

Dedicated to Dr. Robert Mackenzie on the occasion of his 75th birthday

KEROGEN AS A GEOCHEMICAL MARKER OF THE THERMAL HISTORY OF ROCKS

Application of thermal analysis

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Abstract

The study presents examples of the application of oxyreactive thermal analysis to the geological prospecting of bitumen deposits. Thermal analysis performed under properly chosen analytical conditions allows determination of characteristic features of organic matter and, at the same time, estimation of the thermal history of rocks. Thermal oxyreactivity curves document whether rocks were heated before or not. The results of the oxyreactive thermal analysis correlate well with the results of routine chemical analyses of organic matter (e.g. the composition of kerogen and bituminous fraction, Rock-Eval analysis and others). Our study clearly demonstrates that the composition of organic matter in facially, lithostratigraphically, and biogenetically identical rocks depends on their thermal history.

Keywords: kerogen, rockmass thermal history, thermal analysis

Introduction

Organic matter, which was formed during the biological history of the Earth in a variety of natural environments [1] is found as natural caustobioliths only in 0.0016%–0.0x% of global amount [1]. Its major mass is dispersed in small quantities in different sedimentary rocks, mainly in pelitic rocks (94.7% of its mass [2]). The organic matter underwent transformation in three stages [3]:

1. Diagenesis – a process which occurred at low temperatures in the sediment. About 8% of hydrocarbons evolved from organic matter at this stage.

2. Katagenesis – occurred in the range 90–200°C (probably higher). 92% of hydrocarbons contained in primary organic matter evolved at this stage.

3. Metamorphism – occurred above 200°C. At this stage the kerogen was transformed into methane and highly condensed structures of coal, such as anthracite

and anthraxolite [4], which may be further converted into shungite, tucholite and graphite.

Organic matter provides information on the environment of its formation, accumulation and transformation processes. Recently, investigations of numerous components of organic matter as biomarkers have been developed intensively. Spectroscopic, chromatographic and comparative GC-MS methods have been predominantly used. In order to make proper use of the results of these investigations it is essential to have a good recognition of the transformation processes which affected the organic matter.

During such investigations one can encounter special difficulties in recognizing the katagenesis process [5–9]. Microscopic methods of the coloration changes of conodonts and micropalynomorphs and also reflectance of coal macerals are generally used to solve this problem.

Thermal analysis, using Rock-Eval apparatus, is routinely applied. Recently, also other methods of thermal analysis [10–17] have been introduced. Results presented in our report are an example of application of oxyreactive thermal analysis to examine the thermal history of rocks. This method permits investigation of the effect of transformations of kerogen caused by increase of the rock temperature [18]; differentiation of genetic features of organic matter [19–21]; determination of the amount of volatile components and differentiation of pyrobitumina.

Methods

In the oxyreactive TA method, the sample of the investigated organic substrate is heated at a constant specific rate in dynamic air atmosphere. During the analysis, effects of the thermal reactions related to the decrease in mass and to the absorption or liberation of certain amounts of heat, are recorded with high sensitivity and separately in temperature intervals of several degrees. Several conditions should be fulfilled for the effect of reaction to be in correlation with the composition and structure of compounds. The composition of atmosphere must be stable, and both the oxygen diffusion and the effusion of the gas products must be optimally fast.

Thermal analyses were performed using a derivatograph, system F. Paulik, J. Paulik, L. Erdey, (MOM, Hungary) in an air atmosphere. We used dynamic conditions with air suction of $1.9 \text{ cm}^3 \text{ min}^{-1}$ and inflation $1 \text{ cm}^3 \text{ min}^{-1}$. Multiplate sample holders were used with sets of 3, 5 or 10 Pt plates. The weight of the samples and the number of plates depended on the content of organic matter. Proper preparation of samples for analysis, and maintenance of the proper analytical conditions are essential to obtain suitable results. The most important analytical conditions of oxyreactive thermal analysis (OTA) are as follows: maximum increase of the reactive surface of grains of the analysed substance – which means their disintegration to a size smaller than 0, x micrometer, excess of oxygen in the furnace atmosphere at every moment of the reaction (dynamic atmosphere), maximum oxygen access to grains of the analysed substance – which means dilution of the sample with a granular Al_2O_3 material to increase porosity and to form very thin layers on the plates.

