

# Comparison of organic geochemical and palynofacies methods: Example from the Upper Triassic Gassum Formation in Denmark

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Disseminated organic matter from the Upper Triassic to Lower Jurassic Gassum Formation in the Gassum-1 deep well has been analyzed by palynological and organic geochemical methods. The paper compares the effects of the different preparation methods on the organic matter. The kerogen isolation process (demineralisation by HF) is found to cause major changes in the Rock-Eval parameters, but not in carbon isotope composition of organic matter.  $T_{max}$ - and HI-values determined from kerogen concentrates are more consistent with the palynofacies data than those determined from whole rock samples. The differences are ascribed to analytical problems when dealing with low-TOC whole rock samples. Palynofacies data obtained from unfiltered and filtered kerogen concentrates demonstrate a variable loss of amorphous organic matter during filtration (up to 100%). Other palynomorph distributions are not seriously affected by filtration. The loss in amorphous organic matter has no influence on the Rock-Eval data and carbon isotope composition. Comparison of palynofacies and carbon isotope data identifies three organic matter sources with characteristic isotopic composition.

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## Introduction

In recent years, disseminated organic matter (in the following abbreviated by OM) in sedimentary rocks has received much attention as part of hydrocarbon-related basinal studies. Morphological type and geochemical composition of OM are valuable parameters in source potential evaluations, while color and reflectivity are basic tools in thermal studies.

Generally, either optical or geochemical methods are applied in studies of sedimentary organic matter. Optical studies are usually performed on polished chips of whole rock samples (coal petrographical techniques) or on strew slides of isolated kerogen (palynological techniques). In most cases geochemical methods are based on whole rock samples.

On the one hand, it has been a standard procedure to integrate coal petrographical and organic geochemical methods as a part of coal bed investigation (e.g. van Krevelen 1981; Stach et al. 1982). On the other hand, comparison of palynological and organic geochemical methods has

been limited, and only a few papers have attempted to integrate palynological and organic geochemical data in the classification and interpretation of OM types (e.g. Powell et al. 1982; Lewan 1986; Nøhr-Hansen 1989).

It is the purpose of this study to evaluate the effect on the OM composition of the different preparation techniques applied by palynologists and organic geochemists, and to suggest methods to ensure optimal compatibility between analytical results. The study is based on core samples from the Gassum Formation in the Gassum-1 deep well in eastern Jutland (fig. 1), which contains both marine and non-marine OM. Lithologic descriptions, as given in fig. 2, are based on the drilling report (Dapco 1951; Norwood et al. 1951) and on our own observations.

The Gassum Formation (Larsen 1966; Bertelsen 1978 and 1980) includes 50 to 200 m of fine- to medium-grained light-grey sandstone with darker claystone and siltstone. Coal seams appear occasionally. The formation represents fluvio-deltaic to marginal marine deposits (Bertelsen 1978) accumulated along the northeastern

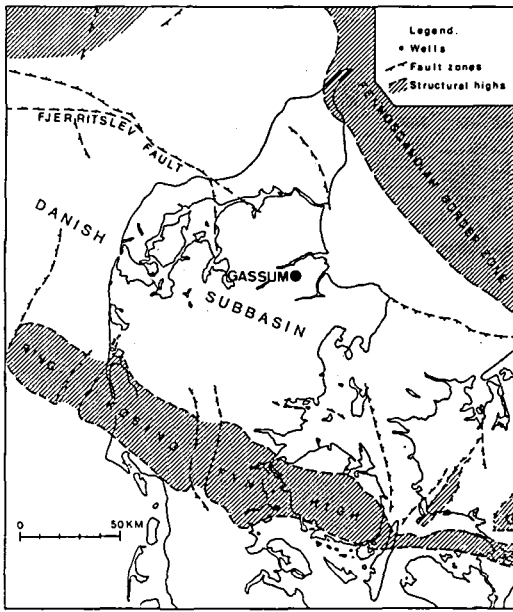


Fig. 1. Localization of the investigated Gassum-1 deep well.

margin of the Norwegian-Danish Basin. The investigated interval corresponds to the G<sub>2</sub>- and G<sub>3</sub>-members of the formation (Bertelsen 1978) and is of Rhaetian to Hettangian age (Sorgenfrei and Buch 1984; Berthelsen 1978 and 1980; Nielsen 1983).

Preparation and analytical methods

a. Kerogen isolation

Kerogen isolation follows standard procedures used at the Paly-Dat Laboratory. Samples are crushed to a grain size of 2 to 10 mm, and 10 to 50 gram aliquots are placed in 250 ml polypropylene centrifuge beakers, treated with 10% hydrochloric acid for from 5 minutes to 24 hours to ensure dissolution of calcite and aragonite, centrifuged at 2500 rev./min and then decanted. The decalcified samples are then reacted with 40% hydrofluoric acid for 5 days, heated in a water bath until further reaction stops, centrifuged and

| Lithostratigraphy | Chronostratigraphy           | Depth of samples  | Lithology  | cores sample no.   | Lithological description of the samples.                               |
|-------------------|------------------------------|---|--|--|--|
| GASSUM FORMATION  | EARLY JURASSIC<br>Hettangian | 1534  | [Dotted signature: sandstone, dashed signature: clay/mudstone] | G 7  | Medium dark grey unconsolidated easily cleavable sandstone.            |
|                   |                              | 1536  |  | G 8  | Dark green grey claystone with silt, concoidal fracture.               |
|                   | 1544                         | G 9   |  | Grey black to brown black finegrained micaceous unconsolidated siltstone with light grey sand. |  |
|                   | 1559                         | G 10  |  | Grey to olivegrey claystone with mica.   |  |
|                   | LATE TRIASSIC<br>Rhaetian    | 1577  |  | G 11   | Olive black easily cleavable micaceous claystone. Smelly when crushed. |
|                   |                              | 1578  |  | G 12   | Medium dark grey uniform easily cleavable shale.                       |
|                   |                              | 1584  |  | G 13   | Grey black to brown black claystone concoidal fracture.                |
|                   |                              | 1585  |  | G 14   | Olive grey claystone with concoidal fracture. Smelly when crushed.     |
|                   |                              | 1587  |  | G 15   | Dark grey claystone, concoidal fracture. Smelly.                       |
|                   |                              | 1588  |  | G 16   | Dark grey claystone, concoidal fracture.                               |
| 1589              | G 17                         | Yellow grey siltstone with coal seams.                  |  |  |  |
| 1591              | G 18                         | Dark grey shale with light grey irregular seams of sand |  |  |  |

Fig. 2. Lithology and stratigraphy of the investigated interval of the Gassum-1 well. Dotted signature: sandstone, dashed signature: clay/mudstone. Chronostratigraphy based on Nielsen (1983).

