THE APPLICATION OF THE OTA OF KEROGEN TO THE EVALUATION OF THE ROCKMASS HEATING

S. Cebulak[1], A. Langier-KuÜniarowa[2]* and I. Grotek[2]

[1]Silesian University, Będzińska 60, 41-200 Sosnowiec, Poland
[2]Polish Geological Institute, Rakowiecka 4, 00-975 Warsaw, Poland

Abstract

Oxyreactive thermal analysis (OTA) carried out in the conditions of full access of oxygen to each reacting particle of the sample investigated is a suitable method for the determination of important properties of the organic matter dispersed in the rocks. Its results may be easily evaluated to the form of values to be used in a clear diversification and classification system of organic matter/kerogen, as well as to the evaluation of its transformation process in a rockmass. The OTA also enables the distinguishing of the transformation stages and the investigation of the results of the gaseous products liberation from organic matter and kerogen. The OTA method may be applied as a complementary one for the Rock Eval analysis and be used for the organic geochemical and bituminological studies for geological bitumen prospecting.

Keywords: kerogen, oil prospecting, organic matter, oxyreactive thermal analysis, paleotemperatures

Introduction

The present paper is the first in a series of publications dealing with the possibilities of the oxyreactive thermal analysis (OTA) applied for the investigation of dispersed organic matter (DOM) in the rocks, involving the thermal history of the rockmass. Such an application of OTA has been reported by the authors since 1997 [1–3]. The studies carried out in recent years confirmed it to be very useful method for the studies of kerogen transformation in the rockmass caused by heat flow occurring in the earth crust including also particular events associated with the thermal influence of magmatic intrusions into sedimentary rocks complexes. Recently the results of heating the rocks with thermal waters saturated rock complexes have been studied.

In this paper the influence of the heat flow commonly occurring in the crust earth is considered as resulting in the transformation of DOM in the Old Paleozoic complexes in North Poland. Remarkable differences in degree and course of DOM transformation have been observed.

---

*   Author for correspondence: E-mail: alan@pgi.waw.pl

Experimental

The samples studied were collected from the boreholes located in North Poland, in the area between GoÓdap IG 1 (E) and Słupsk IG 1 (W).

Geological structure of this area allows to anticipate a weak heating in E part of this region due to relatively shallow burial (less than 1600 m) of the sediments under consideration. In contrast, part W exposed to remarkable heating and its influence on the degree of DOM transformation was due to a great NW-SE tectonic faults system resulted in a deep burial (up to almost 4700 m) of the sediments investigated.

The localization of the boreholes from which these samples originated are shown in Fig. 1.

The samples studied represent all stratigraphic stages of Old Paleozoic. The choice of the samples was based on the contents of organic matter. In the cases of a laminar structure of the rock, the bitumen-rich laminae were used for the analyses.

The study involved 210 samples from Old Paleozoic rocks complexes, 180 of them submitted to thermal analysis in tandem as natural ones (untreated) and after treatment with 1 N HCl (24 h). Besides the samples from the boreholes shown in the Fig. 1, other 117 Old Paleozoic samples from the boreholes located on the Polish part of Baltic Sea as well as 278 Zechstein samples representing the Main Dolomite horizon, known as the reservoir rock complex for oil and gas resources, were also investigated by OTA method. In 77 of the these samples also determined microscopically reflectance index of vitrinite (R_0) was evaluated.

