APPLICATION OF OXYREACTIVE THERMAL ANALYSIS TO THE EXAMINATION OF ORGANIC MATTER ASSOCIATED WITH ROCKS

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Abstract

Organic matter associated with rocks was examined by means of thermal analysis using a new methodology in oxidising conditions. This procedure has been named "Oxyreactive Thermal Analysis" (OTA). The OTA results presented in this study characterise samples from sedimentary rock complexes in terms of their age, and of variations in the associated organic matter arising from different precursors and degree of severity of subsequent transformation processes to which it has been subjected.

The results of the OTA method make it possible to estimate the temperature of maturation, to describe the process of evolution of the organic matter, and to distinguish genetic features of its carbonised and metamorphosed products.

Keywords: organic matter of rocks, OM maturation, OM transformation, thermal analysis

Introduction

The evolutionary development of living organisms during the early history of the Earth resulted in their penetration into almost every natural environment occurring on its surface, and this expansion process was related to the geological and tectonic processes occurring during the Earth's development. In the course of this process, these organisms adapted to a wide variety of physico-chemical conditions, and this variety of environments resulted in large differences in the nature of the organic compounds forming the organisms and therefore in the composition of the organic matter resulting from their decomposition.

Studies of the types of living organisms found in sediments are the basis of stratigraphic chronology of the history of the Earth using the methods of paleobotany and paleozoology which have been employed for many years. In the last few decades, these studies have been assisted by investigations of the or-

ganic matter accumulated in the rock strata by the decomposition of organisms using the traditional techniques of organic analysis, and in this area, thermal analysis (mainly DTA and TG) combined with other techniques, and thermal analysis alone, may prove in the authors' opinion, to be very useful.

Experimental

The application of thermal analysis in air atmosphere to the study of organic matter was developed extensively in the 1970's. A review of literature on the subject carried out in 1981 [1] contains many papers giving examples of TA as applied to the investigation of petroleum products, and a further review in 1989 [2] covering coal and organic matter contained in rocks confirms the great interest in this topic at that time. After this period there was a significant drop in the number of papers, reflecting a decrease in interest in the area, perhaps associated with the notorious unrepeatability of analytical results between laboratories frequently reported at the time. Cumming and McLaughlin [3] showed in 1982 the applicability of thermal analysis in air atmosphere to the proximate analysis and characterization of coals, provided that a rigid experimental protocol was adhered to. Thermal analysis in flowing oxygen atmosphere has also been used for the examination of organo-clay complexes [4], and in this paper, we present the results of an application of such "oxyreactive" thermal analysis (OTA) [5] to this area of study.

The course of reaction of organic substances during heating in air was not in itself the reason for the unrepeatability of results mentioned above; in fact the main reason was a lack of precise definition of the experimental conditions. The parameters of the heating method and the reaction conditions are the main items to be taken into consideration in defining an experimental method, and the most important factors influencing the oxidative reaction process of organic compounds in air are the optimization of the thermal dissociation of the components of the sample and the subsequent reaction with the oxygen.

We have shown that precise and optimum selection of analytical conditions, together with carefully defined heating parameters give repeatable TA results. In consideration of the major influence of the oxidative process in the progress of these reactions, and the fact that a reactivity pattern for the analyte is obtained as a result of the operation, the method is termed "oxyreactive thermal analysis", or OTA.

The OTA method presented in this paper assumes free access of oxygen to the substance being analysed throughout the heating process, and that the course of the reaction is a function of its structure and composition. This type of analysis is of great utility in research work on organic compounds, as an adjunct to the more conventional use of oxidation in the standard methods of organic analysis.

In order to achieve repeatability of OTA results and establish the dependence of the oxyreactivity of the sample on the structure and composition of its components, the following conditions have to be fulfilled:

1) Ultra-fine grinding of the sample to create conditions as close as possible to the molecular reactions between the oxygen in the atmosphere and the sample components.

2) Deployment of the grains of the sample such that oxygen access is uninhibited and in excess of the stoichiometric proportions for the reaction.

3) The establishment of very high gas diffusion rates within the sample bulk, not only to ensure free access of oxygen, but the removal of gaseous reaction products.

4) The establishment of conditions within the sample holder to ensure full oxidation of carbon and hydrogen to CO_2 and H_2O.

5) The optimization of the oxidative conditions covered in points 3) and 4) can also be achieved by varying the oxygen content of the flowing gas atmosphere; this does not always require to be the concentration occurring in normal air.

It must be emphasized that in addition to these points listed above which are of prime importance, others such as heating rate, sample mass, sample holder mass and thermal conductivity, etc., are all of vital importance and influence the results of analysis.