Table 1. Comparison of organic matter type classifications.

| Types of organic material (OM). after Burgess (1974) and Witley et al. (1981) |  | Categories after Bujak (1977a & b) | Kerogen types after Tyson (1984) |
|---|--|------------------------------------|----------------------------------|
| Black wood  | Opaque, angular to blocky fragments with straight fractures and no visible structures. Coaly OM.                                   | Melanogen                          | IV                               |
| Brown wood  | Translucent, brown, angular to blocky fibrous plant material of woody origin. Woody OM.  | Hylogen                            | III                              |
| Cortex, cuticle membranes   | Yellow to brown thick spongy cellular material and pale thin, epidermal fragments. Herbaceous OM.                                  | Phyrogen                           | II                               |
| Freshwater palynomorphs   | Botryococcus and other freshwater algae.   |                                    |                                  |
| Non-saccate microspores   | Spores and pollen grains.  |                                    |                                  |
| Saccate pollen  |  |                                    |                                  |
| Dinoflagellates   |  |                                    |                                  |
| Marine pal. morphs  | Leiospheres, tasmanites, acritarchs and foraminif. linings.  |                                    |                                  |
| Amorphous   | Grey and yellow to brown saprobel with no visible structure. May be finely disseminated fluffy OM or coagulated into lumpy masses. | Amorphogen                         | I/II                             |

decanted. After this treatment, hydrochloric acid is added to the samples, which are then reacted in a water bath at 60°C for 30 min in order to remove fluorides, and finally washed twice in distilled water. No permanganate oxydation of the kerogen concentrate has been applied.

The kerogen concentrate obtained by this procedure was divided into two parts, of which one was filtered on 10 micron nylon filters. Where the filtering was difficult, ultrasonic treatment was used and, if necessary, addition of peptisator to disperse lumps. Finally, both unfiltered and filtered samples were evaporated in glycerine and slides were made and sealed.

#### b. Palynofacies methods

Microscope investigation of the slides was undertaken in transmitted light at 400 × or 1200 × magnification. In all slides approximately 300 particles were counted in a 24 × 36 micron rectangle using a point-counting technique where differences in particle size were disregarded.

In many papers dealing with palynofacies studies, the OM is grouped into four categories, as suggested by Bujak et al. (1977a and b): amorphogen, phyrogen, hylogen and melanogen (table 1). The classification is insufficient for paleoenvironmental interpretations, as the phyrogen category includes both terrestrial and marine palynomorphs. In the present study the organic particles have been grouped into nine organic matter types as listed in table 1 (following Witley et al. 1981; Hansen 1984 and N. Poulsen (pers. comm.) 1986). The Bujak-classification has been applied for simplification in figures and tables. The thermal maturity of the OM has been evaluated by determination of the maturity-related spore and pollen coloration (TAI-index, Pearson 1984) in the kerogen slides.

#### c. Geochemical methods

The geochemical investigations include determinations of total organic carbon content

ORGANIC TYPE CHARACTERISTICS AND PALYNOFACIES ANALYSIS.

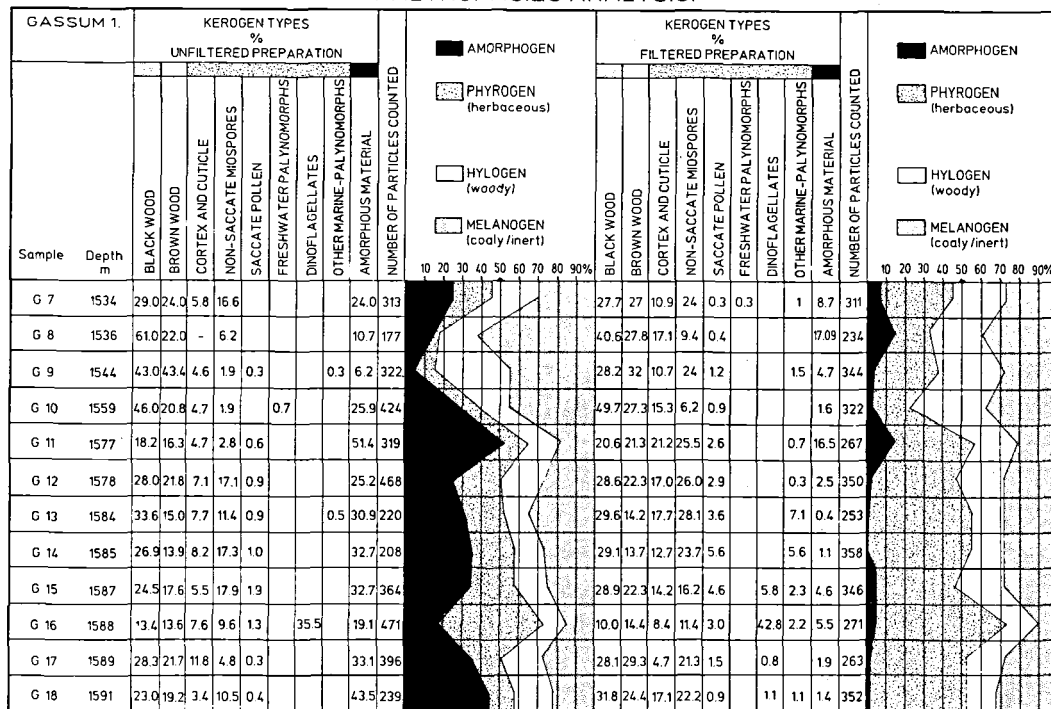


Fig. 3. Organic type characteristics and palynofacies analysis. Sample numbers refer to fig. 2, organic matter categories to Bujak et al. (1977a and b) and table 1.