Thermal analyses were carried out by means of the derivatograph (MOM, Hungary) [4], especially modified for requirements of the OTA method. The experimental conditions applied were as previously described [1]. The essential requirement was to assure a full oxygen access to each organic matter (OM) particle through all the course of analysis. The grain size should assure the possibility of the oxidation during all the heating processes without any formation of the coalification products covered on the sample grains. The experimental conditions should obey the following requirements: grain size<0.5 mm, the dilution of OM with thermally neutral substance in the ratio of 1:3 or more, the distribution of the sample in the form of a very
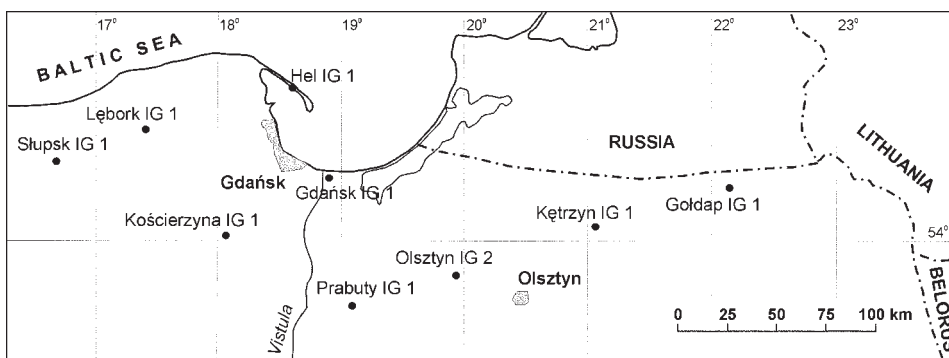

Fig. 1 Map of the localization of the mentioned boreholes in Northern part of Poland

thin layer due to the use of the multiplate sample holders [4], dynamic air atmosphere, relatively low heating rate. The number of plates and their size in the sample holders depended on the dilution of OM in the sample and oscillated between 2 small plates used in the case of OM-rich samples to 10 larger plates when the dilution of OM was greater. As the diluent Al_2O_3 was used. Heating rate was $10°C\ min^{-1}$. Dynamic atmosphere was obtained by the suction above $1.9\ L\ min^{-1}$.

Results and discussion

OTA is a method that enables the determination of the stoichiometry of the oxidation reactions in the sample thus it can serve for the determination of the composition and consititution of the organic matter (kerogen) present in rock samples. Therefore the convergence of the diversification of its oxyreactive properties with that of the provenance of rock samples from different areas and depths as showing different heating events may be expected. This assumption has been confirmed by the results of the present studies.

Thermal curves of the rock samples weakly heated show a distinct exothermic peak with the maximum at 280–300°C. The presence of weaker peaks or only dents at higher temperatures emphasizes the heterogeneity of the composition and constitution of OM in the rocks studied. Higher temperatures of this strong peak maximum (above 300°, even 335–340°C) reveal the OM transformation due to the heating of the rockmass. It maybe due to the OM transformation consisting in the formation of various compounds which are typical of kerogen.

Further increase of heating temperature results in the formation of subsequent strong exothermic peaks proving an advanced transformation of organic compounds into higher condensates, i.e. having higher bond energy and showing different configuration of the constituents and functional groups.

When the temperature of rockmass increases to the limiting value for the preservation of particular bonds and corresponding components become decomposed, the thermal curves of these samples display only high temperature peaks at 360–390 and 400–500 and even above 500°C.

These phenomena are illustrated by the thermal curves shown in Fig. 2. The OTA curves of the samples from the boreholes Gołdap IG 1 and Kętrzyn IG 1 located in the E part of the area under consideration, demonstrate the oxyreactivity of the OM (or more precisely – kerogen) that has been submitted to low-grade transformation only, due to a weak heating of rockmass. The R_0 value of vitrinite in these samples is 0.45–0.50%.

OM occurring in the samples from the boreholes Lębork IG 1 and Słupsk IG 1 (W part of this area) yields thermal curves characteristic for the higher transformation degree indicating higher temperatures that influenced the rockmass in part E of the region. The presence of these peaks at 450–540°C is shown in Fig. 2.