Some fuller notes on the above 5 points are given below in numerical order:

1) Fine grinding of the sample is necessary to ensure thermal equilibrium throughout the particles during heating, thus ensuring that reactions proceed in a controlled manner. It also avoids the possibility of the reacting surface becoming occluded with solid reaction products which might inhibit access of oxygen and escape of gaseous products. Experiments on differently-sized samples of the same material under identical conditions have established that the required particle size is under 0.2–0.3 µm.

In order to avoid agglomeration, a common phenomenon in finely-divided powders, it has been found necessary to dilute the sample with some inert substance such as alumina (Al_2O_3) powder which is inert to oxidation, thermally inert, and incidentally acts as a grinding aid. It has been established empirically that the required optimum analytical conditions can be met by grinding together 300–350 mg of a mixture of Al_2O_3 powder (particle size ca. 0.2 mm) and the substance to be analysed. The proportion of analyte to alumina should be between 1:2 and 1:3 and the grinding time, 30–60 min.

2) The best inert diluent has been found to be Al_2O_3 powder.

3) The required conditions of gas diffusion for oxygen access and product removal can best be achieved by spreading a thin layer of the sample on each of several sample support plates stacked on a single core (in the Derivatograph in-

strument). It is also advantageous in establishing optimum conditions, to arrange aspiration of the product gases from just above the sample holder with simultaneous injection of air in the same area.
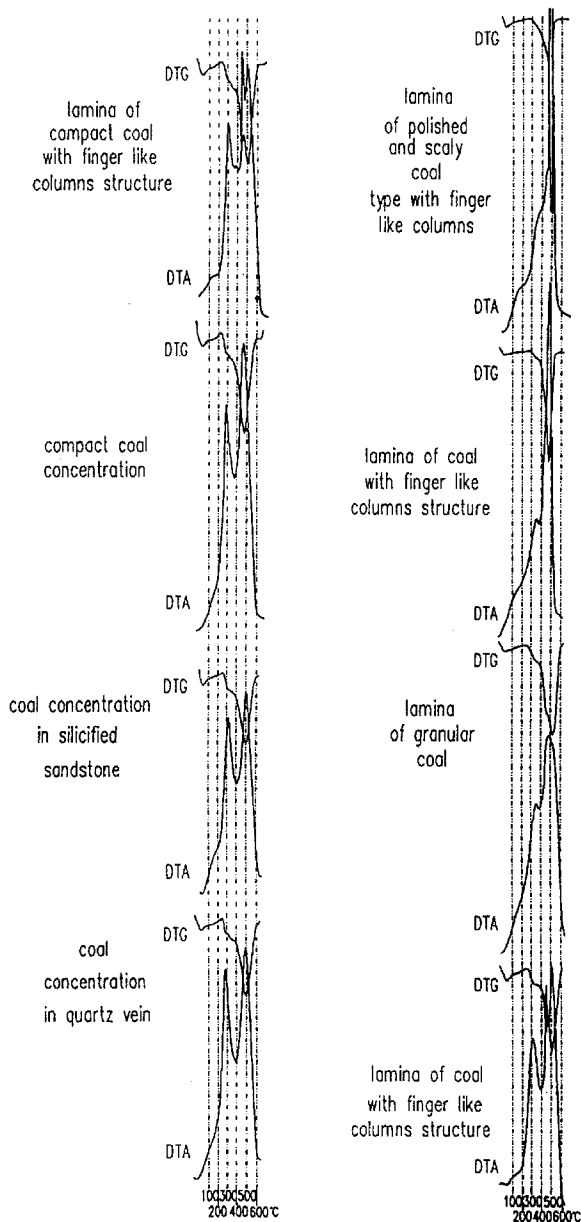