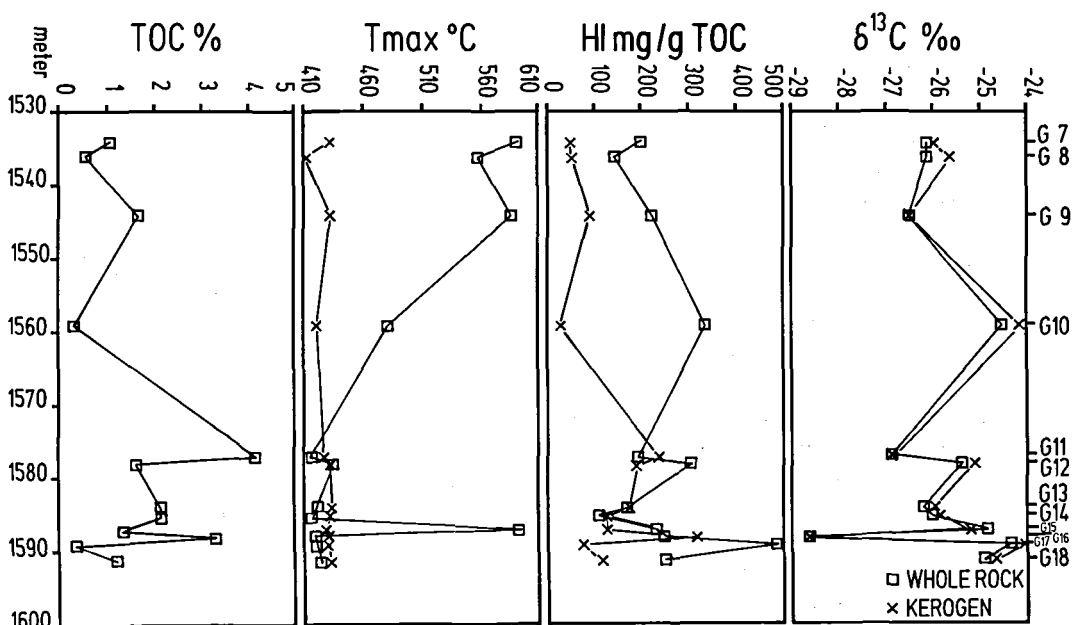


Fig. 4. Organic geochemical results for whole rock and unfiltered kerogen concentrate samples. TOC refers to total organic carbon content, T<sub>max</sub> and HI to maximal pyrolysis yield in °C and hydrogen index in mg hydrocarbons/gram organic carbon in the Rock-Eval procedure and δ<sup>13</sup>C to the carbon isotope composition in ‰ deviation from the PDB-standard.

(TOC %), carbon isotope composition ( $^{13}\text{C}/^{12}\text{C}$ -ratios) and programmed pyrolysis (Rock-Eval).

The TOC-determinations were performed on a LECO-combustion furnace at the Geological Survey of Denmark following standard procedures (Bojesen-Kofoed 1989). Carbon isotope composition was determined at the stable isotope laboratory at the Department of Geology, University of Copenhagen (Buchardt et al. 1986). Dichloromethane-extracted and acid-treated whole rock samples, as well as filtered and unfiltered kerogen concentrates, were analyzed. Combustion to  $\text{CO}_2$  took place in an oxygen-helium atmosphere at  $900^\circ\text{C}$ . The  $^{13}\text{C}/^{12}\text{C}$  ratios of the evolved  $\text{CO}_2$  were determined on a Finnigan MAT-250 gas ratio mass spectrometer. The carbon isotope compositions are given as  $\delta^{13}\text{C}$ -values (‰ deviation in  $^{13}\text{C}/^{12}\text{C}$ -ratios) relative to the PDB-standard. Reproducibility is better than  $\pm 0.05\text{‰}$  (2 $\sigma$ ).

Pyrolysis analyses were performed on a Delsi Rock-Eval II instrument at the Geological Survey of Denmark. Procedures followed Espitalié et al. (1985a and b). Determinations of  $T_{\text{max}}$ ,  $S_1$ - and  $S_2$ -peaks were made on whole rock samples and on unfiltered and filtered kerogen concentrates. The hydrogen index HI was calculated as the TOC-normalized  $S_2$ -peak (mg hydrocarbons/g TOC).

## Results and discussion

The palynological results given in fig. 3 include data from unfiltered and filtered kerogen concentrates. Evaluated values for maturity-related spore and pollen coloration (TAI-index) are between 2 and 2+, corresponding to immature to marginally mature conditions with regard to hydrocarbon generation. A corresponding vitrinite reflectance would be below 0.5% (Pearson 1984).

The geochemical results (table 2 and fig. 4) include TOC-values for whole-rock samples, and carbon isotope values, pyrolysis  $T_{\text{max}}$  and hydrogen index HI for whole rock samples, unfiltered kerogen concentrates and filtered kerogen concentrates.

As mentioned earlier, organic geochemical analyses are usually carried out on whole rock samples, even if the concentration of OM is low, while palynological investigations are based on

kerogen concentrates. These methodological differences may complicate direct comparison of the two data types. In order to evaluate the effects of the kerogen isolation procedure on the geochemical composition of the OM we have compared carbon isotope composition and Rock-Eval data of whole rock samples and corresponding unfiltered kerogen concentrates.

The difference in carbon isotope composition between whole rock and isolated kerogen is less than 0.5‰. In all but one case the isolated kerogen has suffered minor enrichment in  $^{13}\text{C}$  as compared to whole rock samples, indicating loss of  $^{13}\text{C}$  depleted OM during kerogen isolation. The enrichment is most pronounced for samples low in TOC. When compared to the total range in carbon isotope composition the observed enrichment is seen to be small (less than 0.5 ‰ compared to 4.5‰). Therefore, the demineralization procedure has only little influence on the isotopic composition of the OM, and comparable carbon isotope data can be obtained from whole rock samples and corresponding kerogen concentrates. However, detailed isotopic studies performed on low-TOC samples (less than 1.5% TOC) should preferably be based on whole rock samples.