Considering in detail the kerogen oxyreactivity diversification, the samples from the boreholes located between these utmost regions of the area under consideration and from the rocks complexes occurring at different depths, some characteristic correlations have been found. Thermal curves of the samples from the borehole
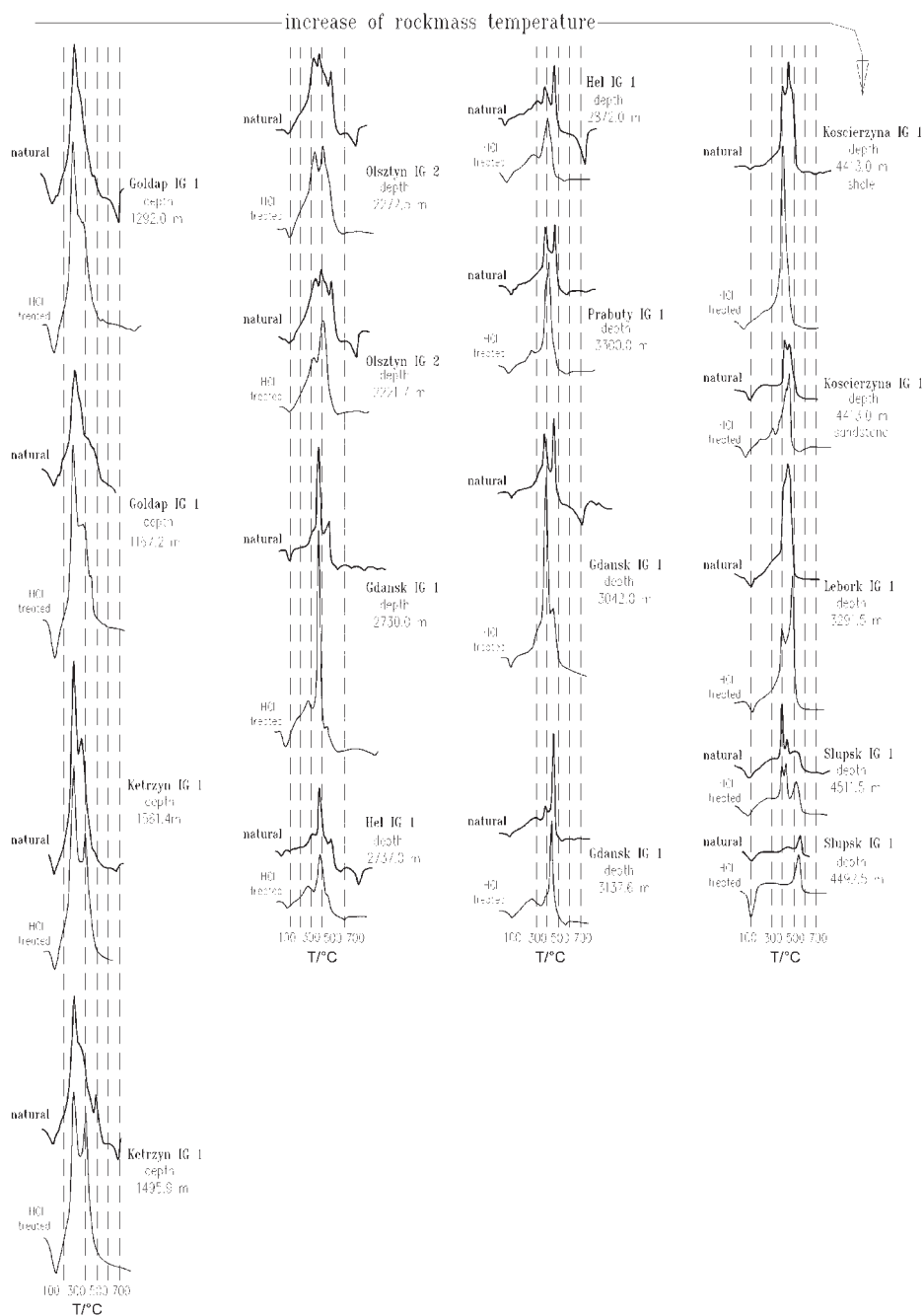
Fig. 2 Exemplary DTA curves of selected samples, both natural and HCl treated

Olsztyn IG 2 (depth 2272.5 and 2221.7 m) show still a distinct peak at 320–335°C as well as a strong peak at 370–400 and a weak one at 480–495°C, as shown in Fig. 2 (the second column of the DTA curves). The R_0 value of vitrinite is here 0.50–0.63%.

On the DTA curves of the samples from the intermediate part of the area studied (boreholes Hel IG 1, Gdańsk IG 1 and Prabuty IG 1; Fig. 2 – the second and third column of the curves) the peak at 300–335°C does not appear, whereas two separate peaks at 370–390 and 460–490°C occur. Very characteristic is the preponderance of the first of these peaks on the thermal curves shown by the samples from smaller depths, where the R_0 value is 0.60–1.21%. The second peak predominates on the DTA curves of samples from greater depths, with R_0 values in the range of 1.26–1.60%.