Fig. 1 DTA and DTG curves of sapropelic coal from "Carbon Leader" horizon (Witwatersrand – age 2600–2800 Ma). Various samples of coal laminae and concentrations in various rocks
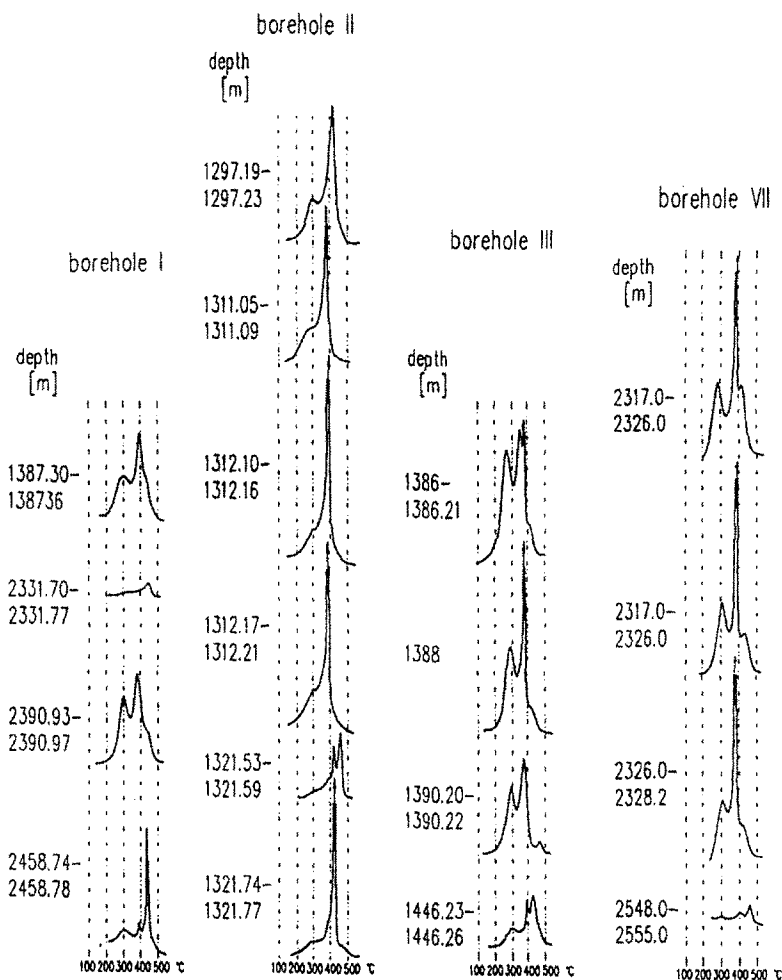
Fig. 2 DTA curves of kerogen concentrate from early Paleozoic rock samples (Baltic area) from different heating zones within the rock mass. Samples demineralized in HCl/HF

With a plate-type sample holder it has been found that the best results for samples with a very high organic matter content are obtained when using two plates, a sample mass weight of 20–30 mg, and a sample dilution of 2:1 or 3:1. For materials of lower organic content the sample mass should be increased to ensure a total content of at least 20–30 mg of organic matter, and a greater number of support plates on the single core should be used. With a crucible-type sample holder, sample masses must be small such that only a very shallow layer lies on the bottom, and higher dilution ratios should be used.

4) Full oxidation of the gaseous reaction products can be achieved by use of large dilutions and additionally, by covering the weighed, diluted sample layer with an upper layer of pure calcined alumina powder. This latter should be of a

particle size less than 1–2 μm. The total ratio of Al_2O_3 (i.e both mixed with the sample and in the covering layer), plus the mineral constituents of the rock sample, to organic matter should be in the region of 5:1 or 6:1.

5) It has been found that higher oxygen concentrations can cause modifications in the structure of carbonization products, and in general the oxygen concentration is an important parameter. However this effect is minimal if it is only a few percent higher than that in normal air (21%), if all the other considerations mentioned in points 1–4 are fulfilled.
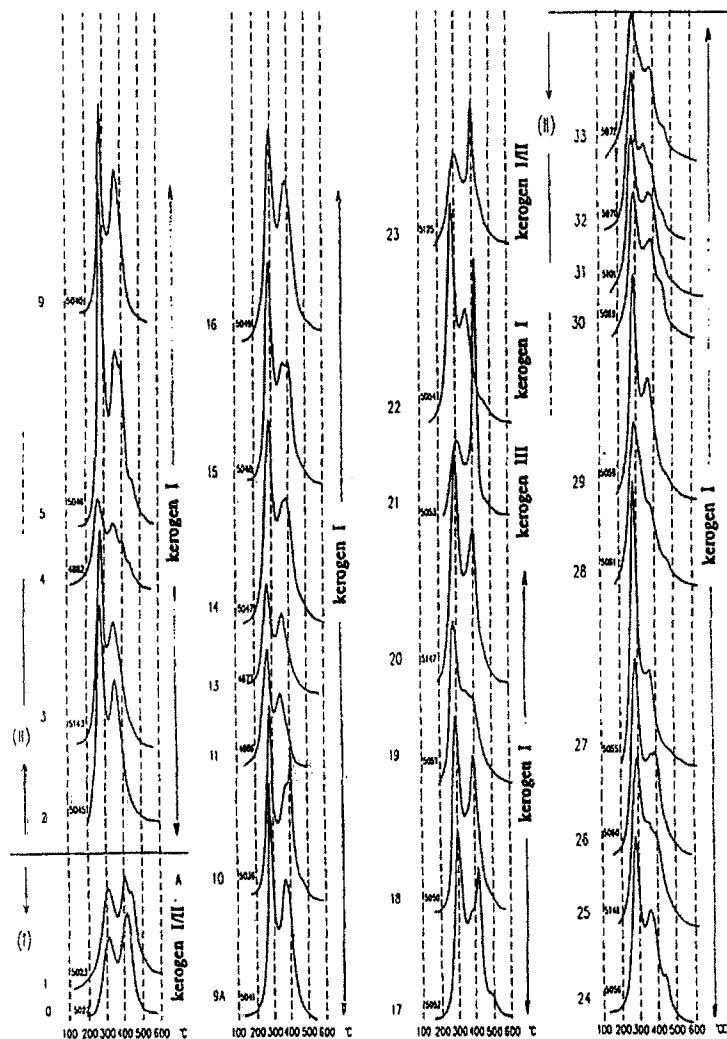