Pyrolysis  $T_{\text{max}}$ -values determined from whole rock samples are highly variable ( $415\text{--}593^\circ\text{C}$ ), while  $T_{\text{max}}$ -values determined from kerogen concentrates are relatively uniform ( $411\text{--}433^\circ\text{C}$ ). Inspection of the pyrolysis traces reveals major differences in shapes of  $S_2$ -peaks from whole rock samples, while pyrolysis of kerogen concentrates provides well-defined  $S_2$ -peaks. The  $T_{\text{max}}$ -values obtained from kerogen concentrates compare favorably with thermal maturity as determined from TAI-values (immature to marginally mature with regard to hydrocarbon generation). Accordingly, the drastic variability in whole rock  $T_{\text{max}}$ -values is likely due to matrix effects rather than to real differences in maturity. Matrix effects in pyrolysis of low-TOC samples have been described by Katz (1983) and by Peters (1986), who claimed absorption on clay minerals to be the most important factor in retaining the pyrolysate and thereby increasing the observed  $T_{\text{max}}$ .

Calculation of hydrogen index, HI, is based on the pyrolysis  $S_2$ -peak, and poorly-defined peaks may lead to erroneous HI-values. This effect probably explains the marked differences be-

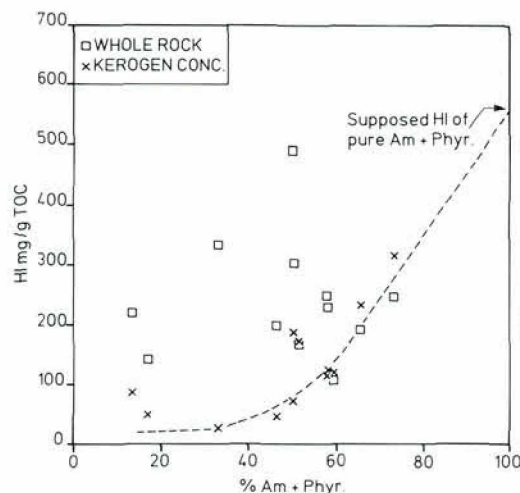


Fig. 5. Hydrogen index values (HI in mg hydrocarbons/gram organic carbon) as determined for whole rock and unfiltered kerogen samples plotted against the percentage of the hydrogen rich OM categories (amorphogen and phytolite, see table 1). Note the better defined relationship for kerogen concentrates than for whole rock samples.

tween HI-values obtained from whole rock samples and kerogen concentrates (fig. 4). The validity of the two sets of HI-values can be evaluated from the palynofacies composition. In general,

the  $S_2$ -peak is sensitive to the amount of hydrogen in the OM. Immature OM, rich in hydrogen, is characterized by a high fractional content of amorphous and herbaceous OM (Tissot 1984; Hartman-Stroup 1987). High HI-values should therefore correlate to high amounts of amorphogen (Am) and phytolite (Phyr). As seen from fig. 5, a relationship of this type exists between OM-types and HI-values for analyses based on kerogen concentrates. Samples with less than 45% Am+Phyr have low HI-values, while samples with 50% or more Am+Phyr show a positive correlation to HI-values. No such relation is found for the whole rock values. The very high HI-values found in this group probably reflect the combined effect of matrix interference (Katz 1983; Dembicki et al. 1983) and contamination by drilling mud. The data lead to the conclusion that more representative HI-values of low-TOC samples can be obtained from Rock-Eval analyses of kerogen concentrates than from whole rock samples.

#### b. Effects of filtering

The palynological preparation as used in this study includes 10 micron filtering of the kerogen

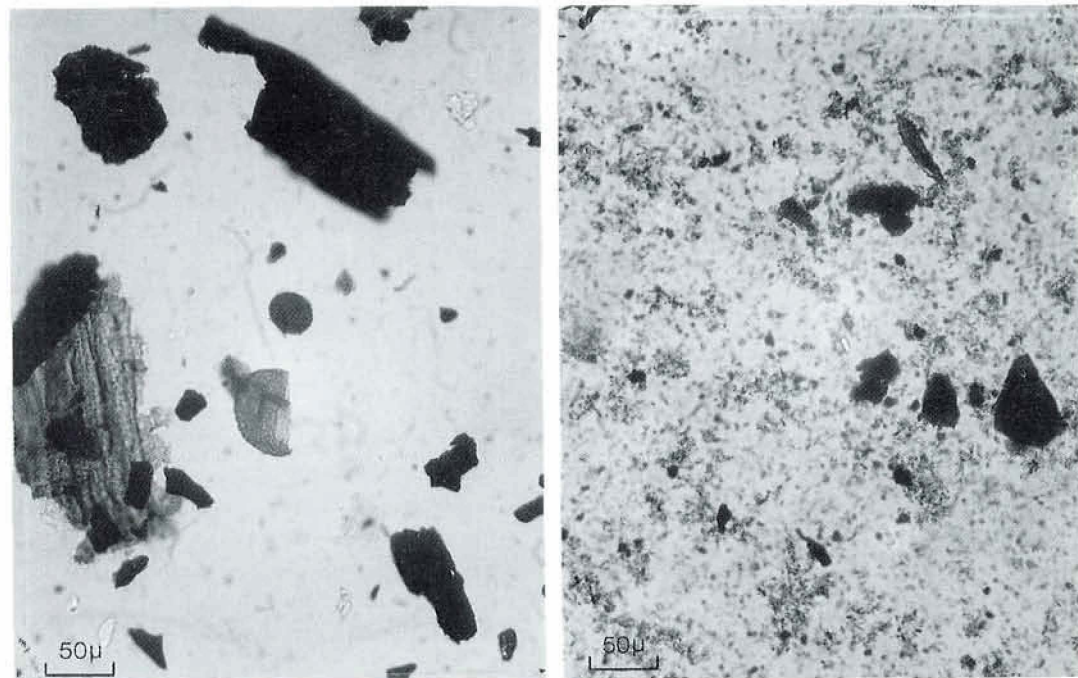


Fig. 6. Photomicrographs of kerogen concentrates (sample G10) before (right) and after (left) 10 µm filtering. Note the high loss of fine grained, so-called amorphous OM after filtration.