Thermal curves of the samples from the boreholes Kościerzyna IG 1 and Lębork IG 1 (the fourth column of the DTA curves in Fig. 2) show 2 or 3 peaks in the temperature range 400–490°C, the first at the temperature up to 420°C. The R_0 value of vitrinite of these samples has been determined as 1.68–1.70 and 1.83–2.30% for the boreholes Kościerzyna IG 1 and LÄbork IG 1 respectively.

The samples showing the preponderance of the thermal peaks at 460–490°C give also a weak effect slightly above 500°C.

Oxygen reactivity of kerogen of the samples from the Słupsk IG 1 borehole representing the W border of the area under consideration is characterized by two thermal peaks at 390–440°C besides a strong one about 500°C. The R_0 value determined in two samples from the rock complex under consideration in Słupsk IG 1 is 3.66 and 4.05%.

Another problem has to do with the different OM reactivity of HCl treated samples. Namely on the OTA curves of these samples when they were weakly heated in the rockmass, the high-temperature peaks disappear, whereas the low-temperature peaks intensity increases showing also a slight lowering of peak temperatures. This may be interpreted as a result of the reactions analogous to the depolymerization of a geopolymer, resulting from the HCl treatment. It is particularly well expressed in the thermal curves of the samples from Hel IG 1, Gdańsk IG 1 and Kościerzyna IG 1 (shale) representing a rockmass of heating degree higher than that of Gołdap IG 1 and Kętrzyn IG 1 boreholes as shown in Fig. 2 (the DTA curves of natural samples and of the HCl treated ones are marked by different fonts).

On the contrary, thermal curves of the HCl treated samples representing the boreholes Kościerzyna IG 1 (sandstone), Lębork IG 1 and Słupsk IG 1, i.e. from the rockmass heated in still higher degree, show a different phenomenon: the intensities of their high-temperature peaks, sometimes also their peaks temperatures, slightly increase in comparison with OTA curves of natural samples. It allows to presume that probably the HCl treatment in this case gives rise to the further transformation reaction occurring in the geopolymers i.e. the activation of the transformation processes. This phenomenon may be employed for the elaboration of the indices of the presumable OM transformation. It may be useful for the documentation of the stepwise changes of the OM properties occurring due to its heating transformation in the natural environment.

It is worth mentioning that in the Koícierzyna IG 1 borehole two varieties of the rock occur at the same depth (4413.0 m): a shale and a sandstone, which due to HCl treatment show adverse results. The HCl treated shale shows the thermal effects proving depolymerization, whereas those shown by HCl treated of sandstone indicate the coalification increase in spite of the same heating temperature influencing the rockmass under consideration during its geological history. This phenomenon may be interpreted as a result of lithologic differences between these sample varieties as density, porosity and other properties which are most important for the outflow of gaseous products of reactions, much easier in the case of sandstone and very slow in a compact shale. The easy liberation of decomposition products from the sandstone sample accelerates its coalification. Furthermore the catalytic properties of clay minerals may be the reason for the heteropolymer system preservation.

Due to a high number of experiments consisting of 1180 OTA analyses (605 of natural samples and 575 of HCl treated ones), enriched with the R_0 of vitrinite determinations in 77 samples, geological recognition of rocks complexes under consideration, especially regarding the intensity of heating, and taking into considerations the general geological information about the rock complexes under consideration, the authors could make many observations. On this basis the authors evaluated kerogen according to the OM oxidation reactivity.

Such an evaluation can be helpful for the determination of paleotemperatures of rock complexes from OTA results for geological purposes. One of us (S.C.) commenced these studies based on the generalized observations of a very remarkable number of OTA results and their relations to R_0 values as well as to clay minerals XRD determination.

The principles of kerogen evaluation based on the OTA results

The general relationship between the differentiated OM oxidation reactivity and the heating degree of rocks complexes confirmed by geological data and R_0 of vitrinite values has been evaluated as the basis for the determination of the essential kerogen characteristics as acquired by OTA technique. Thus following OTA exothermic stages have been distinguished as showing the presence or lack of characteristic peaks:

I – up to 360°C
II a – 360–420°C
II b – 420–460°C or slightly above
III – above 460°C

The peaks occurring in each of these intervals result from the oxidation reactions indicated by different kerogen constituents.