The variability of the thermal curves i.e. the temperature of peaks and their shape as well as the relations between the thermal (DTA) curves and weight loss (TG) curves show differences in the composition and structure of the components of organic matter. The temperature range of the reactions is a function of the bonding energy of radicals (functional groups) or structure elements. The oxyreactive thermal analysis (OTA) has already been used in some studies. Another basic condition, i.e. the correct choice of the optimal amount of organic matter should be determined experimentally.

Results

We present our results of application of the method in the investigation of the degree of generation of bitumina from rocks sampled in the areas of oil prospecting carried out by the 'Petrobaltic' Oil and Gas Company Exploration-Production and the Polish Geological Institute. Figures 1 and 2 show significant differences of DTA patterns between two groups of samples - one from boreholes I, III and VII and the other one from boreholes II and VIII. While the first group is characterized by a distinct peak in the DTA curves in the temperature range 280-310°C and by the presence of the next peak in the range 370-480°C, samples of the second group reveal either one or several peaks in the temperature range 370-480°C. No peaks are present or only a weak shoulder is seen on the DTA curves of the second group in the range 280-310°C. The absence of the low temperature peak is explained by the heating of the rock formation above 200°C (borehole II; Fig. 1) or to temperatures even higher than 300°C (perhaps up to 350-360°C) as in the case of the borehole VIII (Fig. 2). In borehole II, evidence for heating is seen in samples from the depth of 1312.10-1312.16 m. Samples collected at lower depths show significant contents of lower energy bonds in the organic matter. In comparison with samples from boreholes of the first group, their content of lower energy bonds is distinctly lower.

The results correlate very well with results of chemical analyses of the organic matter. Chemical analyses were made by using classical methods such as the determination of bituminous fraction composition, Rock-Eval analysis and also the determination of the degree of kerogen coalification.

Borehole VIII belongs to a zone of dry gas with bitumina. The upper part of borehole II belongs to a zone of wet gas and its lower part belongs to a zone of dry gas. The other boreholes belong to zones of generation of oil.

The maximum temperature, $T_{\max}=439-449^{\circ}\text{C}$ (Rock-Eval analyses), suggests that the petroleum maturity degree has been achieved in all analysed samples. Results of vitrinite reflectivity confirm this. Analyses of the organic matter which occurs in the vicinity of boreholes I, II and VII show its initial phase of hydrocarbons generation. Organic matter in borehole VIII underwent strong geochemical transformation.

Interesting results have been obtained from analyses of rock samples from borehole IX (Fig. 3). They precisely determined the temperature of heating of rock complexes in the investigated area. A peak in the DTA curves at 300-310°C disap-

pears with the depth of sampling. Distinct bending of the DTA curve at 230°C is observed for a sample taken from the depth of 1310.10 m. In samples taken from the deepest places, the bending on the DTA curve turns downward and shifts to 360–370°C. The second peak (370–400°C) and the third (435–465°C) one occur as characteristic double peaks. The changes of the DTA curves show that some components or the organic matter exhibit structural bonds both dissociated and oxidized with increasing depth. The amount of bonds characterized by the lower temperature of reaction decreases with increasing depth, whereas the amount of bonds with higher temperatures of reaction increases with increasing depth. This mirrors the direct effect of heating in deeper beds up to the temperature just below the threshold temperature for the decomposition of the components, or the split of bonds of the

