data clearly suggest the Upper Permian Ravnefjeld Formation as source rock (see Fig. 9).

Pale oozing material has been reported from partly agate filled cavities in Tertiary basalts on Hold-with-Hope (W.S. Watt, personal communication 1989). Gas chromatograms of this material indicate a high degree of biodegradation.

Highly coalified residual material (R_o > 4%) has been reported from Laplace Bjerg, Geographical Society Ø where a 'palaeo oil accumulation' at least 35 m thick was observed in Jurassic sandstones unconformably overlain by Cretaceous shales (Marcussen *et al.*, 1987). This locality, and a locality in a similar setting in Mols Bjerge on Traill Ø have been mentioned by the CASP in an unpublished report.

High coalified organic matter (R_o> 2.5%) has also been reported from a dolomite bed in the Gråklint Beds of the Gipsdalen Formation in Mols Bjerge on Traill Ø. This solid bitumen occurs in vugs partly filled with millimetre- to centimetre-sized crystals of dolomite, calcite and quartz (Marcussen *et al.*, 1987).

East Greenland

Bitumens and seeps have been reported several places in East Greenland in connection with ARCO's oil exploration in Jameson Land and GGU's oil-related studies of the region. Most of the observations are from uplifted and exposed sediments of the Late Palaeozoic–Mesozoic rift basin, with some records from Tertiary basalts or Quaternary sediments overlying this basin.

Solid black bitumen is very common in vugs and fractures in Upper Permian carbonates on Wegener Halvø (Stemmerik *et al.*, 1989; Scholle *et al.*, 1991). These bitumens represent relics of hydrocarbons which were generated from the closely associated Upper Permian Ravnefjeld Formation source rocks. The hydrocarbons were generated in the Late Cretaceous time and altered by hot hydrothermal fluids (Stemmerik, 1991). The Upper Permian sediments in this area are thermally postmature with vitrinite reflection values between 1.4 and 1.8% (Christiansen *et al.*, 1990b).

The sandstones of the Kap Stewart Formation occasionally contain highly coalified bitumen. In Horsedal (northern Jameson Land) an at least 7 m thick impregnated zone near a Tertiary sill was noted by G. Dam. All the primary pore porosity is plugged by a complex intergrowth of graphite and illite (F. C. Mengel, personal communication, 1991).

Oil-stained sandstones have been discovered in several of GGU's shallow core wells penetrating the organic-rich Upper Jurassic Hareelv Formation (Piasecki, 1987). These interlayered black shales and sandstones have been studied in detail by Requejo *et al.* (1989) using various organic geochemical methods. The oils in the sandstone were generated from the associated shales, probably at some distance down-dip.

Coarse grained sandstones with a petroliferous odour have been found in the Jurassic Charcot Bugt Formation in Milne Land (M. Larsen, personal communication 1994). This impregnation has so far not been confirmed by analytical work.

Tar-like material has been found on a Tertiary basalt block on Savoia Halvø south of Scoresby Sund (Watt & Wrang, 1984). This material is severely biodegraded but C-isotope and py-GC data are in accordance with an Upper Jurassic source rock (Requejo *et al.*, 1989).

A gas seep has been recorded by ARCO in Colorado Dal in central Jameson Land (ARCO confidential reports). Only little analytical data is available due to contamination of samples. Measurements of the isotopic composition of the methane suggest a thermogenic origin.

Oil seepage has also been mentioned, but not confirmed by GGU, in the Caledonian basement in Stauning Alper west of Jameson Land (C. Harris, RTZ, personal communication to H. K. Schønwandt, 1992).

West Greenland

Several old observations on oil and gas seepage in the Nuusssuaq and Svartenhuk Halvø area have been mentioned already by Rosenkrantz *et al.*, (1942, p. 42), Mikkelsen

(1954, 1993), and Rosenkrantz (1962, p. 271). These descriptions and other local rumours on oil seepage have been difficult to confirm and see in a petroleum geological context prior to 1992 when the first indications of the Marraat seepage were found on the south-west coast of Nuussuaq. Results from the field work and drilling in 1993 and subsequent analytical programme are not included in this report. The reader is referred to Christiansen (1993), Christiansen *et al.* (1994a,b,c,d) and Dam & Christiansen (1994) for further details on the history, organic geochemistry and implications of the Marraat oil.

Prior to the Marraat discovery only a few solid bitumens or carbonaceous residues have reported from the Cretaceous-Tertiary onshore basin in West Greenland. One sample (GGU 49759) of bitumen-impregnated brecciated sandstone was collected from non-marine Upper Cretaceous sandstones on the island Qeqertarssuaq by G. Henderson in 1963 (Henderson, 1969). The locality was revisited and resampled by G. Henderson and N. B. H. Stevens in 1971 and the petrography of the sandstones was described by Stevens *et al.* (1974). Highly coalified carbonaceous residue has also been reported from a hydrothermal vein cross-cutting basaltic flows in the Marraat Killiit area on Nuussuaq (Pedersen, 1986). Escape of gas has been observed in a mud volcano in the Auvfarssuaq valley on Nuussuaq. Analyses of gas and water samples collected by A. Rosenkrantz (published in Henderson, 1969) show high contents of methane and an enrichment of noble gases. The mud volcanoes are being studied in further detail during the current field campaign (Christiansen, 1993), and a modern analytical programme is under completion.

South Greenland

Solid bitumen has been mentioned from the Ilímaussaq intrusion in South Greenland (Steen Andersen, personal communication, 1993). Such material is typical in uraniferous deposits and is probably not related to petroleum generated from a source rock.

Offshore

Marine oil seeps have not yet been recognized offshore Greenland. However, systematic geochemical surveys with airborne 'sniffers' or laser fluorescence have not been carried out. It should be noted that an oil seep has been recognized offshore Baffin Island (MacLean *et al.*, 1981; Levy & MacLean, 1981). This seep is close to onshore areas with

Cretaceous-Tertiary sediments and in a tectonic setting comparable to the Svartenhuk-Melville Bugt region on the opposite side of Baffin Bay.

Geochemistry

The aim of the organic geochemical studies carried out on bitumens from Greenland has been to assess the intensity of thermal alteration and biodegradation, and if possible to obtain parameters applicable to correlation with a possible source rock.

For screening purposes Rock Eval pyrolysis has provided important data especially on thermal alteration. Although bitumen-impregnated source rocks should be avoided or treated with care using these data (Clementz, 1979; Christiansen *et al.*, 1989), T_{max} values, Production Index (S_1/S_1+S_2), and Hydrogen Index (S_2/TOC or HI′ = S_1+S_2/TOC) are applicable for maturity ranking (Fig. 6). T_{max} values of the least altered material is below 415°C and many oil stained samples have values between 420° and 430°C. The associated Production Index values are high (0.2-0.5). Also the Hydrogen Index values are high, but probably not always reliable due to analytical problems with obtaining accurate TOC values (loss during preparation). With increasing thermal alteration well defined trends are observed in the T_{max} versus PI, T_{max} versus HI, and PI versus HI cross plots (Fig. 6), in principle comparable to source rock trends. Moderately to strongly thermally altered samples have T_{max} > 480°C, PI < 0.2 and HI < 150.

The separation of extracts into fractions (saturated and aromatic hydrocarbons, NSO-compounds, and asphaltenes) provides a good preliminary estimate of the biodegradation. The hydrocarbons (especially the saturated) are easier degraded than other compounds and during progressive degradation the material is relatively enriched in NSO-compounds and asphaltenes (Fig. 7). The degradation trend in this triangular diagram however depends on the primary composition. As an example both the North Greenland samples and the Upper Jurassic samples from Jameson Land have a relatively low saturated:aromatic ratio compared to for example the Devonian samples from North-East Greenland (Fig. 7).

The gas chromagrams of the saturated hydrocarbons may be tentatively used for classification of the intensity of biodegradation (Fig. 8, Table 4). Especially the relative abundance of *n*-alkanes and isoprenoids is important, and with more intense biodegradation where these compounds have been lost, the shape of the 'naphthenic humps' and possible resolved biomarkers provide possibilities for evaluation of biodegradation (Fig. 8).

GC/MS analysis of saturated hydrocarbons, especially of the m/z 191 and 217 which provide data on terpane and sterane distributions, is important for bitumen-source rock correlations. Only severe biodegradation alters the sterane and hopane distribution, as is the case with the Germania Land and the Savoia Halvø seeps.

Correlation studies to either a known source rock or an inferred source rock (information on depositional environment) using biomarkers have been successfully carried out on Cambrian and Silurian bitumens from North Greenland (Christiansen *et al.*, 1989), Devonian-Carboniferous-Permian-Triassic bitumens in North-East Greenland (Christiansen *et al.*, 1990, unpublished data, see also Fig. 9), and Jurassic oil stains in Jameson Land (Requejo *et al.*, 1989).

Future studies of seeps and bitumens in Greenland

All the previous studies of seeps and bitumens in Greenland which are reviewed in this report are based on material which has been observed with the naked eye, either in the field or under the microscope. This sort of work, which typically is combined with general oil-related studies (sedimentology, stratigraphy, mapping), is expected to continue in the coming years, especially in the Disko-Nuussuaq-Svartenhuk Halvø region in West Greenland and during specific oil-related studies in Jameson Land and in the Wandel Sea Basin in North Greenland.

It may be that systematic geochemical surveys of microseepage will be successfully applied during future exploration in on- and offshore basins in Greenland. Some of the techniques involved are relatively cheap to use in Greenland where the remoteness and harsh environments make drilling operations in particular very costly.

Most onshore areas are well exposed with only little Quaternary cover and vegetation, and there is a very limited risk of contamination from introduced material (roads, building material, storage tanks etc.). Consequently remote sensing systems (especially infrared spectroscopy showing coloured haloes) and airborne sensor systems (especially light hydrocarbon detection and magnetics) have a strong potential. Sampling programmes of surface soils and water could be effective but they are expensive due to logistic difficulties. In particular, analysis of light gases, including their isotopic composition, and content of selected trace metals is likely to provide useful data.