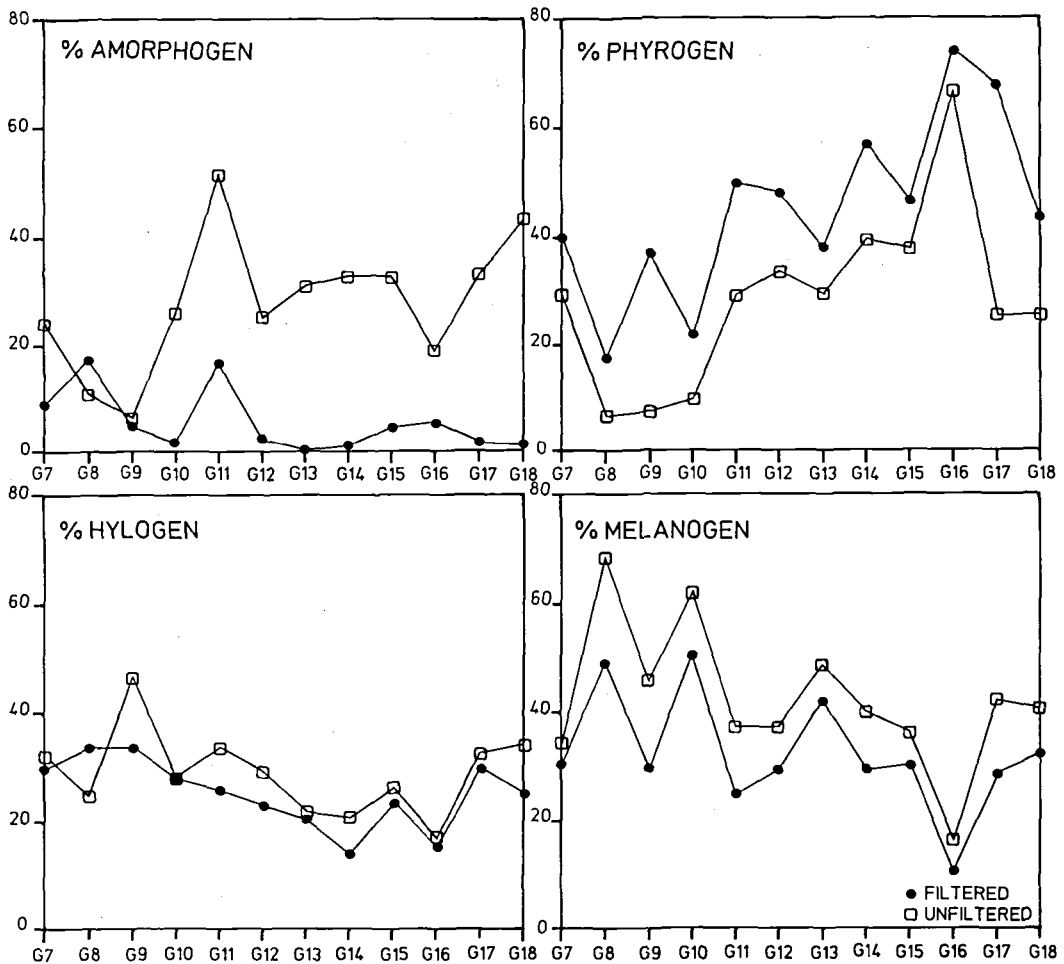


Fig. 7. Comparison of palynofacies distribution before and after 10  $\mu$ m filtering. Calculation based on the four Bujak-categories for organic matter (Bujak et al. 1977a and b): Amorphogen, phyrogen, hylogen and melanogen, see also table 1. Loss of the phyrogen, hylogen and melanogen categories are calculated on an amorphogen-free basis. Numbers on x-axis refer to samples. Note the large and unsystematic loss of amorphogen during filtering.

concentrate. The filtering is a standard procedure carried out in order to produce samples with a maximum content of spores, pollen and dinoflagellates and – if possible – nothing else. As seen from fig. 6, identification of individual palynomorphs is greatly enhanced by removal of the fine-grained organic fraction. Unfortunately, the filtering procedure may also introduce problems in the interpretation of the data. Thus, unfiltered and filtered kerogen concentrates may differ considerably in chemical composition. Direct comparison between palynological results, based on filtered samples, and geochemical results, based on either whole rock samples or unfiltered kerogen concentrate, may be misleading. Moreover,

palynofacies analyses based on total composition of filtered kerogen may be biased by the selective loss of certain kerogen types.

Figs. 3 and 7 demonstrate that the filtering process leads to a large (up to 100%), but variable, loss of the OM-group described as amorphous. The effect can be ascribed to preferential loss of certain OM-subtypes during filtration. Microscopy demonstrates that fine-grained and fluffy amorphous OM have been lost, and coarser, lumpy aggregates of strongly degraded amorphous OM have been physically degraded during the filtration. The amorphous OM remaining in the filtered samples belongs to less degraded, and therefore more resistant, types. The effect of fil-

Table 2. Geochemical results.