Fig. 3a DTA curves of organic matter in residue from Devonian (Famennian) rocks from Kowale opencast pit after demineralization in HCl. 1–50: Numbers of samples I–IV: Numbers of series

Fig. 3b DTA curves of organic matter in residue from Devonian (Famennian) rocks from
Kowale opencast pit after demineralization in HCl. 1–50: Numbers of samples
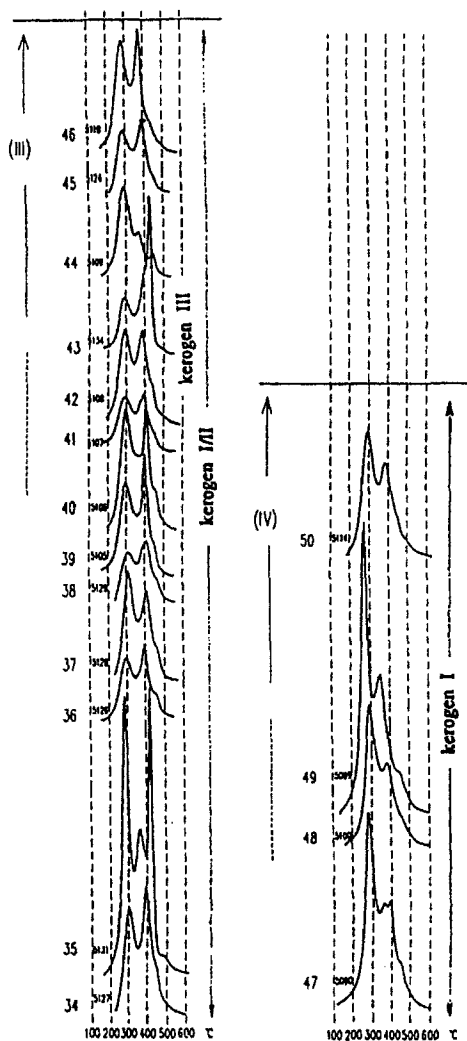I–IV: Numbers of series

The characteristics of the thermal curves obtained, e.g. their shapes, the
temperatures of the peaks, and the relationships between the DTA and mass
loss (TG) traces, are indicators of the composition and structure of the organic
matter in the sample. For example, the temperature range over which the reac-
tions take place are a function of the bonding energies of the various functional
groups or other structural elements within the matrix. The use of similar oxyre-
active thermal analysis (OTA) methods has been reported in other publications
[6–10]. In all such work, it is of fundamental importance to make the correct
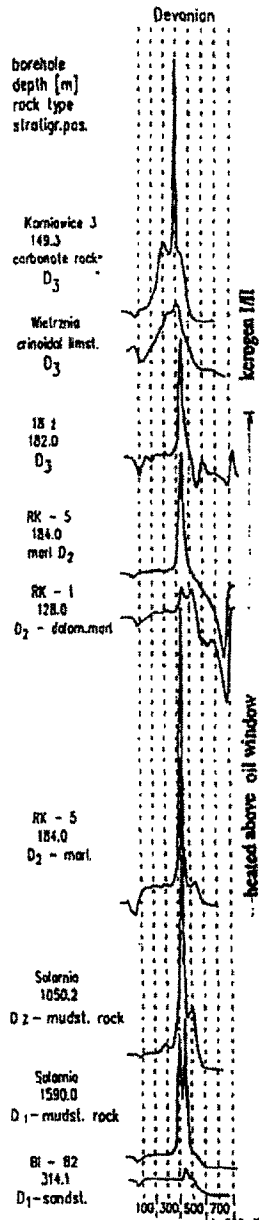
Fig. 4 DTA curves of early Paleozoic rocks from the margin zone of USCB (Poland) as an example of kerogen characterization