In the offshore areas the use of geochemical methods are most promising in areas where conventional seismic data or shallow geophysical data (eccosoundings, side scan sonar, boomer, pinger etc.) indicate abnormal features (gas in sediments, minor buildups, pockmarks or bubbles in the water column). Furthermore major faults or areas on top of major structures with a possible trapping configuration for hydrocarbons are likely targets for beginning geochemical surveys, e.g. by airborne laser fluorosensor.

A subsequent sampling programme, both at sea bed and at water surface, should be carried out in any area with geochemical anomalies. Under the present economic climate, where the oil industry desperately tries to reduce the risk of their operations, geochemical surveys are likely to take place early in an exploration phase before costly drilling.

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Table 1. Changes in physical properties and geochemistry during progressive degradation

	Thermal alteration and deasphalting		Water washing	Biodegradation	Inspissation and oxidation
	(oil)	(residue)	(residue)	(residue)	(residue)
Carbon numbers	↘	(–)	↗	↗	↗
Sa / aro	↗		↗	↘	↘
Hc / non-Hc	↗	↘	↘	↘	↘
asphaltenes	↘	↗	↗	↗	↘
H / C	↗	↘	↘	↘	↘
S, Va, Ni	↘	↗	↗	↗	↗
pour point	↘	↗	↗	↘	↗
density	↘	↗	↗	↗	↗
viscosity	↘	↗	↗	↗	↗
solubility	↗	↘	↘	↘	↘
volatiles	↗	↘	↘	↘	↘
reflection	–	↗	–	(↗)	(↗)
fluorescence	–	↘	–	↘	↘
$\delta^{13}C$ whole oil / bitumen	↗	–		↗	↗
sa	↗	–		↗	↗
ar	–	–		–	↗
asphalt	–	–		↘	–

Other properties which change during strong degradation (solid bitumens): colour, streak, lustre, hardness, fracture pattern, feel, odour, fusibility.

Other properties which change during early degradation (still in the liquid stage): many different specific compound ratios from GC and GC/MS, functional group ratios from IR and NMR.

Table 2. Classification of crude oils versus bitumens

		Viscosity[1] (pas)	Density (g/cm^3)	API gravity (°)
CRUDE OIL	light to intermediate	<10	<0.934	>20
	heavy		0.934-1	20-10
	extra heavy		1-1.029	10- 6
BITUMEN		>10	>1.029	<6

[1] Viscosity measured at 37.8°C (100°F) for degassed material.

Modified from Cornelius (1987).

Table 3. Classification of bitumen species in the asphaltite and pyrobitumen family on the basis of physical properties and H/C ratio

	Reflection (%)	Fluorescence (%)	Solubility[1] (%)	Volatile matter[2] (%)	H/C[3]
Asphaltite family					
Asphalt	0.02 - 0.07	4 - 0.4	>90	>90	~1.5
Gilsonite	0.07 - 0.1	0.4 - 0.05	>90	90-80	~1.4
Glance pitch	0.1 - 0.3	<0.2	>90	80-65	~1.2
Grahamite	0.3 - 0.7	<0.05	90-20	65-45	~1.0
Epi-impsinite	0.7 - 2.0	<0.02	<10	45-20	~0.8
Meso-impsinite	2.0 - 3.5	0	0	20- 8	~0.6
Cata-impsinite	3.5 - 6(10)	0	0	8- 1	~0.4
(Graphite)	> 6(10)	0	0	<1	~0.1
Pyrobitumen family					
Ozocerite + Elaterite	< 0.1	30-1	highly variable	>95	~1.7
Wurzlite	< 0.1	2-0.1	<20	95-75	~1.4
Albertite	0.1 - 0.7	<0.1	<10	75-50	~1.1
Epi-impsinite	> 0.7	<0.01	<10	50-20	~0.8

[1] Solubility in CS_2 (weight %).

[2] Volatiles at 900°C (weight %).

[3] Typical H/C values, no clear separation.

Modified after various sources, especially Jacob (1975, 1983) and Cornelius (1987).

[1]Thermal maturity of bitumen

= sum of source rock history prior to migration + reservoir history after trapping

IM	immature	(hopanes not in equilibrium);
EM	early mature	(hopanes in equilibrium, steranes not in equilibrium);
M	mature	(steranes in equilibrium);
PM	postmature	(biomarkers not present, $R_o > 1.3$).

[2]Biodegradation of bitumen

limited	*n*-alkanes unaltered;
slightly	*n*-alkanes partly removed;
moderate	*n*-alkanes completely removed, but isoprenoids present;
strong	isoprenoids complete removed, biomarkers present;
severe	steranes and hopanes altered.

Table 4. Bitumen samples from Greenland with information on lithostratigraphy, host rock lithology, appearance, thermal maturity and biodegradation

GGU No.	Unit	Host rock	Appearance	Thermal maturity[1]	Biodegradation[2]
North Greenland					
324200	Portfjeld Fm	carb	black, seeping/solid	M	slightly-strong
322102	Buen Fm	sst	brown staining	M	moderate
322205	Buen Fm	sst	brown staining	M	slightly
324453	Buen Fm	sst	brown staining	M	
315172	R G Gp	sst	black staining	M-(PM)	slightly-moderate
315199	R G Gp	carb	black solid	M	strong
317378	R G Gp	sst	black staining	M	strong
322117	R G Gp	sst	black staining	M	strong
315857	Aft. Fm	carb	black staining	M-PM	limited
324337	Aft. Fm	carb	black solid	PM	slightly
324256	H G Fm	sst	dark staining	M-PM	
324269	H G Fm	sst	dark staining	PM	
324309	H G Fm	sst	dark staining	M-(PM)	slightly
324343	H G Fm	sst	dark staining	PM	
324355	H G Fm	sst	dark staining	PM	limited
316055	W L Gp	carb	black solid	M	moderate-strong
316067	W L Gp	carb	black solid	M	slightly
Gauss Halvø, North-East Greenland					
289809	M. Dev.	carb/sst	black solid	M	limited
289810	M. Dev.	carb/sst	black solid	M-PM	limited
289811	M. Dev.	carb/sst	black solid	M-PM	limited
289814	M. Dev.	carb/sst	black solid	M	limited
289815	M. Dev.	sst/carb	black solid	M-PM	limited
289816	M. Dev.	carb/sst	black solid	M-PM	limited
289817	M. Dev.	carb/sst	black solid	M-PM	limited
289890	M. Dev.	sst/carb	black solid	M	limited-slightly
289891	M. Dev.	sst/carb	black solid	PM	
289900	U. Dev.	carb/sst	black solid		limited
291202	U. Dev.	sst	black solid	PM	limited
Germania Land, North-East Greenland					
365085	basement	breccia	dark oozing	M	strong-severe
365091	basement	breccia	dark oozing	M	strong-severe
Savoia Halvø, central East Greenland					
215848	Tertiary	basalt	dark oozing	M?	severe
Hold with Hope, North-East Greenland					
194161	Tertiary	basalt	pale oozing	M?	strong
Sjællandselv, Jameson Land					
303114	U. Jurassic	sst	dark staining	M	moderate-strong
303115	U. Jurassic	sst	dark staining	M	moderate-strong
303116	U. Jurassic	sst	dark staining	M	moderate-strong

Table 5. LECO, Rock Eval, extraction and reflection data of bitumen samples from Greenland

	LECO - Rock Eval								Extraction				
GGU No.	TIC %	TOC %	T_{max} °C	S1 mg/g	S2 mg/g	PI	HI	HI'	SOM ppm	Sa %	Ar %	non-HC %	R_o %
324200													0.10
322102	0.27	0.83	427	2.72	6.09	0.31	734	1061	8560	13	18	69	0.11
322205	1.90	0.97	423	3.09	4.43	0.41	457	775	11070	12	10	78	0.20
324453	0.19	0.81	427	3.40	4.72	0.42	583	1002					
315172	2.19	0.25	440	0.77	1.54	0.33	616	924	980	23	24	53	0.43
315199	12.59	0.79	429	3.80	7.51	0.34	950	1432	11645	19	21	60	0.18
317378	2.24	1.85	428	2.51	10.78	0.19	583	718	10350	5	9	86	0.16
322117	0.51	2.26	429	2.78	11.88	0.19	526	649	14250	4	13	83	0.16
315857	8.47	0.71	425	0.45	1.19	0.27	168	231	940	26	43	31	0.84
324337	8.26	2.45		0.05	0.22	0.19	9	11	1070	46	21	33	
324256	4.69	0.24	445	0.01	0.16	0.06	66	71					
324269	3.46	0.66	459	0.27	0.55	0.33	83	124					
324309	2.73	0.66	428	1.28	1.52	0.45	230	417	1600	33	28	39	1.19
324343	2.85	0.61	482	0.08	0.26	0.24	43	56					
324355	3.26	0.63	453	0.40	0.80	0.33	127	190	1710	67	18	15	1.41
316055	11.58	0.88	429	1.94	4.97	0.33	565	785	6850	8	20	70	0.59
316067	11.01	2.11	437	3.18	25.20	0.11	1194	1567	14490	5	23	72	0.16
289809	9.34	1.06	443	1.54	4.00	0.28	337	523	1650	71	12	17	
289810	8.61	0.34	454	0.24	0.70	0.26	206	276	655	54	27	19	
289811	5.12	0.15	459	0.05	0.20	0.20	133	167	188	55	16	29	
289814	7.25	1.55	458	1.54	3.20	0.32	206	306	2255	71	9	20	
289815	5.78	0.20	460	0.06	0.20	0.23	100	130	430	72	4	24	
289816	9.26	0.49	460	0.18	0.70	0.20	127	180	475	63	11	26	
289817	11.19	0.91	450	0.24	1.60	0.13	176	202	472	55	11	34	
289890	4.21	0.53	437	0.86	1.30	0.40	245	408	72	13	15	72	
289891	3.93	0.27	499	0.00	0.10	0.00	37	37	73	4	19	77	
289900	8.17	0.52	504	0.02	0.02	0.09	38	42	2173	60	14	26	
291202	1.66	0.12	437	0.07	0.10	0.41	83	142	345	55	15	30	
365085 (B163)	low	0.55	411	4.88	1.18	0.81	216	1101	9700	32	19	49	
365085 (B164)									10100	32	18	50	
365085 (B165)									2800	33	18	49	
365091 (B166)									20700	38	19	43	
215848	low								1498	17	22	61	
194161													
303114-09 (10.56)	low	0.69		0.78	0.93	0.46	135	248	4803	25	11	62	0.62 (vit)
303115-22 (29.41)	low	0.64		1.50	0.93	0.62	145	342	3813	32	40	28	0.63 (vit)
303116-28 (18.60)	low	0.55		2.07	1.01	0.67	184	560	4581	30	34	36	0.61 (vit)
303116-29 (19.04)	low	0.56		1.65	1.21	0.58	216	511	4276	31	38	31	0.61 (vit)
303116-30 (20.51)	low	0.76		3.33	2.43	0.58	320	758	7185	29	34	37	0.61 (vit)
303116-11 (18.79)	0.28	0.37		4.55	1.13	0.80	305	1535					