| sample # | TOC % | $T_{\max}$ °C |         | $\delta^{13}\text{C}_{\text{‰}}$ |         | HI mg/g TOC |         |        |      |
|----------|-------|---------------|---------|----------------------------------|---------|-------------|---------|--------|------|
|          |       | wr.           | ker.uf. | wr.                              | ker.uf. | wr.         | ker.uf. | ker.f. |      |
| G-7      | 1.1   | 590           | 432     | -26.12                           | -26.02  | -26.16      | 200     | 48     | n.d. |
| G-8      | 0.6   | 557           | 411     | -26.12                           | -25.65  | -25.96      | 143     | 51     | 46   |
| G-9      | 1.6   | 585           | 432     | -26.56                           | -26.54  | -26.77      | 221     | 88     | 66   |
| G-10     | 0.3   | 481           | 421     | -24.54                           | -24.16  | -24.26      | 334     | 28     | 32   |
| G-11     | 4.1   | 415           | 427     | -26.93                           | -26.89  | -27.19      | 193     | 234    | 218  |
| G-12     | 1.6   | 435           | 433     | -25.40                           | -25.16  | -27.37      | 304     | 188    | 166  |
| G-13     | 2.1   | 420           | 432     | -26.22                           | -26.01  | -26.12      | 168     | 174    | 158  |
| G-14     | 2.1   | 415           | 429     | -26.04                           | -25.85  | -25.99      | 109     | 122    | 149  |
| G-15     | 1.4   | 593           | 428     | -24.86                           | -25.19  | -25.35      | 231     | 126    | 142  |
| G-16     | 3.3   | 421           | 430     | -28.64                           | -28.61  | -28.82      | 248     | 317    | n.d. |
| G-17     | 0.4   | 421           | 430     | -24.34                           | -24.08  | -24.21      | 492     | 75     | n.d. |
| G-18     | 1.2   | 424           | 429     | -24.87                           | -24.70  | -25.02      | 250     | 116    | n.d. |

wr: whole rock samples

ker.uf.: unfiltered kerogen concentrate

ker.f.: filtered kerogen concentrate

n.d.: no determinations

tering on the relative amount of the other OM-categories is small and systematic (fig. 7). It should be noted that the phyrogen category has been enhanced, thereby demonstrating the success of the filtering process as viewed by the biostratigrapher.

The influence of the filtering procedure on the chemical composition of the kerogen has been evaluated by carbon isotope and Rock-Eval analyses (table 2). The hydrogen index, HI, is affected only to a minor degree by filtration (table 2), largest shifts being between 10 and 15%. No systematic change is observed, leading to the conclusion that the fraction lost by filtration is heterogeneous and not composed solely of hydrogen-rich amorphous OM.

The difference in carbon isotope composition between the unfiltered and filtered kerogen is insignificant. All filtered samples have suffered a small (<0.4‰) depletion in  $^{13}\text{C}$  as compared to the unfiltered samples. The isotopic shift has no relation to the varying, but large amount of amorphous OM lost during filtration, indicating that the isotopic composition of the amorphous OM lost during filtration is similar to that of the remaining OM in the individual samples. As was the case for the demineralization procedure, the bias introduced on the carbon isotope composition by filtration is small compared to the total range in isotopic composition.

The data emphasize the limitations to indirect geochemical interpretations based on palynofacies observations. In many palynological assess-

ments of source rock quality amorphous OM has been taken as equivalent to hydrogen-rich OM, and the high content of amorphous OM has been taken as an indication of good source potential. As has already been pointed out by Powell et al. (1982), amorphous OM has to be understood as a heterogeneous OM-group including both hydrogen-rich and hydrogen-poor OM-types. Our data support this concept.

### c. Paleoenvironmental aspects

Traditionally, palynofacies analyses are applied as the most important organic matter parameter in paleoenvironmental interpretations (Hansen 1984). Recently, efforts have been made to integrate palynofacies data and organic geochemical analyses into an "organic facies" concept (Jones 1987). This approach is based mainly on TOC and Rock-Eval data and only to a minor degree on carbon isotope results. Our data enable interpretation of the  $\delta^{13}\text{C}$ -values in a palynofacies context, and the study has been expanded to demonstrate the advantages of a combined palynological and organic geochemical approach to organic matter classification.

The carbon isotope composition of OM reflects the origin (Dean et al. 1986; Lewan 1986; Bucharadt and Cederberg 1987). In the material studied, the only sample dominated by marine palynomorphs (G16, see fig. 3) is significantly depleted in  $^{13}\text{C}$  as compared to those dominated by non-marine OM-types (fig. 4). This effect probably reflects the high content of  $^{13}\text{C}$ -depleted lip-



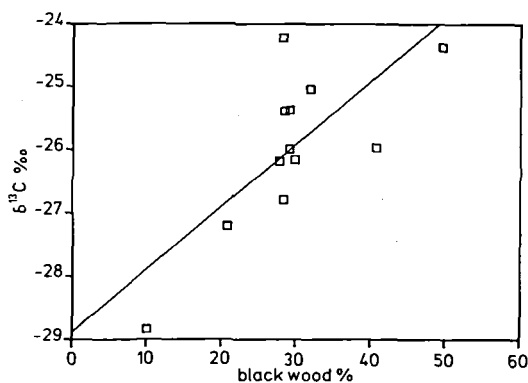


Fig. 8. Carbon isotope composition of filtered kerogen concentrate plotted versus amount of the black wood OM category. Note the good correlation between black wood content and carbon isotope data (correlation coefficient  $r = 0.76$  for  $n = 12$ ).

ids (Deines 1980) in the dinoflagellates as confirmed by high HI-index in the sample (317 mg/g TOC).

No relation is found between carbon isotope composition and relative variation of the non-marine OM types except for the black wood component (fig. 8), which shows a significant positive correlation (1% level) to  $\delta^{13}\text{C}$  values (correlation coefficient  $r = 0.76$  for  $n = 12$ ). This relationship must reflect the isotopic composition of the modified lignin in the black wood, which is significantly enriched in the heavy carbon isotope as compared to the marine OM.

The present carbon isotope data do not indicate any characteristic isotope composition of the amorphous OM. As discussed earlier, this OM-type is interpreted to be a heterogeneous mixture of decomposition products from different primary OM-groups, and the carbon isotope composition probably reflect this mixed origin.

Based on these observations the isotopic distribution can be explained from a mixture of the main OM-groups with different isotopic composition:

- 1) a marine component dominated by dinoflagellates strongly depleted in  $^{13}\text{C}$  ( $\delta^{13}\text{C}$ -values  $< -28$  ‰);
- 2) a terrestrial, allochthonous component dominated by black wood enriched in  $^{13}\text{C}$  ( $\delta^{13}\text{C}$ -values  $> -24$  ‰); and
- 3) a mixed, dominantly terrestrial component consisting of brown wood, spores, pollen, cuticles

and cortex, which has intermediate  $\delta^{13}\text{C}$ -values (between  $-27$  and  $-24$  ‰).