choice of the amount of organic material in the analysis sample, depending on its nature and concentration in the original sample. This is best decided upon by carrying out preliminary empirical experiments. In the case of demineral-
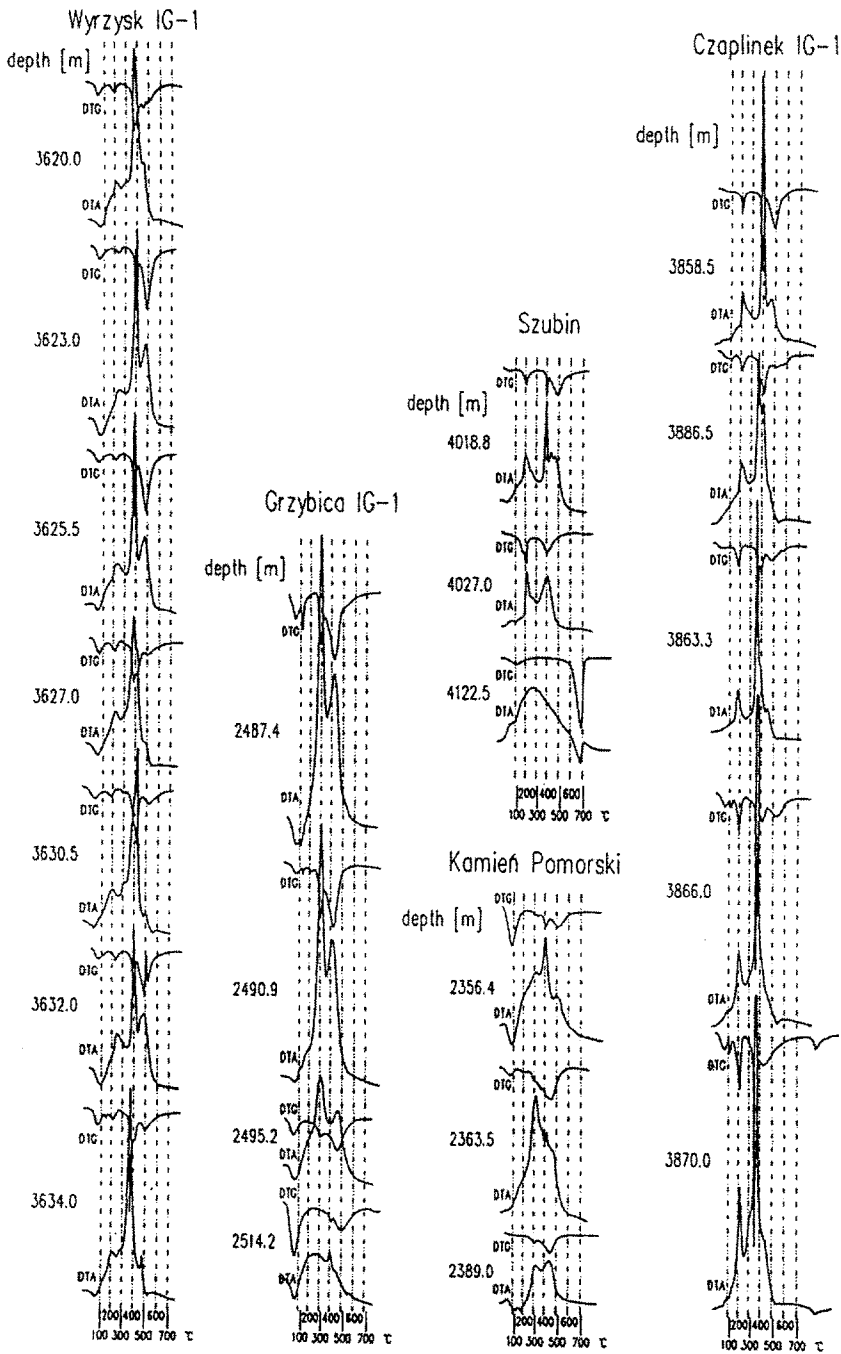
Fig. 5 DTA and DTG curves of kerogen from rock samples after demineralization in HCl

ized samples, the organic content is of course higher than in the parent materials, and this should be taken into account in deciding upon the sample mass and dilution factor.

In the investigations here reported, the Hungarian "Derivatograph" simultaneous TG/DTG/DTA instrument, developed by F. Paulik, J. Paulik, and L. Erdey [11], was used. A flowing atmosphere of air was injected into the sample chamber at a rate of $1.0 \, l \, min^{-1}$, and waste gases extracted by suction at a rate of $1.9 \, l \, min^{-1}$. A multiplate sample holder was fitted with sets of 1–10 plates as required. Sample mass and number of plates used depended on the organic content of the sample.