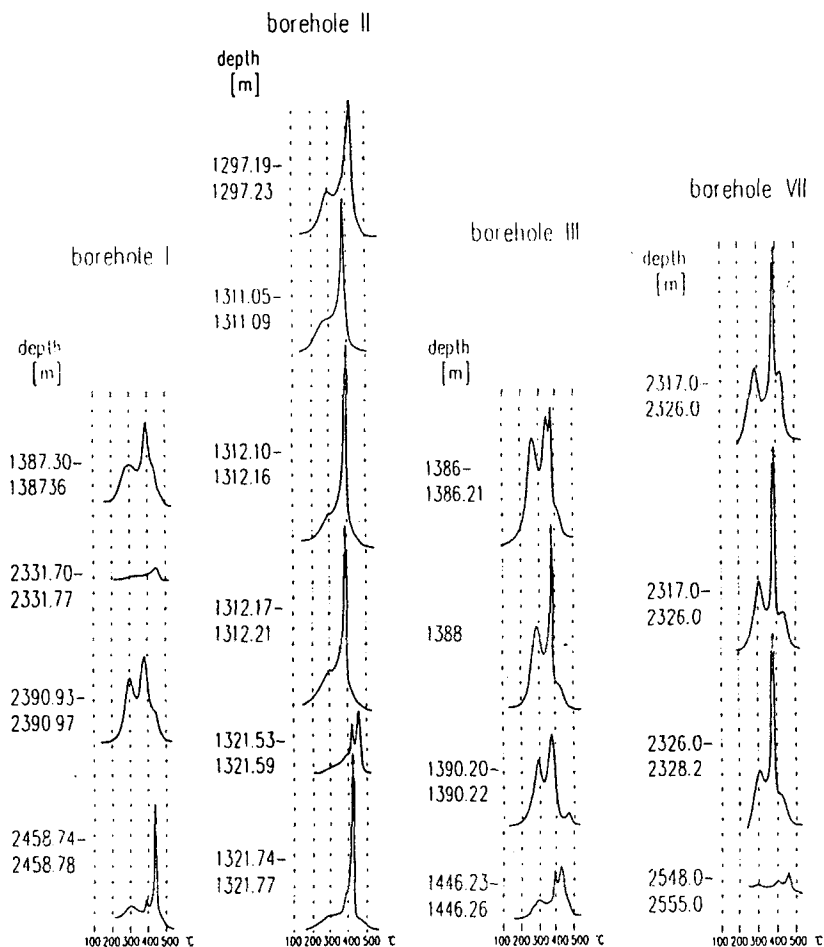


Fig. 1 DTA curves of the kerogen concentrate from old Paleozoic rock samples from rock-mass from different heating zones (the Baltic Sea). (Samples after demineralization in HCl/HF)

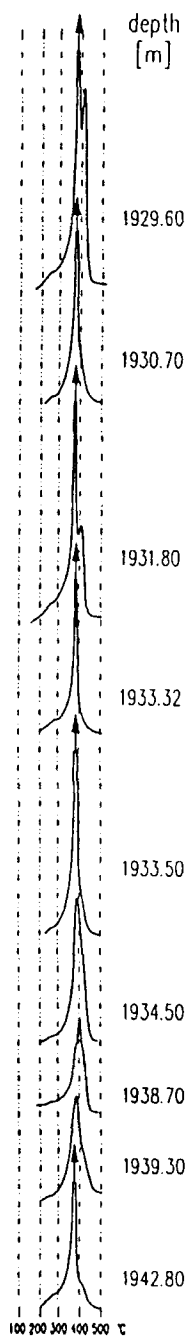


Fig. 2 DTA curves of kerogen concentrates from old Paleozoic rock samples from rockmass heated up to 300–320°C (the Baltic Sea). (Samples after demineralization in HCl/HF)

first peak (350–370°C). The time of heating is also important for the effect mentioned above.