This distribution differs from that of modern OM (Hunt 1966; Gearing et al. 1984), but is in accordance with the above mentioned studies of fossil OM.

## Conclusions

The study has investigated the advantages of combining palynofacies and organic geochemical methods. The following observations are of special interest:

1. Rock-Eval data ( $T_{max}$  and hydrogen index HI) obtained from unfiltered kerogen concentrates differ considerably from whole rock data. The kerogen concentrate data are in agreement with palynofacies results and are considered more reliable than whole rock data.
2. Carbon isotope composition of organic matter are not significantly affected by palynological preparation (hydrofluoric acid treatment) or by 10 micron filtering including ultrasonic and peptisator treatment. Largest deviations (up to 0.5 ‰) are observed in samples with low content of organic carbon. For such samples, isotope data from whole rock samples are to be preferred.
3. The geochemical results indicate that the organic matter classified as amorphous OM is a heterogeneous OM-group including both degraded lumps of hydrogen-rich OM and fine-grained debris of hydrogen-poor OM-types. Therefore, amorphous OM is considered unreliable as a quantitative palynofacies parameter, and source rock evaluations based on palynological quantification of amorphous OM should be avoided.
4. A large, but variable proportion of the amorphous organic matter group including both fine-grained structured debris and coarse-grained, lumpy OM is lost during filtering. Consequently, quantitative palynofacies evaluations based on filtered kerogen should not include amorphous OM.

5. The organic carbon isotope data reflects the organic matter types as determined by palynological methods. Dinoflagellaterich OM is strongly depleted in  $^{13}\text{C}$  ( $\delta^{13}\text{C}$ -values less than  $-28\text{‰}$ ), while OM rich in black wood is enriched in  $^{13}\text{C}$  ( $\delta^{13}\text{C}$ -values more than  $-24\text{‰}$ ). Amorphous OM has carbon isotope compositions similar to the dominating OM-types in the individual sample.

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## Dansk sammendrag

Organisk materiale (OM) fra den øvre triassiske – nedre jurassiske Gassum Formation i Gassum 1 boringen (fig. 1) er analyseret palynologisk og organisk geokemisk. Afhandlingen sammenligner de ændringer i geokemisk og palynologisk sammensætning, der skyldes de forskellige præparationsmetoder.

Kerogenkoncentrations-proceduren (deminerisering med HF) påvirker Rock-Eval bestemmelse, men ikke kulstofisotopsammensætningen af OM (tabel 1 og fig. 4).  $T_{\text{max}}$  og HT-værdierne bestemte fra kerogenkoncentration er i større overensstemmelse med palynofacies data end målinger fra bjergartsprøver. Forskellene tilskrives metodemæssige problemer ved analyse af bjergartsprøver med lavt TOC-indhold. De palynologiske data, baseret på punkttællinger af 9 OM-typer (tabel 1), viser en markant forskel mellem ufiltrerede og filtrerede prøver (fig. 3), idet op til 100% af det amorfe OM tabes ved filtreringen. Den indbyrdes fordeling af de andre OM-typer ændres derimod ikke (fig. 7). Tabet af amorft OM har ingen indflydelse på Rock-Eval data eller på kulstofisotop-sammensætningen.

Det organiske materiale i ufiltrerede prøver, der tælles som amorft OM, er en heterogen OM-gruppe omfattende både brintrigt OM og finkornede ( $<10\ \mu\text{m}$ ) rester af brintfattige strukturerede OM-typer. Da tabet af amorft OM ved filtreringen umuliggør kvantitative vurderinger af det relative indhold af denne OM-type i normale palynologiske prøver, må det konkluderes, at palynologisk bestemmelse af indholdet af »ægte« (dvs. brintrigt) amorft OM er behæftet med stor usikkerhed.

Kulstofisotop-sammensætningen af det organiske materiale afspejler de OM-typer, der bestemmes ved palynologiske metoder. Der kan opdeles i tre grupper baseret på kilde: 1) en marin komponent domineret af dinoflagellatcyster kraftigt forarmet i  $^{13}\text{C}$  ( $\delta^{13}\text{C}$ -værdier  $<-28\text{‰}$ ), 2) en terrigen, allokton komponent domineret af black wood beriget i  $^{13}\text{C}$  ( $\delta^{13}\text{C}$ -værdier  $>-24\text{‰}$ ), og 3) en blandet, dominerende allokton komponent bestående af brown wood, sporer, pollen, cuticula og cortex med  $\delta^{13}\text{C}$ -værdier mellem  $-27$  og  $-24\text{‰}$ .