Differences in the horizontal scales of some of the thermal curves presented arose from a purely technical reason. The earlier analyses were carried out at a slower recording speed than those for the Ascophyllum (Fig. 7), but in all cases
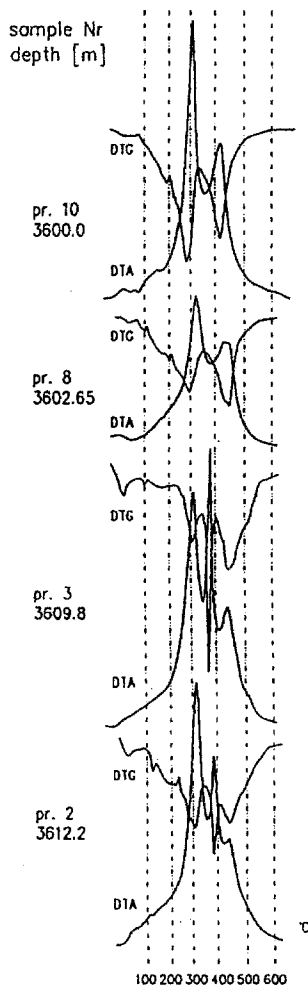

Fig. 6 DTA and DTG curves of Permian rock samples from the Czarne 3 borehole

the vertical scales are identical, allowing direct comparisons. The differences in the horizontal scales could not be compensated for with the available "Autocad" software.

Materials

The objective of this study was to assess the ability of oxyreactive thermal analysis (OTA) to characterize organic matter in rocks. Samples represented a variety of sedimentary environments and included:

– 12 samples of hard coal from "Carbon Leader" horizon, Witwatersrand, Republic of South Africa (Fig. 1).
– 58 samples of Early Paleozoic marine sediments (pelites and carbonate rocks) from deep boreholes in northern Poland and the Baltic Sea (Fig. 2).
– 53 samples of Famennian limestone and marl of the algal limestone series from the IGCP (International Geological Correlation Program) reference profile in Kowale (Figs 3a and 3b).
– 45 samples of Devonian rocks representing different facies in S.W. Poland (Fig. 4).
– Over 200 samples of Zechstein rocks collected from 15 deep boreholes in N and NW Poland. These represented different facies of a sedimentary basin selected for oil prospecting (Figs 5 and 6).
– 19 samples of algae from the Baltic Sea (15 samples) and the N Atlantic Ocean (4 samples) (Fig. 7).

The numerous OTA curves presented in this paper and generated from these samples demonstrate that they can be used as "fingerprints" to identify the organic matter extracted from rocks of different ages and originating in different sedimentary environments. All the thermal analyses were performed under a set of identical conditions which was established as being the most suitable for OTA.

Dispersions of organic matter in rocks, particularly carbonate rocks, required specially developed concentration techniques to obtain samples suitable for thermal analysis. Experiments carried out by one of us (S. Cebulak, supported by USA Congress, M. Sklodowska-Curie Grant), suggested that physical separation or leaching in hydrochloric acid are the only satisfactory methods of concentrating the organic matter. Use of a mixture of hydrochloric and hydrofluoric acids, as is common in demineralisation work, was found to result in a significant coalification of many of the constituents of the organic phase. Moreover, the high temperatures (70–100°C) involved in the HCl/HF leaching process was found to affect certain of the inorganic constituents, particularly sulfides. Thus, leaching in 2 molar HCl was chosen as the best technique appropriate to the present study, although it must be emphasised that even this can result in the hydrolysis and transformation of weakly matured organic matter.
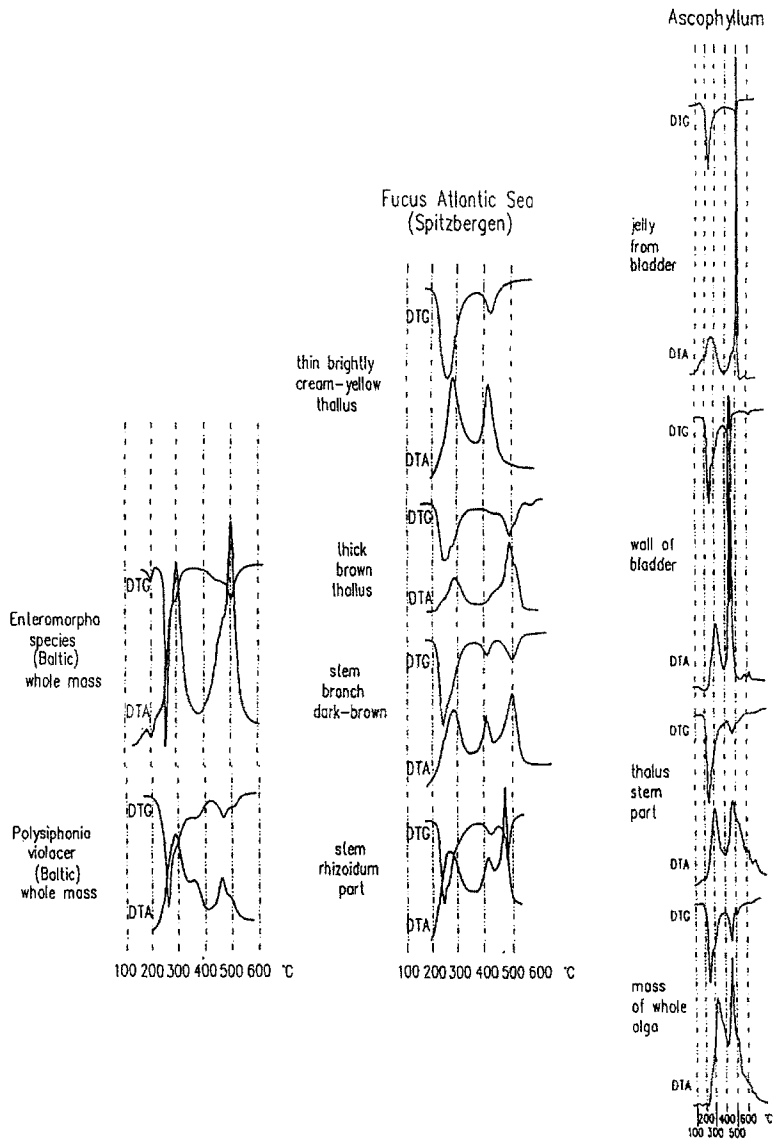
Fig. 7 DTA and DTG curves for various algae