The shape of TG and DTG curves at temperatures 200–300°C (Fig. 3 – the right column of curves) adds some additional information. The curves show an increase

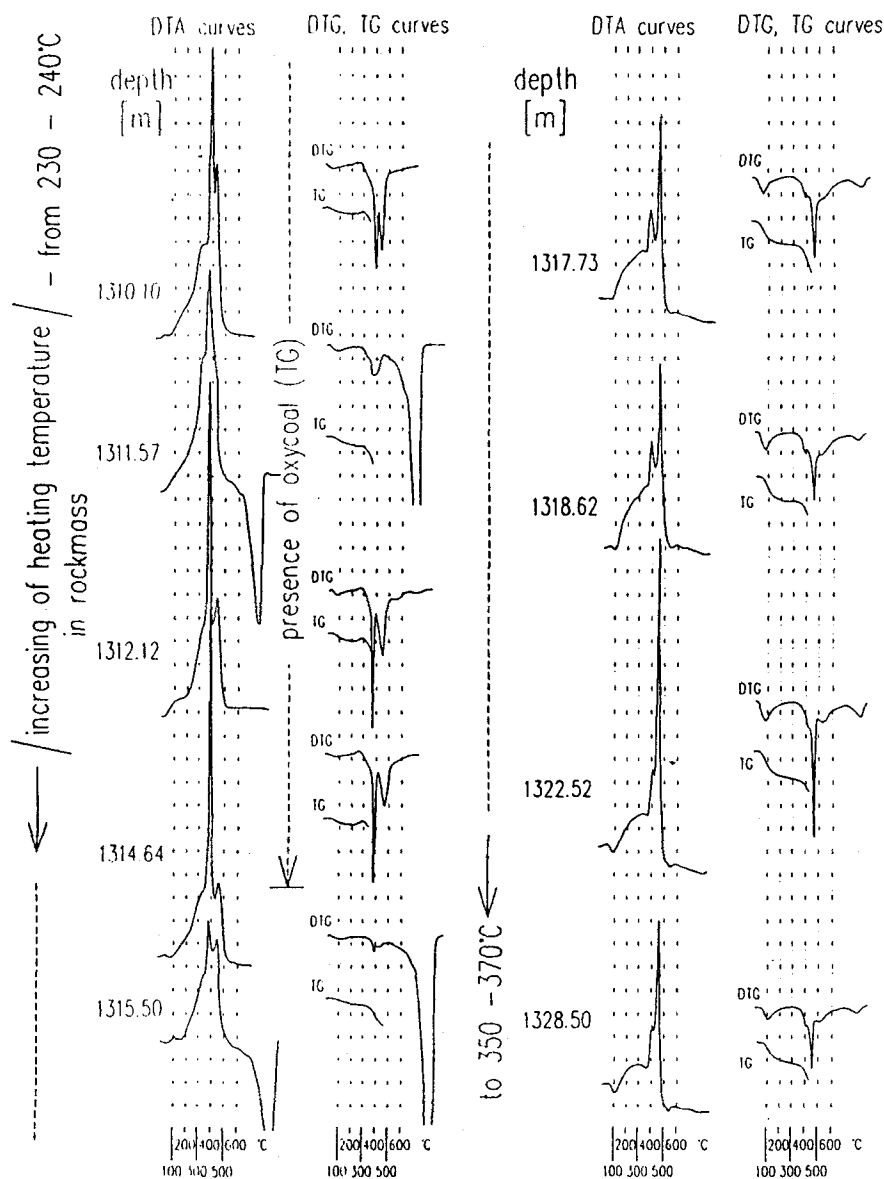


Fig. 3 DTA, DTG and TG curves of old Paleozoic rocks from heating zones probably 230–240°C to 350–370°C (the Baltic Sea, borehole IX). (Untreated samples)