See Table 4 for geological details.

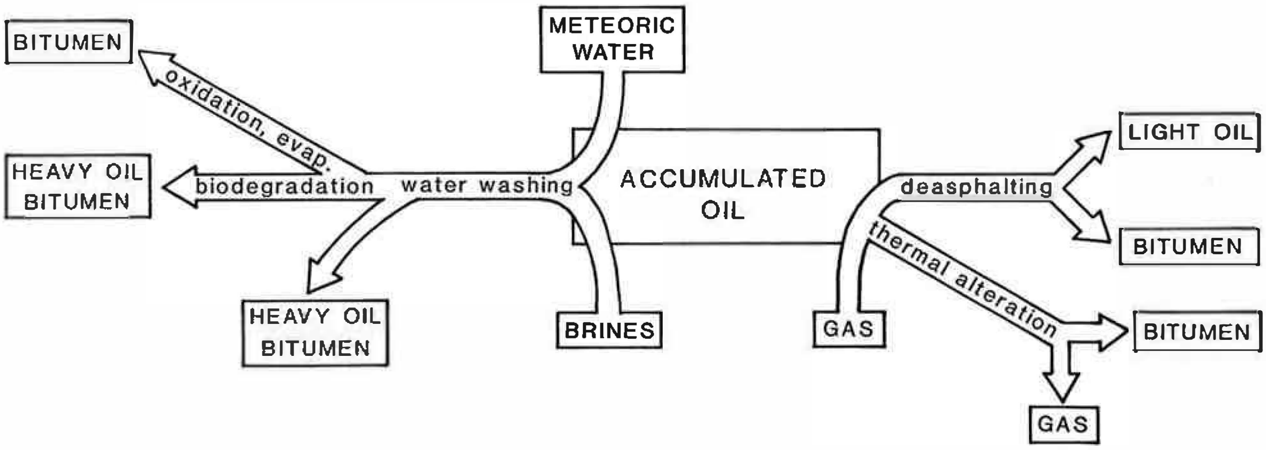

Fig. 1. Processes of degradation. Modified after Milner *et al.* (1977) and Connan (1984).

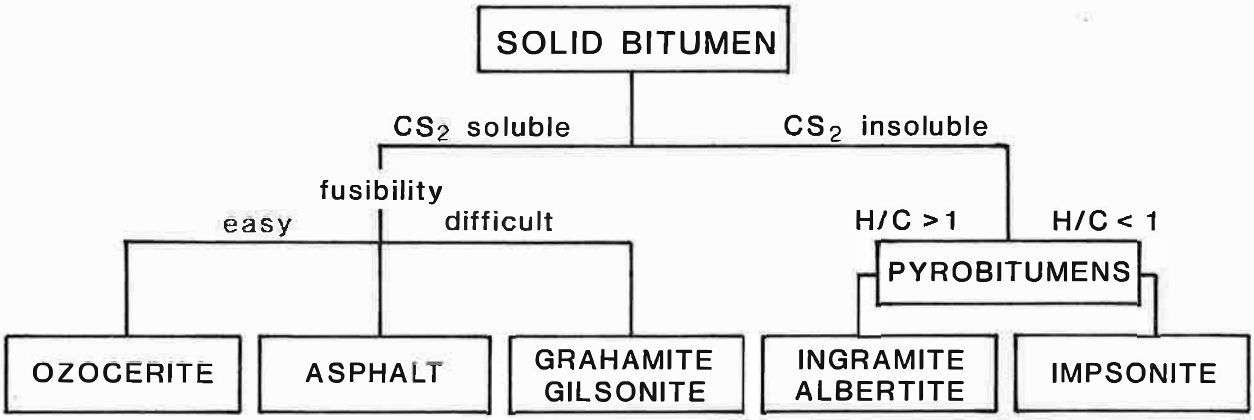

Fig. 2. Old generic classification. Modified after Abraham (1960).

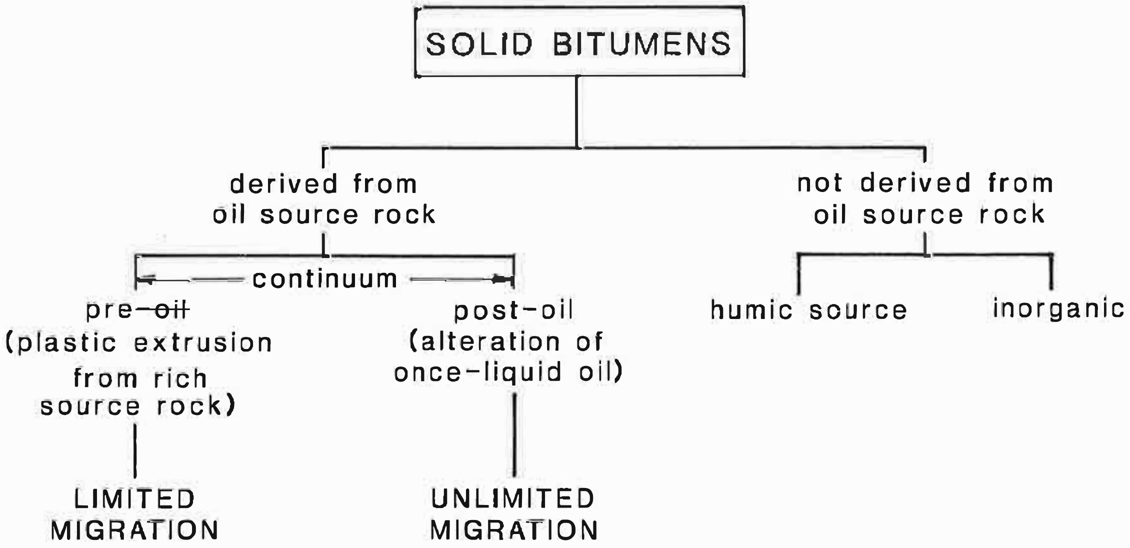

Fig. 3. New genetic classification. Modified after Curiale (1987).