## References

- Berthelsen, F. 1978: The Upper Triassic-Lower Jurassic Vinding and Gassum Formations of the Norwegian-Danish Basin. *Danm. geol. Unders. Serie B*, 3, 26 p.
- Berthelsen, F. 1980: Lithostratigraphy and depositional history of the Danish Triassic. *Danm. geol. Unders. Serie B*, 4, 59 p.
- Bojesen-Koefoed, J. 1989: Organisk-geokemiske screening-analyser, metoder og resultater. Analysemetoder ved DGU's source-rock laboratorium. *Danm. geol. Unders. Intern Rapport nr. 5*, 36 pp. 1-39.
- Buchardt, B., Clausen, J. and Thomsen, E. 1986: Carbon isotope composition of Lower Palaeozoic kerogen: Effects of maturation. *Org. Geochem.* 10, 127-134.
- Buchardt, B. and Cederberg, T. 1987: *Stabil isotop geokemi i moderbjergarter, olie og gas i Danmark*. Afsluttende rapport, EFP-83 projekt, København, 33 p. (In Danish)
- Bujak, J. P., Barss, M. S. and Williams, G. L. 1977a: Offshore East Canada's organic type and color and hydrocarbon potential I. *Oil and Gas Journal* 75, (14), 198-202.
- Bujak, J. P., Barss, M. S. and Williams, G. L. 1977b: Offshore East Canada's organic type and color and hydrocarbon potential II. *Oil and Gas Journal* 75, (15), 96-100.
- Burgess, J. D. 1974: Macroscopic examination of kerogen (dispersed organic matter) in petroleum exploration. *Geol. soc. Amer. Spec. Paper*, 153, 19-30.
- Dapco 1951: Gassum No. 1, Weekly Reports 1-47. Core Descriptions. Internal Report. *Geol. Surv. Denmark*.
- Dean, W. E., Arthur, M. A. and Claypool, G. E. 1986: Depletion of  $^{13}\text{C}$  in Cretaceous marine organic matter: Source, diagenetic or environmental signal? *Marine Geol.*, 70, 119-157.
- Deines, P. 1980: The isotopic composition of reduced organic carbon. In P. Fritz and J. C. Fontes (eds.) *Handbook of Environmental Isotope Geochemistry*, Volume 1, The Terrestrial Environment, A. Elsevier, Amsterdam, 329-406.
- Dembicki, H., Hornsfield, B. and Ho, T. T. 1983: Source rock evaluation by pyrolysis-gas-chromatography. *Amer. Assoc. Petrol. Geol. Bull.* 67, 1094-1103.
- Espitalié, J., Laporte, J. L., Madec, M., Marquis, F., LePlat, P., Paulet, J. and Boutefeu, A. 1977: Methode rapide de caractérisation des roches mères de leur potentiel pétrolier et leur degré d'évolution. *Revue de l'Institut Français du Pétrole*, 32, 23-42.
- Espitalié, J., Deroo, G. and Marquis, F. 1985a: La pyrolyse Rock-Eval et ses applications, première partie. *Revue de l'Institut Français du Pétrole*, 40, 563-579.
- Espitalié, J., Deroo, G. and Marquis, F. 1985b: La pyrolyse Rock-Eval et ses applications, deuxième partie. *Revue de l'Institut Français du Pétrole*, 40, 755-784.
- Gearing, J. N., Gearing, P. J., Rudnick, D. T., Requejo, A. G. and Mutchins, M. J. 1984: Isotope variability of organic carbon in a phytoplankton-based, temperate estuary. *Geochim. Cosmochim. Acta*, 48, 1089-1098.
- Hansen, J. M. 1984: Palynofaciesanalyse på basis af visuel og elektronisk billedanalyse. *Dansk geol. Foren., Årsskrift for 1984*, 127-132. (In Danish)
- Hartman-Stroup, C. 1987: The effect on organic matter type and organic carbon content on Rock-Eval hydrogen index in oil shales and source rocks. *Org. Geochem.*, 11, 351-369.
- Hunt, J. M. 1966: The significance of carbon isotope variations in marine sediments. In G. H. Hobson and G. C. Speers (eds.) *Advances in Organic Geochemistry*. Pergamon Press, New York, 27-35.
- Jones, R. W. 1987: Organic facies. In J. Brooks and D. Welte (eds.) *Advances in Petroleum Geochemistry*, 2, Academic Press, London, 1-90.

- Katz, B. J. 1983: Limitations of 'Rock-Eval' pyrolysis for typing organic matter. *Org. Geochem.*, 4, 195-199.
- Krevclen, D. W. van 1981: *Coal*. Elsevier, Amsterdam. 514 p.
- Larsen, G. 1966: Rhaetin-Jurassic-Lower Cretaceous sediments in the Danish Embayment. *Danm. geol. Unders.* II Rk, 91, 127 p.
- Lewan, M. D. 1986: Stable carbon isotopes of amorphous kerogens from Phanerozoic sedimentary rocks. *Geochim. Cosmochim. Acta*, 50, 1583-1591.
- Nielsen, M. 1983: Palynologisk undersøgelse af ø. trias i Gassum 1 boringen. Upubl. thesis, Århus Universitet. 87 p. (In Danish)
- Norwood, J. A., Nørvang, A. and Elm, C. C. von 1951: Final Report on Gassum 1. Internal Report. *Geol. Surv. Denmark*.
- Nøhr-Hansen, H. 1989: Visual and chemical kerogen analyses of the Lower Kimmeridge Clay, Westbury, England. In D. J. Batten and M. C. Keen (eds.) *Northwest European Micropalaeontology and palynology*. Ellis Horwood Limited, Chichester, England: 118-132.
- Pearson, D. L. 1984: *Pollen/Spore color standard, version #2*. Phillips Petroleum Company, Exploration Project Section. Bartelsville, Oklahoma. 1 p.
- Peters, K. E. 1986: Guidelines for evaluating petroleum source rock using programme pyrolysis. *Amer. Assoc. Petrol. Geol. Bull.*, 70, 318-329.
- Powell, T. G., Creaney, S. and Snowdon, L. R. 1982: Limited use of organic petrographic techniques for identification of petroleum source rocks. *Amer. Assoc. Petrol. Geol. Bull.*, 66, 430-435.
- Sorgenfrei, T. and Buch, A. 1984: Deep tests in Denmark 1935-1959. *Danm. geol. Unders.* III Rk, 36, 146 p.
- Stach, E., Machowsky, M. T., Teichmüller, M., Taylor, G. H., Chandra, D. and Teichmüller, R. 1982: *Stach's Textbook of Coal Petrology*, 3rd ed., Gebrüder Borntraeger, Berlin, 578 p.
- Tissot, B. P. 1984: Recent Advances in Petroleum Geochemistry Applied to Hydrocarbon Exploration. *Amer. Assoc. Petrol. Geol. Bull.* 68, 545-563.
- Tyson, R. V. 1984: Palynofacies investigation of Callovian (Middle Jurassic) sediments from DSDP Site 534, Blake-Bahama Basin, W. C. Atlantic. *Mar. Pet. Geol.* 1, 3-13.
- Whitley, R. K. J., Parry, C. C. and Simpson, R. D. H. 1981: Integration of Palynological and Sedimentological Methods in Facies Analysis of the Brent Formation. In: L. V. Illing and G. D. Hobson (eds.) *Petroleum of the Continental Shelf of North-West Europe*, 205-215.