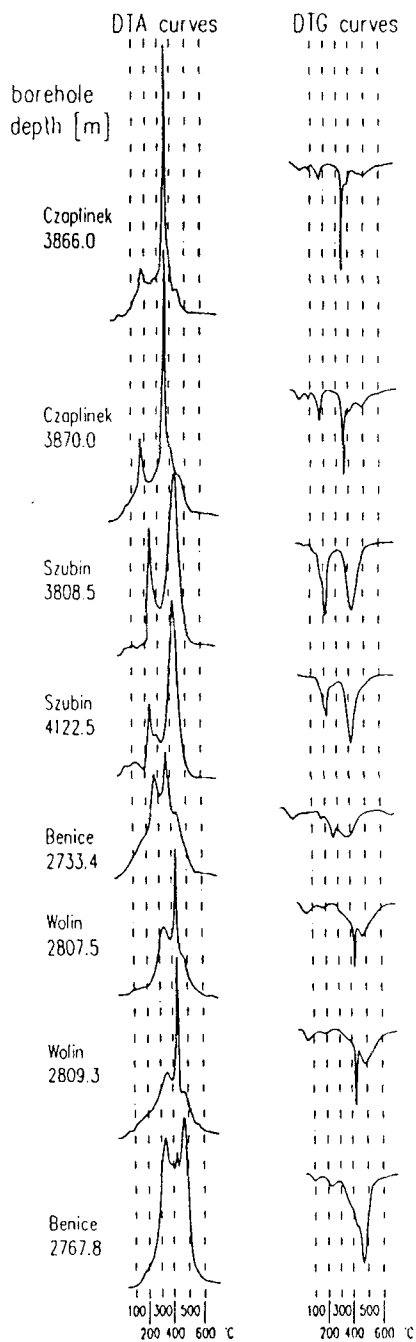


Fig. 4 DTA and DTG curves of kerogen concentrates from young Paleozoic rocks (Zechstein). (Samples after demineralization in HCl)

in weight at temperatures from 240°C to 270–280°C, during heating of samples collected at depths of 1310.10, 1312.12 and 1314.64 m. This is significant for the so-called oxycarbon. The reaction did not occur in samples taken below the depth of 1315.50 m. This suggests that the essential change of primary character of organic matter occurred in upper and lower series, or that the heating temperature changed in both series. The thermal decomposition of oxycarbon occurs at about 270°C.

Characteristic features of the DTA, DTG and TG curves led to the determination of the heating temperatures of the upper beds (samples from depths of 1310.10 and

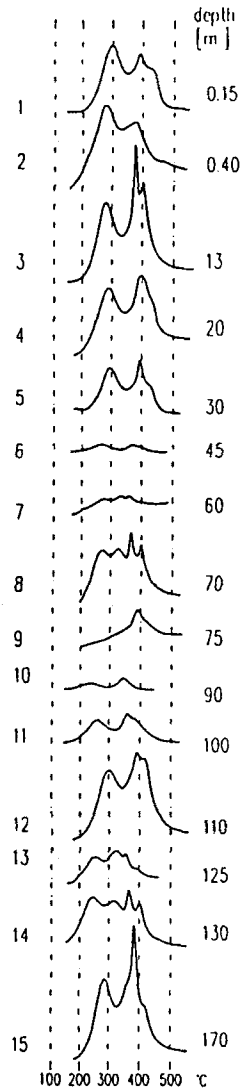


Fig. 5 DTA curves of whole samples of rocks from borehole P-32 from the Barents Sea. Depth of 0.15–170 m. (Untreated samples)

1311.57 m) at about 230–240°C, and the heating temperatures of basal beds (samples from depths of 1322.52 and 1328.50 m) at about 350–370°C. The beds from the depth of 1315.50 m were heated between 230–240°C and 270–280°C.

Thermal curves of the kerogen concentrate (Figs 1 to 3) are a good illustration of the oxyreactivity of the Cambrian and Ordovician sea-derived organic matter. From the viewpoint of its origin the biomass should not contain the organic matter with humic kerogen. Therefore, the kerogen concentrate obtained from these rocks is of sapropelitic origin and shows low variability, both in content and structure (Fig. 1).