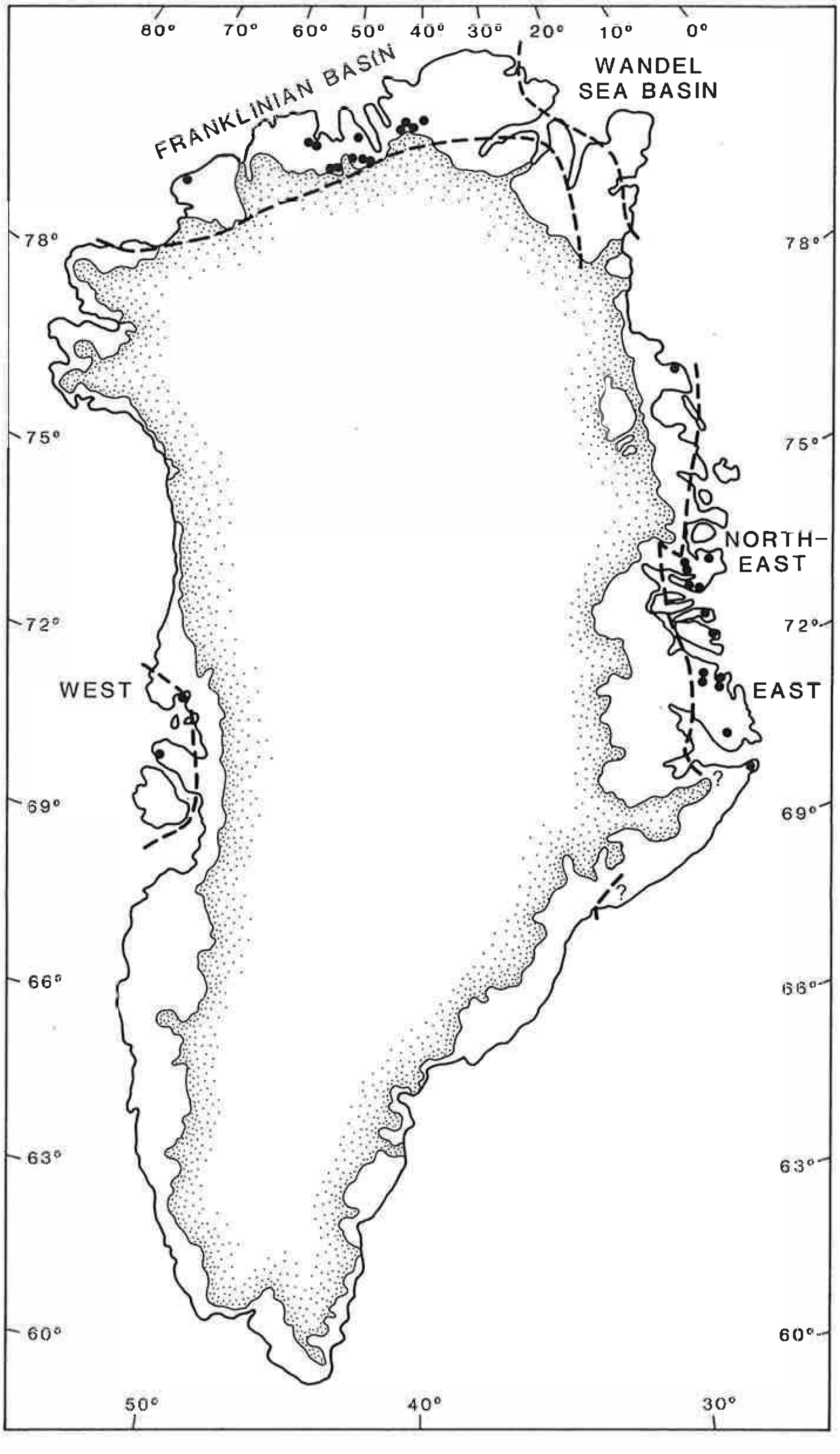

Fig. 4. Map showing sedimentary basins of Greenland and the location of seeps and bitumen occurrences.

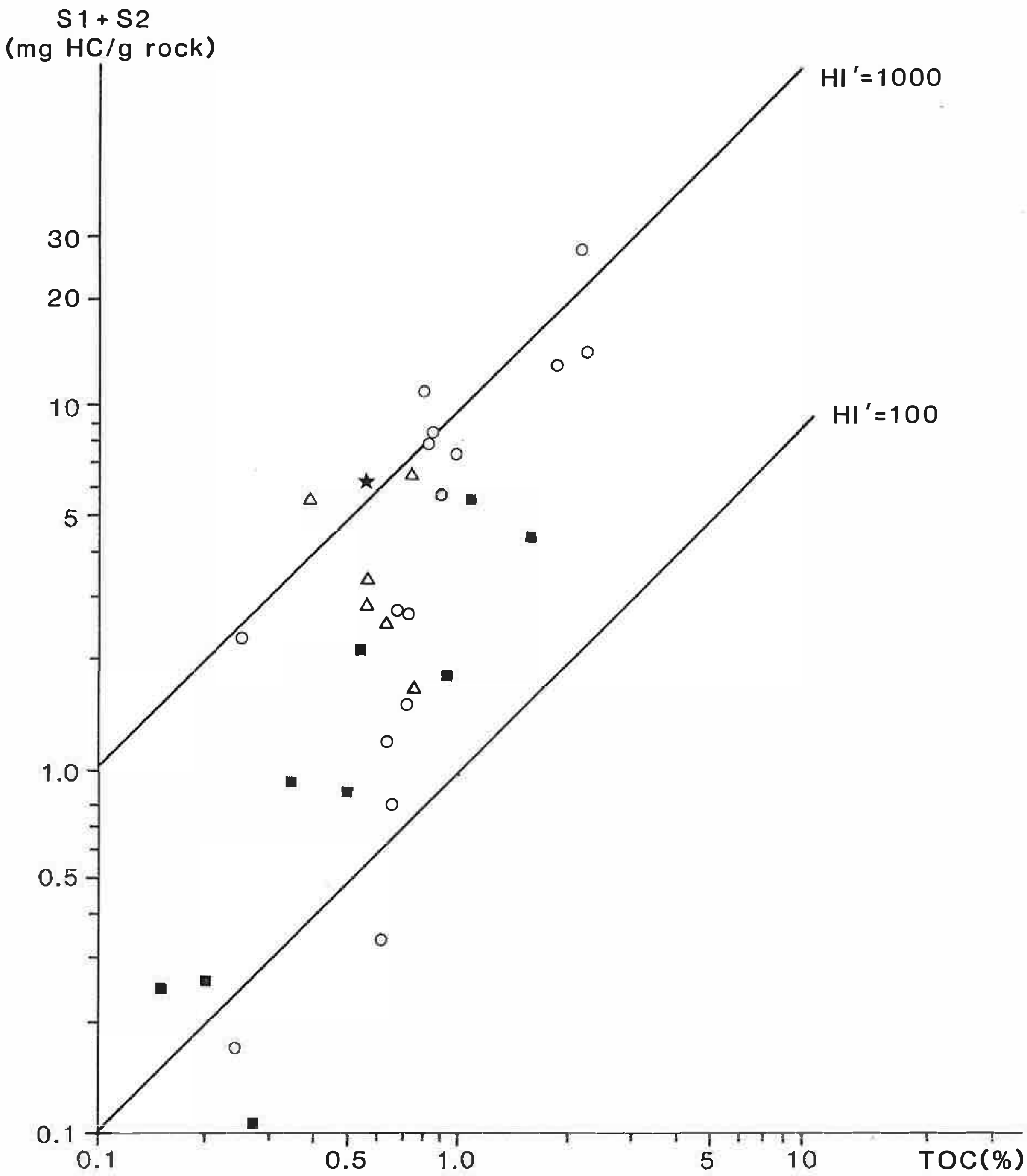

Fig. 5. Plot of TOC(%) vs S_1+S_2 (mg HC/g rock) of bitumen samples from Greenland. See Tables 4 and 5 for details. Open circles: North Greenland, filled squares: Gauss Halvø, North-East Greenland, filled stars: Germania Land, North-East Greenland, open triangles: Sjællandselv, Jameson Land, open star: Savoia Halvø, central East Greenland.

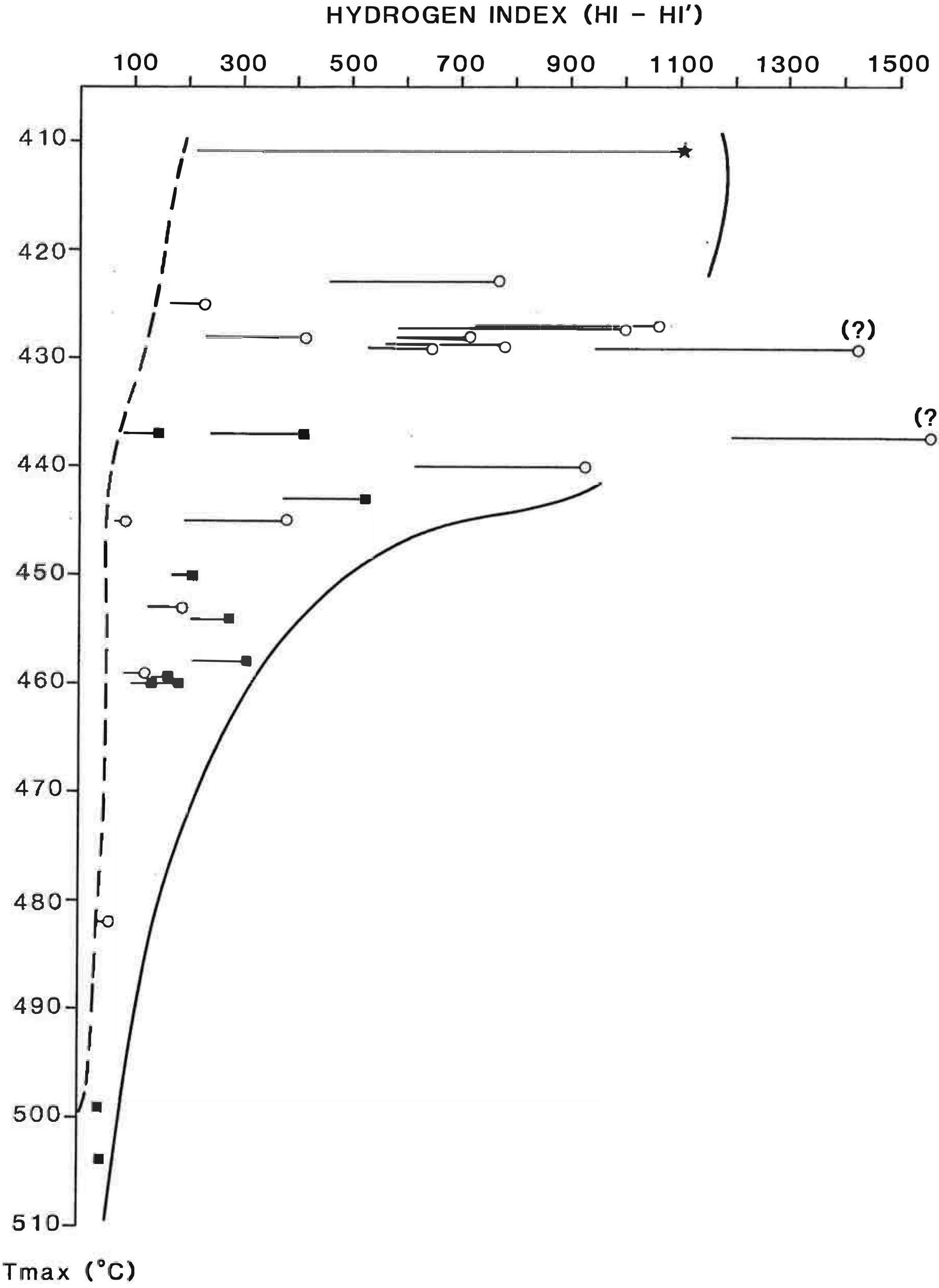

Fig. 6A. Plot of T_{max} versus Hydrogen Index (HI-HI'). Signatures like Fig. 5.