Results

Oxyreactive thermal analysis of the organic concentrate (kerogen) shows significant differences in the responses of materials of different ages. The results obtained reflect variations in the original composition and structure of the or-

ganic matter and differences due to transformations occurring during the geological history of the Earth. This type of interpretation has been made possible by the close interdependence between the oxyreactivity of organic matter and its composition and structure. The oxyreactive characterization of organic matter formed since the beginning of the biotic age in the Earth's history is exemplified by the samples of coal taken from the horizon known as "Carbon Leader" in the Witwatersrand deposits of South Africa, whose age is around 2600–2800 Ma. The significant differences between the various thermal curves for the samples of this particular coal (a boghead) and the products of its anthracitization resulted from a loss of volatile components from the precursor organic compounds, and other transformation processes occurring during its maturation (Fig. 1).

It has been suggested that the hydrocarbon precursors of these Witwatersrand coals were formed by polymerization of liquid and gaseous hydrocarbons as a result of irradiation by uraninite [12]. Snyman [13] has further suggested that the Witwatersrand coal represents a high-rank boghead which has been altered as a result of α-particle bombardment by uraninite. Where uraninite was absent from the coals, this transformation could also result from a katagenesis process within the rock mass, and there may be evidence for this in the presence of phyllosilicates in the form of muscovite, pyrophyllite, and chlorite.

The composition and structure of the organic matter found in coal fragments sampled from quartz-cemented rocks resulted from its primordial composition, and from biochemical and low-temperature geochemical post-sedimentary processes. Cementation by the quartz has prevented the escape of volatile components.

The thermal curves for these coals show that their decomposition occurs at 300 and 500°C (Fig. 1), and it is possible that this represents the oxyreactivity of algal and fungal matter belonging to the Cyanophyceae and Thuchomyces lichenoides [16]. They are in fact very similar to those obtained for contemporary algae (Fig. 7). It is well known that in this primary geological age, only archaeobacteria, primitive fungi, and algae of the Cyanophyceae type existed, and that only such biomatter could form thin layers of coal [13, 16]. The plant-like structure has been termed "columnar" in this type of boghead coal [15, 16].

The OTA results for kerogen samples from Old Paleozoic rocks (590–400 Ma) presented in Fig. 2 show a different type of thermal curve. These are characterized by two or three peaks, the first one occurring around 300°C, the second at between 380 and 400°C, and the third at 420–440°C. Occasionally, a small additional peak appears at about 360–370°C and another at around 470°C. The absence of the first peak in the thermal curves of samples from the deepest parts of drill cores can be explained by geothermal heating of the rock and consequent loss of the more volatile components. This effect of heating is particularly well marked in the analyses of samples from borehole II.

The differences in the results of the thermal analyses obtained for Old Paleozoic samples (Fig. 2) and for samples from the beginning of the Biotic Age are due to the fact that in the Old Paleozoic, the world of living organisms was already well developed and differentiated. Algae had developed into physically large forms with a different morphology and metabolism from the earlier forms, and thus the structure and composition of their organic constituents (and their derivatives) is different. Figure 7 demonstrates the differences in the OTA curveš for the organic matter deriving from the large and morphologically differentiated algae, Ascophyllum and Fucus, from the Atlantic Ocean.

In the world of animals, protective armour and shells of chitin appeared, and this material is very resistant to decomposition and transformation processes. Its presence in fossil organic matter may explain the form of the thermal curves of samples from this section of the stratigraphic profile (Cambrian to Silurian).