The Zechstein kerogen (Fig. 4) was formed during the differentiation of biomass due to biological evolution. The analysed concentrate was also sampled from the marine dolomitic-calcareous facies. Thermal curves of the samples collected from various places of the Pomeranian Zechstein basin suggest the large variability of the biomass. This variability must be taken into account during interpretation of the kerogen oxyreactivity as the indicator of the thermal history of rocks.

The distinct variability of the Zechstein kerogen may have been caused by the changes of composition in the primary marine biomass. The correctness of this hypothesis can be tested by analyses of changes in the oxyreactivity of the recent marine sediments in the Barents Sea (Fig. 5). It is also confirmed by the oxyreactivity curves of the present-day algae biomass (Fig. 6).

On the basis of the presented data we conclude that kerogen is a proper and suitable indicator for the rockmass heating. Oxyreactive thermal analysis applied for the investigation of kerogen as geochemical indicator concerning genetic features of biomass, may be also accepted as a good method for studying the rockmass thermal history.

Figures 1 and 3 suggest that the heating temperature can be assessed on the basis of the mentioned methodology for temperatures above 230–240°C. Similar investigations of the kerogen concentrate from younger Paleozoic (Zechstein) rocks (Fig. 4) showed that kerogen could also be used as an indicator for the heating of rocks above 170–180°C. This use depends on the presence of bonds in Zechstein kerogens which show oxyreactivity at low temperatures. Conclusions drawn from this study are also confirmed by results of the thermal analysis of the kerogen concentrates obtained from the limestone-marl series of Famennian (Fig. 7). Differences between the DTA curves of samples in the profile of the rock formation (the numbers of samples increase upwards the geological profile) enable to distinguish between four series with different characteristics of kerogen. Series III and sample No. 23 show either the change of the composition of algae biomass (Fig. 6) or, perhaps, the increase in the amount of the terrigenous humic matter.

Thermal studies of kerogen concentrates from the Famennian rocks from different places in Poland and Germany illustrate the suitability of thermal analysis for determination of the thermal history of rocks (Fig. 8). A sample from Kowale was not heated. A sample from Łagów was probably heated at a temperature of about 240°C but it had genetic features of the organic matter similar to those of the series No. III of the Kowale profile. A sample from Wzdół was heated at a slightly lower