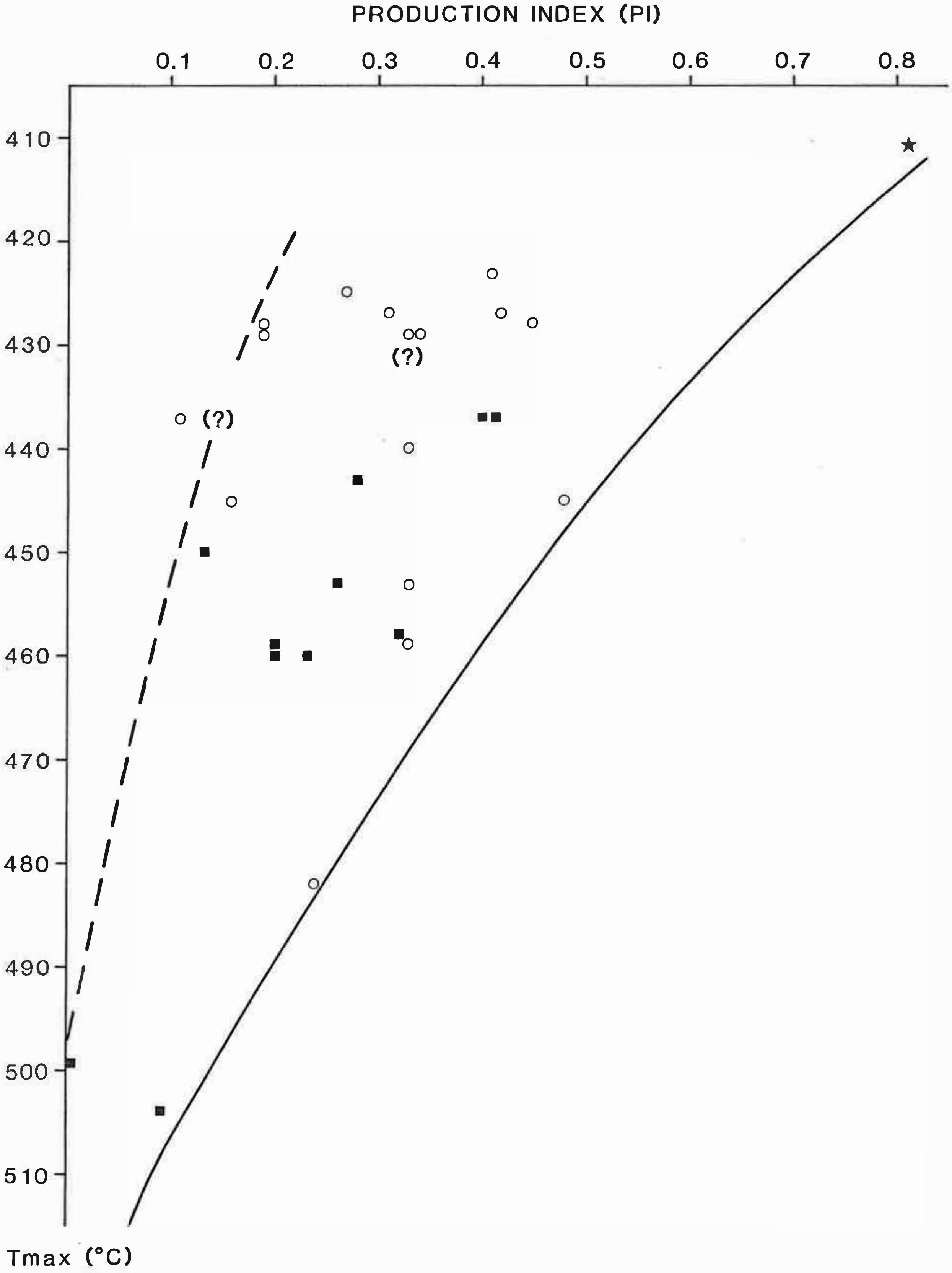

Fig. 6B. Plot of T_{max} versus Production Index (PI). Signatures like Fig. 5.

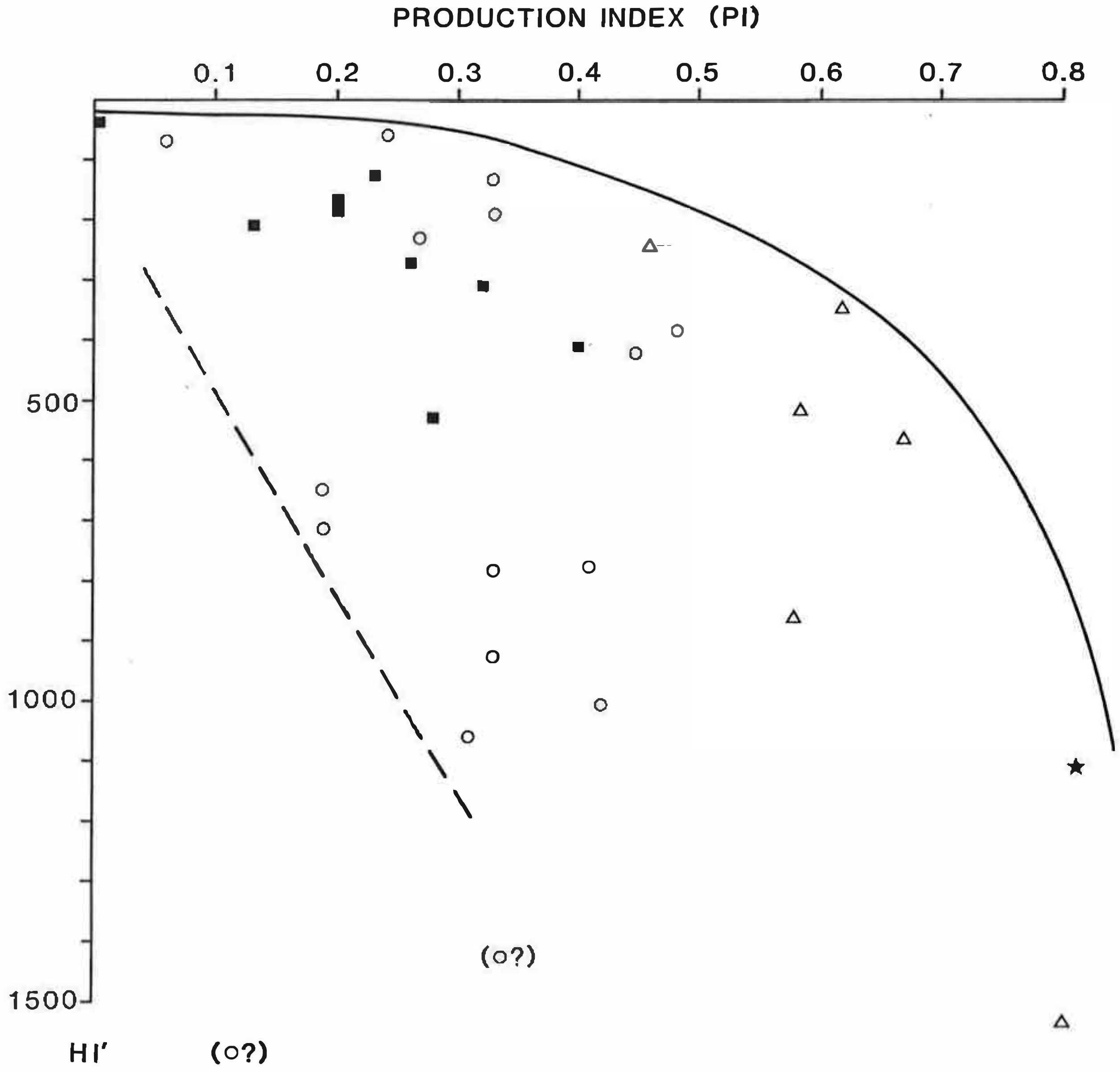

Fig. 6C. Plot of PI versus HI'. Signatures like Fig. 5.