Differences in the oxyreactivity of organic matter in rocks sampled from different environments in a Famennian rock complex are shown in Figs 3a and 3b. The OTA curves for these samples show similar thermal response temperatures to those from the Old Paleozoic, i.e. Peak I about 300°C, Peak II about 370–400°C, and a weak third peak (Peak III) at 450–470°C. Within the geological profile, the differences in the form of these OTA curves allows the discrimination of four series, or rock complexes.

In Series II and IV, algal limestone complexes, the organic matter originated in a similar environment, and on their OTA curves one can see that the first peak predominates over the second. Series III samples are notable for the different oxyreactivity of their organic matter, and it can be seen in this case that the curves are characterized by having a similar magnitude for both peaks or even, in some cases, showing peak reversal where the second peak predominates over the first. This is a heterolite series consisting of alternate layers of limestone, marl, and clayey siltstones formed in a sedimentary basin under oscillatory changes in environmental conditions. As a result, this variability of environment gave rise tò a cyclical variation in the living conditions and consequently, the types of indigenous organisms and the organic compounds arising from their decomposition. This effect is shown in samples 21 and 23 in the Series II rock complexes.

In Series III, the type of OTA curve characteristic of Early Paleozoic sediments (as shown in Fig. 2) is displayed, but in Series II and IV a different type of OTA curve is evident. This is very similar to the curves for algal matter of Carboniferous sapropelic coals of the boghead type (two peaks at about 300 and 400°C, with the first predominating). The organic matter of the samples referred to in Figs 3a and 3b may be classified under three types of kerogen, as indicated in Fig. 3a.

Figure 4 shows the OTA curves of organic matter from Devonian rocks (410–360 Ma) taken from the margin zone of the Upper Silesian Carboniferous Basin. The majority of these suggest significant heating of the rock complex up to a temperature beyond the so-called "oil window". This is demonstrated by the

lack of the first peak (around 300°C) on almost all the OTA curves (Fig. 4), with only two exceptions, Karniowice 3 and Wietrznia.

The nature of the organic matter in the Younger Paleozoic sediments (Zechstein) is dependent both on its primary environment and on subsequent diagenetic processes which have resulted in the formation of significant amounts of bituminous organic compounds. OTA curves for this type of organic matter are shown in Figs 5 and 6, and these are typical of samples with a high degree of maturation of the organic matter (OM) into bitumen. Three types of organic matter can be distinguished on the basis of differences in their thermal curves;

1) OM in samples from the boreholes designated Wyrzysk IG-1, Szubin, and Czaplinek 1.

In these, the first exothermic peak occurs as low as 200°C, the second at about 300°C, a third very large one around 400°C, and finally a fourth of variable size in the region of 500°C.

2) OM in samples from the borehole. Czarne 3.

Two or three thermal effects are seen on the OTA curves for these samples. A very large peak occurs at about 300°C, another large peak at around 400°C occurring in only some samples, and a fairly commonly-occurring final peak at 470–500°C. The volatile losses occurring in the temperature range 100–300°C, (without any exothermic effect), are normally large in these samples.

3) OM in samples from the boreholes Grzybica IG-1 and Kamien Pomorski.

DTA curves for these materials show a variety of shapes, but in general they have three peaks at around 300, 400, and 470–500°C, with the first being usually the largest. No low-temperature evolution of volatile components has been observed in these samples. All these types of organic matter can be classified in the "kerogen I" group.

The organic matter of these sample groups, 1–3 above can give rise to different types of bituminous fractions, each with its own typical volatilizing temperature and degree of flammability, as can be seen from a comparison of their DTA and DTG curves. These obvious differences in the OTA curves could form the basis of a method for estimating the industrial uses of such materials, e.g. the potential bitumen output. They could also give valuable information on the environmental influences involved during the formation of the sediments in which they occur.

Conclusions

The results presented in this paper demonstrate the usefulness of the oxyreactive thermal analysis technique in a wide variety of areas of geological research. It provides a method for determining differences in the mode of formation of sedimentary organic matter, its tendency to generate volatile products on

heating, and the degree of carbonification. OTA can also be used to estimate the degree of geothermal heating to which the rock matrix has been subjected, and the temperatures at which the volatile components are released.

These results have been confirmed by the use of the conodonts temperature index, together with the reflectivity of phytoclasts.

Additionally, OTA allows conclusions to be drawn as to the composition and structure of carbonaceous matter formed by the heating process during carbonification, and as to the nature of its precursors. The concept of the oxyreactivity of carbonaceous materials also leads to a better understanding of the transformation processes leading to its formation, and the OTA method may also prove useful as an adjunct to and extension of the "Rock-Eval" characterization of organic matter.

A further possibility of this method is its application to investigations in the biological field and the examination of different environments in the Biosphere. Investigations using OTA studies of rocks of different ages, along with selected model organic compounds were used as the basis for the interpretation of the results here presented.

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