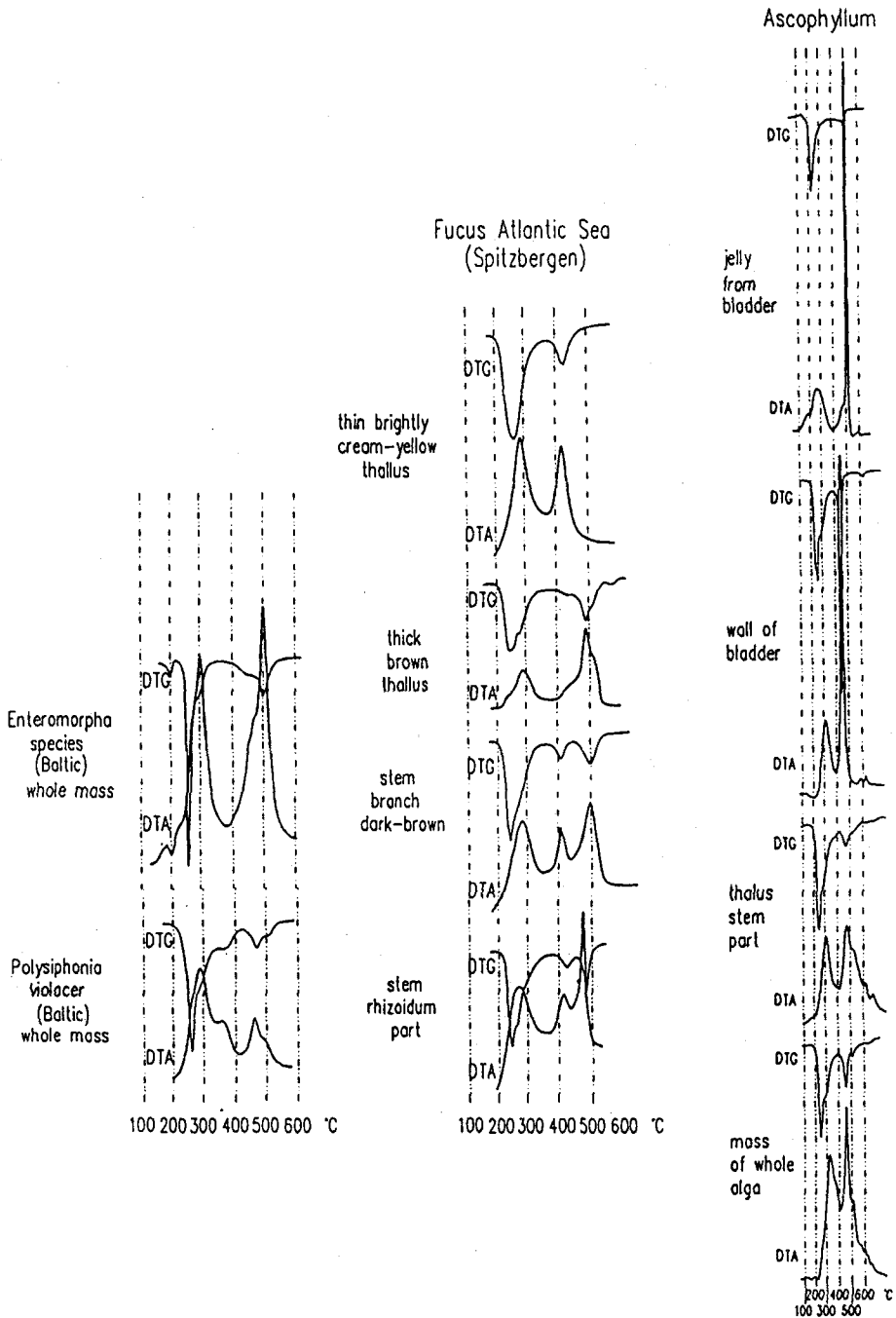


Fig. 6 DTA and DTG curves of some different algae

temperature of about 200°C and it had genetic characteristics of kerogen – type series I, II and IV of Kowale profile. This sample may be the most similar to sample No. 28. A sample from Steinbruch Schmidt was heated at about 300°C and a sample from Kellwasser was heated at temperatures not higher than 320–350°C.