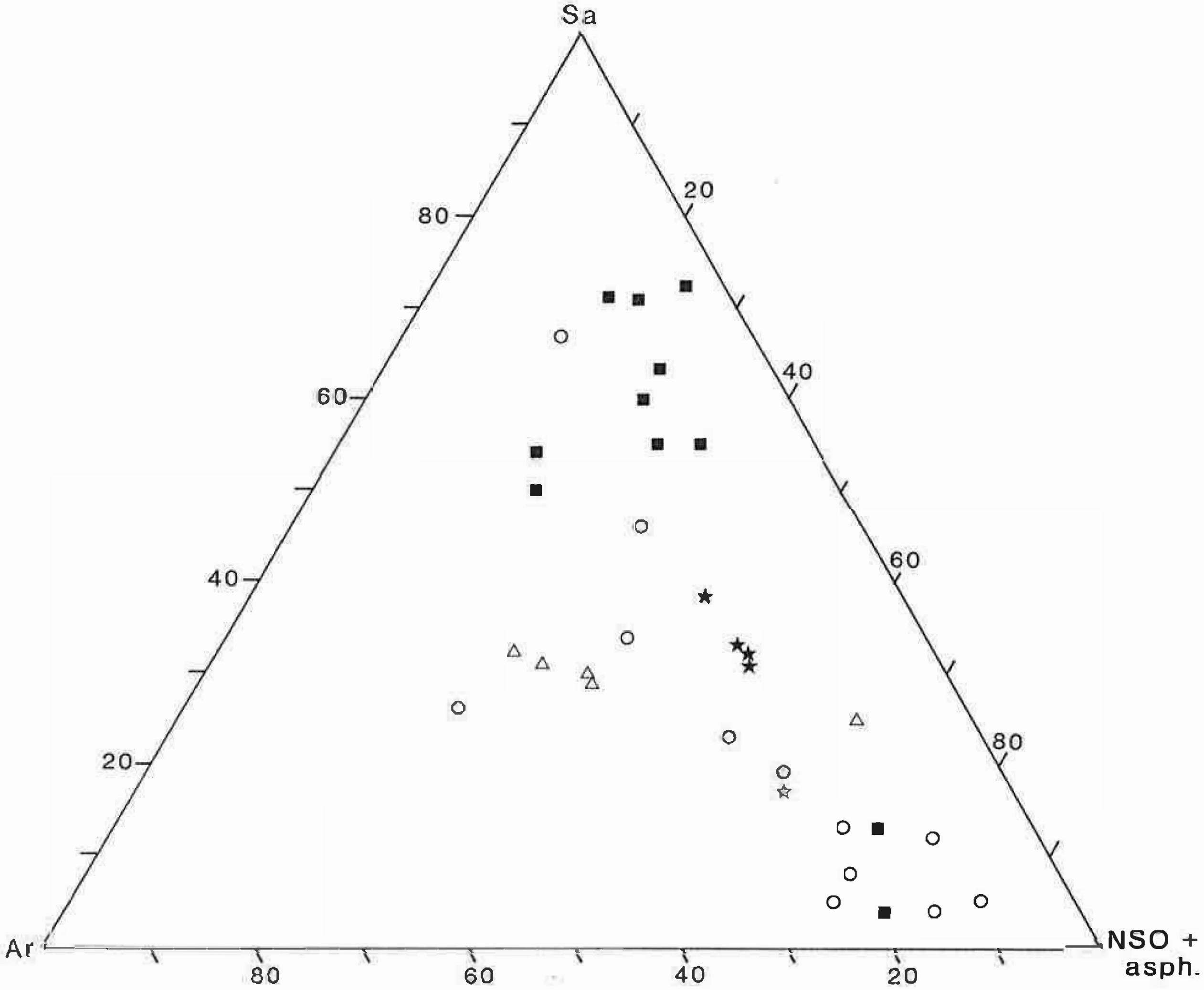

Fig. 7. Triangular diagram showing relative extract composition of saturated hydrocarbons (%), aromatic hydrocarbons (%) and NSO compounds + asphaltenes (%). The general diagram with typical compositions is modified after Tissot & Welte (1984) and Cornelius (1987). For details of Greenland samples, see Tables 4 and 5. Signatures like Fig. 5.

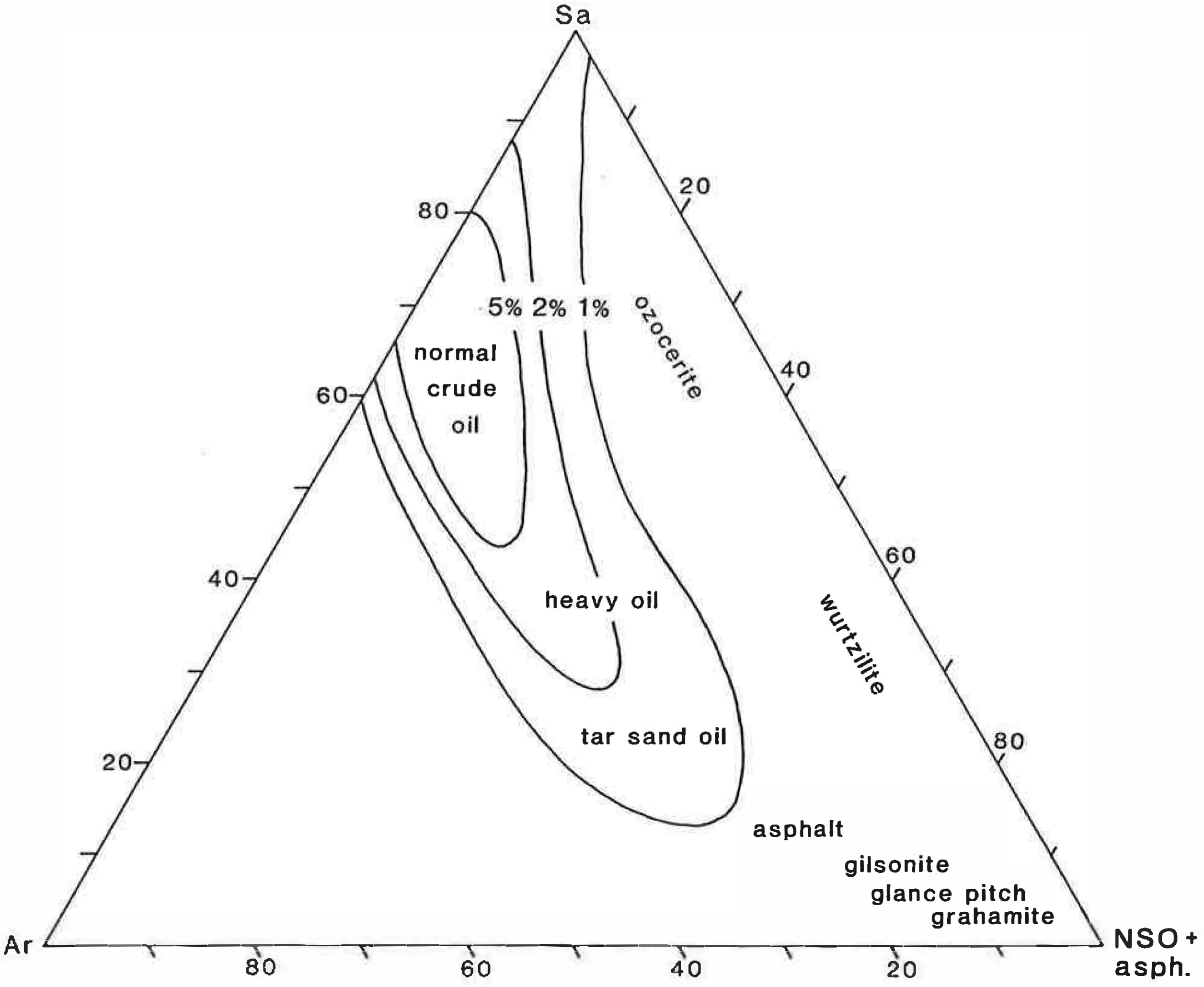

Fig. 7. Continued.

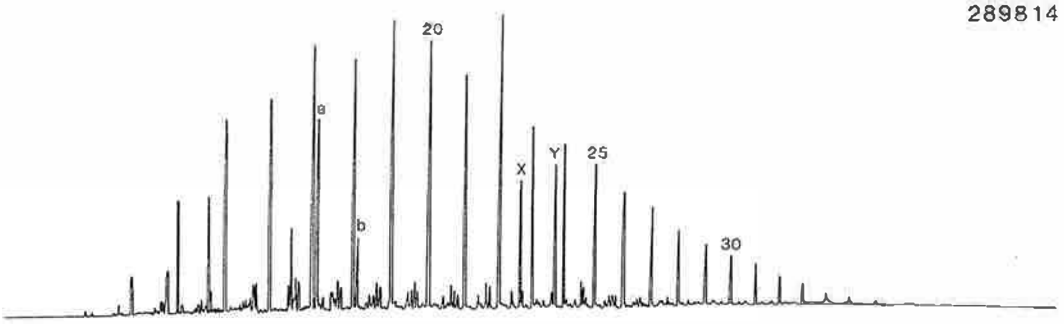

Fig. 8A. Selected gas chromatograms of saturated hydrocarbons from Greenland bitumen samples.
289814 Middle Devonian sandstone, Gauss Halvø.

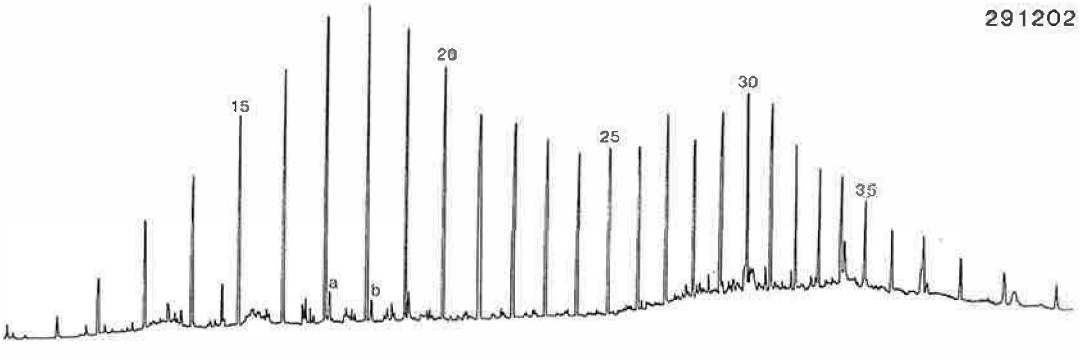

Fig. 8B. Selected gas chromatograms of saturated hydrocarbons from Greenland bitumen samples.
291202 Upper Devonian sandstone, Gauss Halvø.

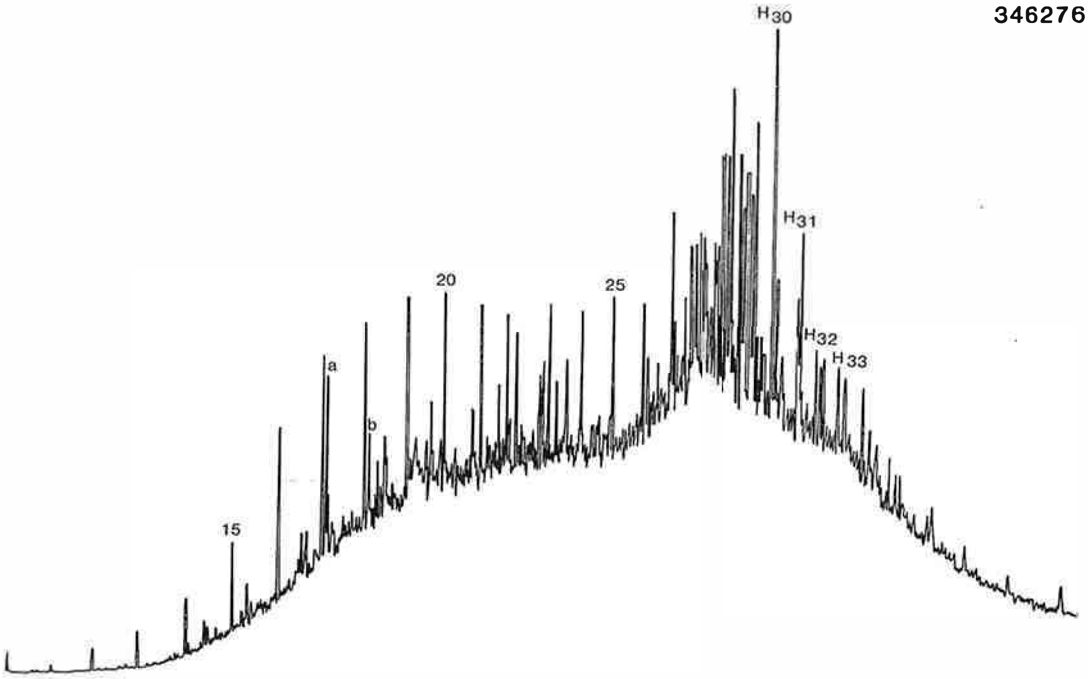

Fig. 8C. Selected gas chromatograms of saturated hydrocarbons from Greenland bitumen samples.
346276 Triassic sandstone, Gauss Halvø.

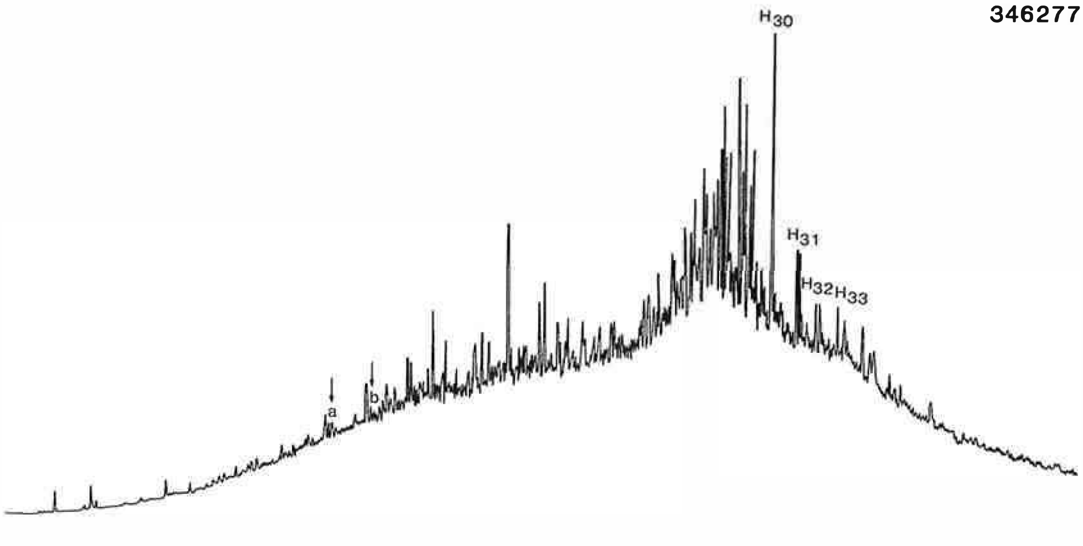

Fig. 8D. Selected gas chromatograms of saturated hydrocarbons from Greenland bitumen samples.
346277 Upper Permian carbonate, Gauss Halvø.

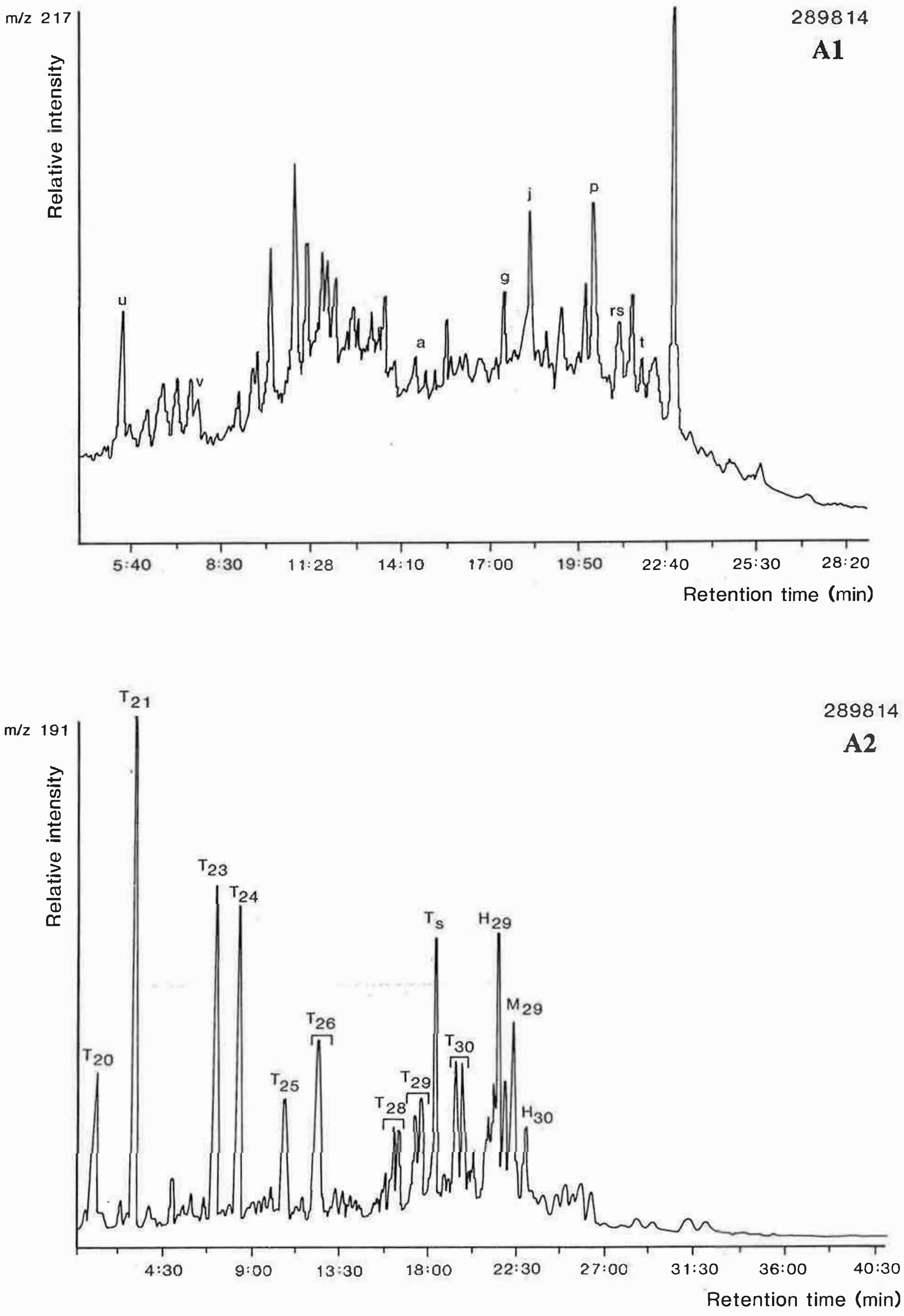

Fig. 9A. Selected GC/MS traces (m/z 191 and 217) of saturated hydrocarbons from Greenland bitumen samples. 289814 Middle Devonian sandstone, Gauss Halvø.