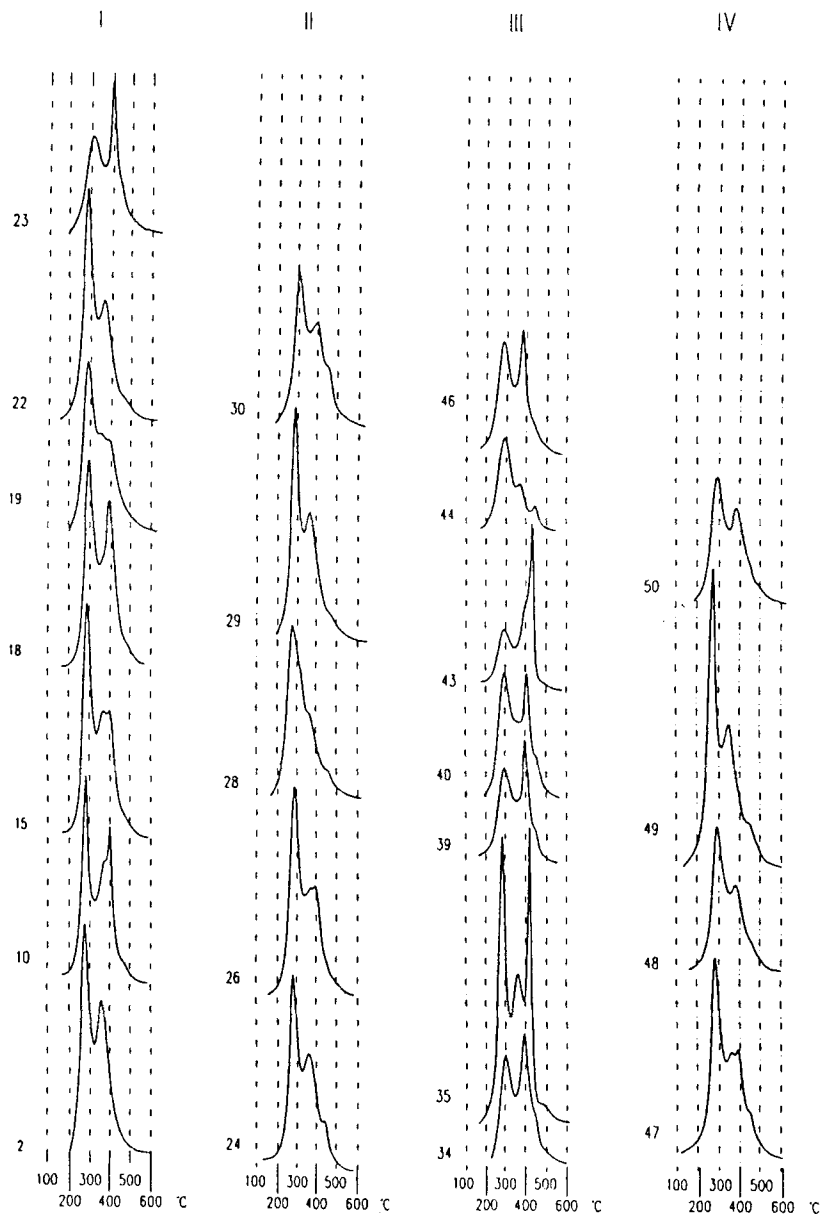


Fig. 7 DTA curves of the kerogen concentrate from Famennian rocks (locality: Kowale). (Samples after demineralization in HCl). 1–50: numbers of samples. I–IV: numbers of series

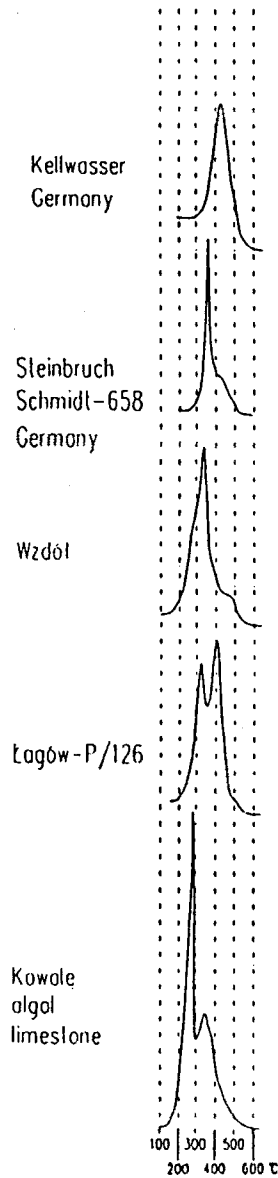


Fig. 8 DTA curves of the kerogen concentrate from Famennian rocks from different Devonian occurrences (Poland and Germany). (Samples after demineralization in HCl)

Conclusions

On the basis of the presented results it can be assumed that kerogen is the rock component that may play a universal role in geological research. Additionally, kero-

gen is not only very sensitive to the thermal history of the rock metamorphism and as such can be used as a good geothermometer, but it also enables the determination of the degree of generation of bituminous matter. Kerogen is a very suitable marker for genetic and paleoenvironmental studies.

We recommend the oxyreactive TA method as a fast and effective analytical tool for kerogen analysis. It is especially effective in studying the kerogen as an indicator for the thermal development of rocks.

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