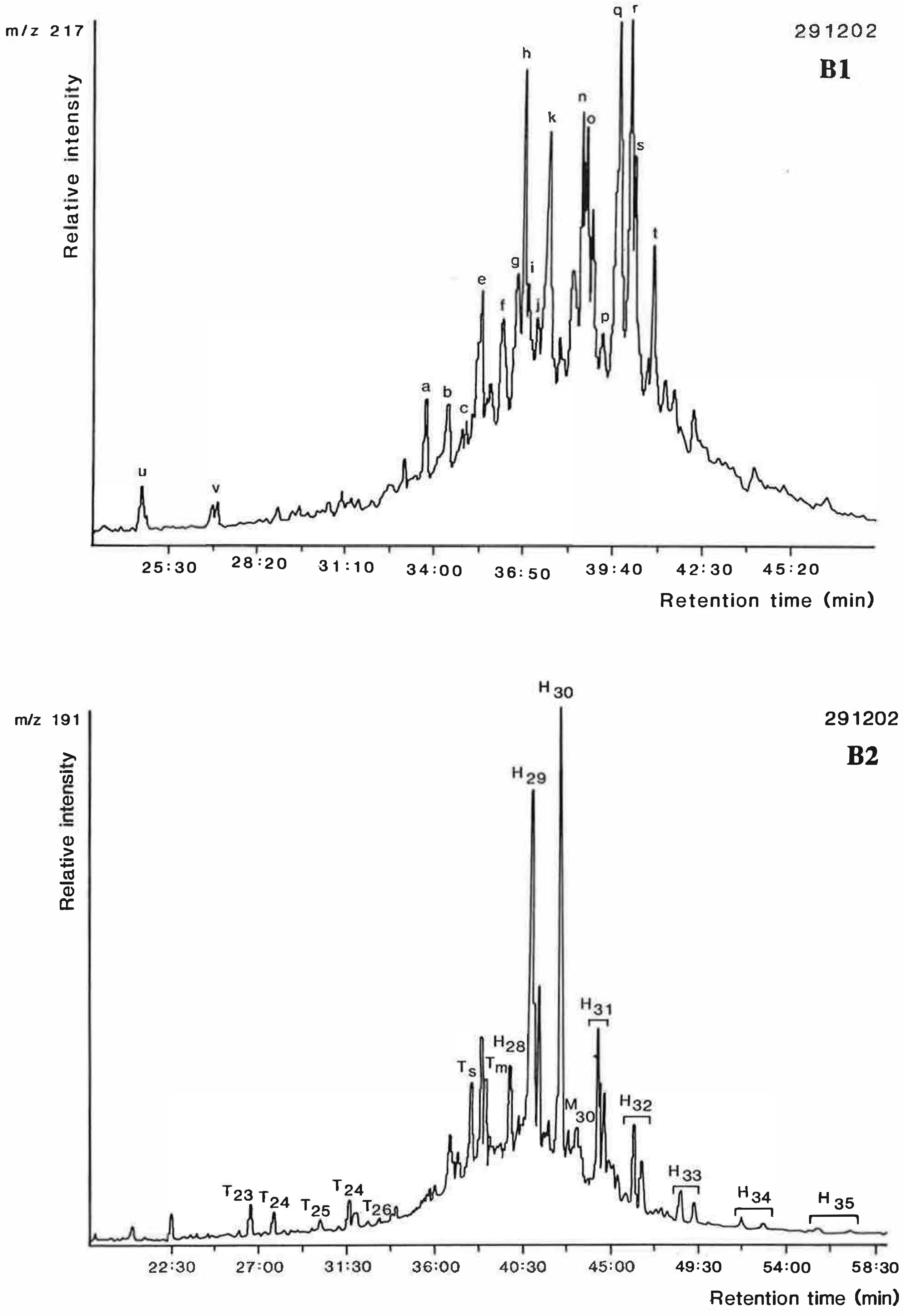

Fig. 9B. Selected GC/MS traces (m/z 191 and 217) of saturated hydrocarbons from Greenland bitumen samples. 291202 Upper Devonian sandstone, Gauss Halvø.

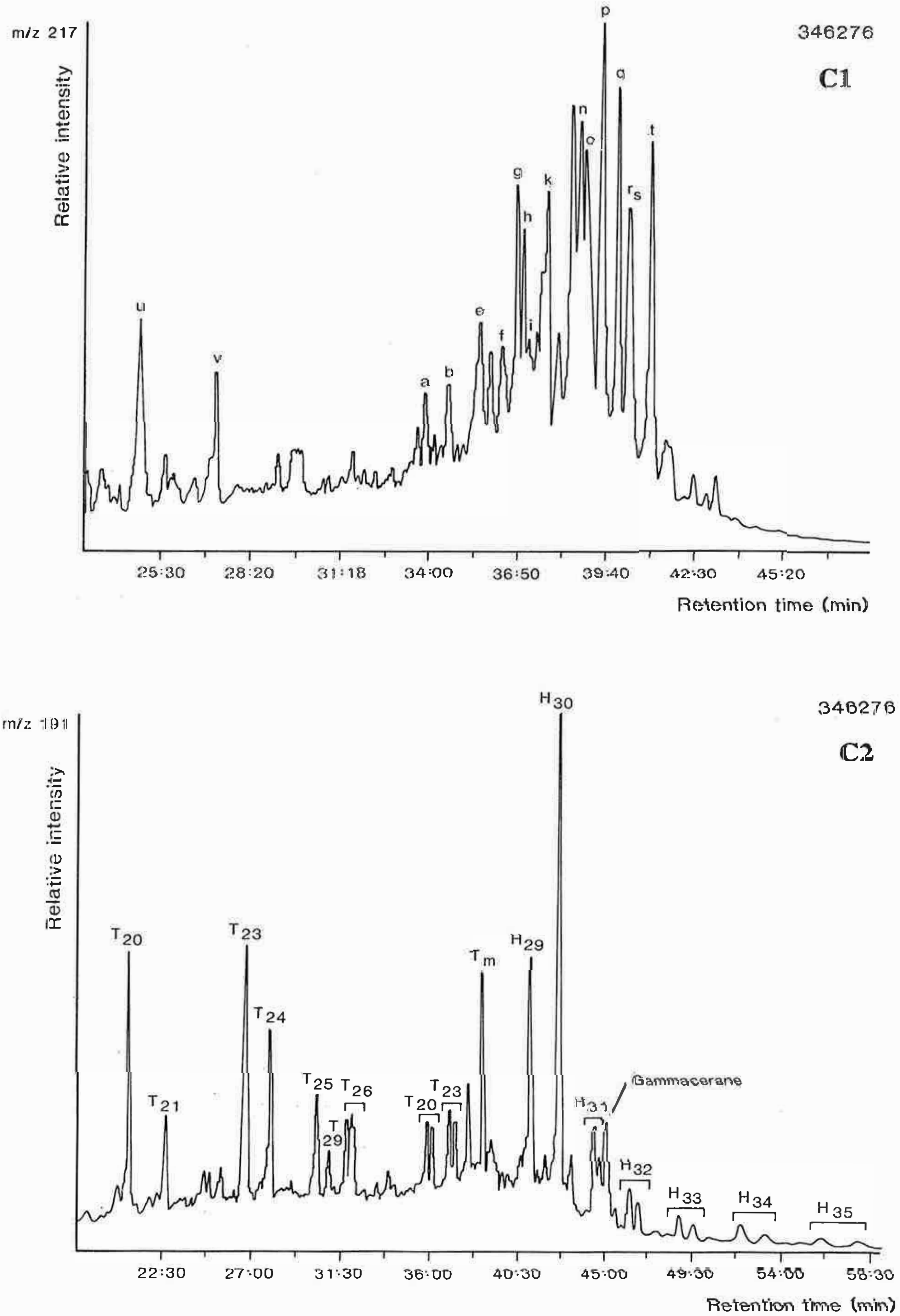

Fig. 9C. Selected GC/MS traces (m/z 191 and 217) of saturated hydrocarbons from Greenland bitumen samples. 346276 Triassic sandstone, Gauss Halvø.

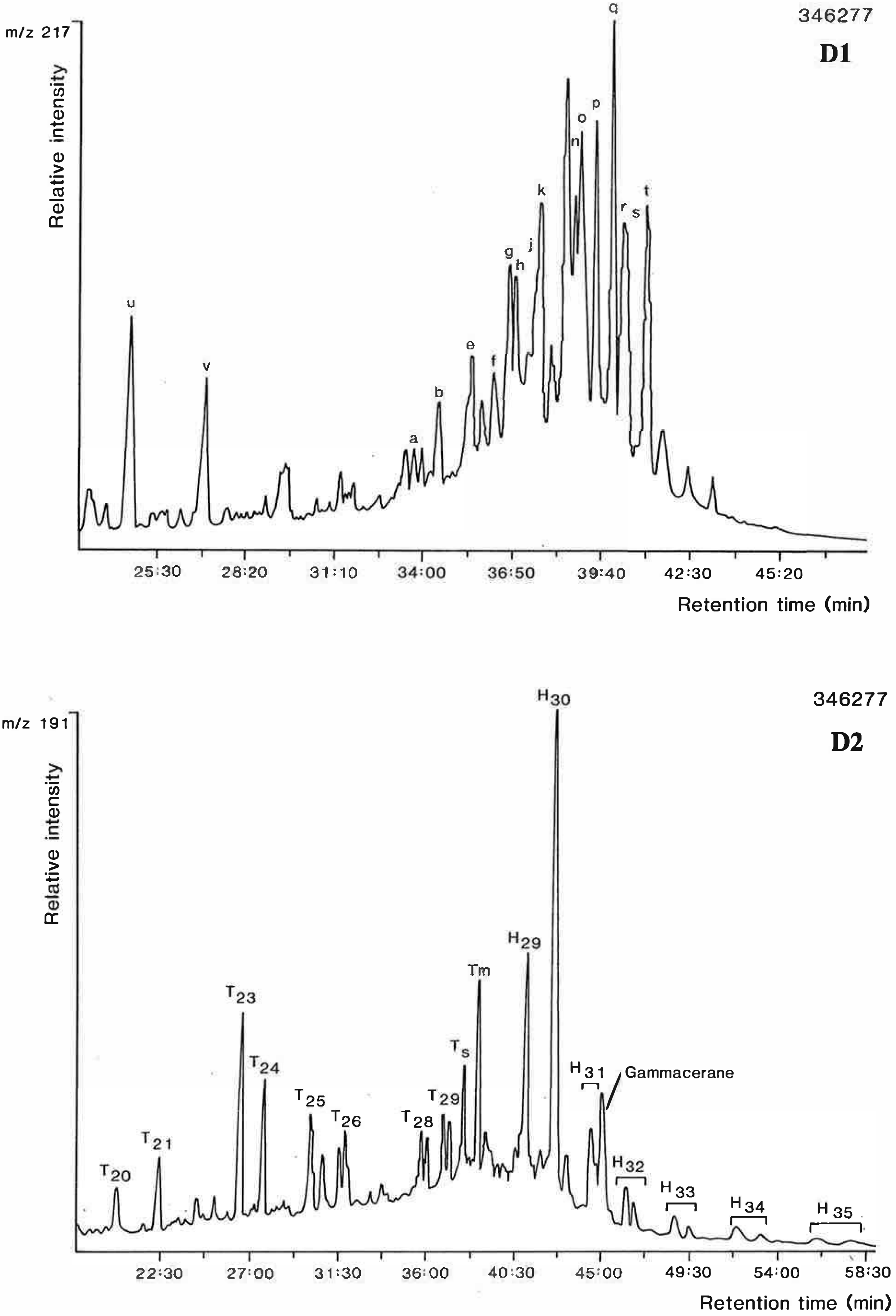

Fig. 9D. Selected GC/MS traces (m/z 191 and 217) of saturated hydrocarbons from Greenland bitumen samples. 346277 Upper Permian carbonate, Gauss Halvø.

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