Generally, it may be assumed that the peaks occurring in the first stage of the OTA curves originate from the liberation and oxidation of the constituents having the lowest bond energy in the geopolymer as well as showing the lowest condensation of the structure. The peaks of higher intervals prove the presence of stronger constituents bonds and more complicated structure configuration as well as its higher conden-

sation. Tracing accurately the differences in the peaks distribution on the DTA curves of natural samples (Fig. 2) indicates that:

1. the first and the fourth temperature interval on the OTA curves is characterized by a relative simplicity,

2. in the second and the third interval there appears a very characteristic correlation of the peaks (Fig. 2, the second and third column of DTA curves).

Simultaneously with the temperature increase the essential peak of the second interval gradually disappears whereas the intensity of the peak of the third interval increases (e.g. samples: Gdańsk IG 1 –2730.0 m, Hel IG 1, Prabuty IG 1 and again Gdańsk IG 1-depths 3042.0 and 3137.6 m), and initially these two peaks are not distinctly separated.
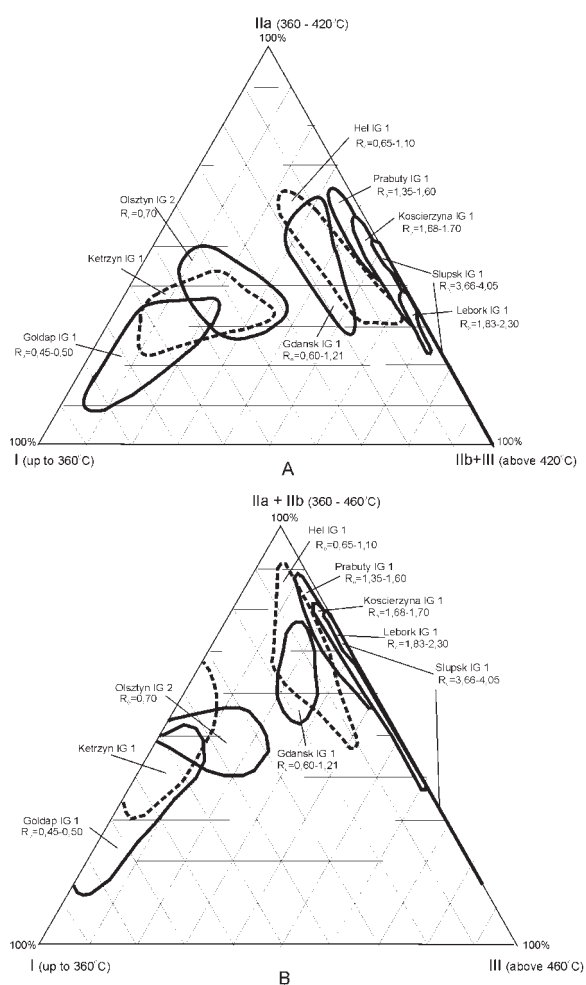

Fig. 3 A, B. Diagrams of the oxyreactive properties of kerogen in the rocks samples investigated – two variants of parameters arrangements

Due to such a mutual behaviour of these peaks, they both are assumed as being interdependent ones. Consequently the peaks occurring in the dististinguished temperature intervals (I, IIa, IIb, III) may be assumed as the parameters determining the stages of kerogen transformation, and its degree may be evaluated by the relationship between the magnitude of these parameters expressed by the area of the appropriate thermal effects occurring in the distinguished temperature intervals.

Another way for these considerations would be the estimation of mass loss corresponding to the oxidation reactions occurring in the appropriate temperature intervals, but the samples investigated usually contain clay minerals as the main rock components and their dehydroxylation reaction would hinder this estimation for the third stage. This dehydroxylation influences also the appropriate exothermic OM peak, but this influence is much smaller than on the mass loss.

The proposed way of the estimation of the essential OTA parameters characterizing kerogen transformation enables the elaboration of many diagrams of the interdependence of selected parameters.

The differences of kerogen transformation processes running in the rockmass may be well illustrated by means of triangular diagram where the vertices present the percentage values of the evaluated parameters as shown in Fig. 3. Parameters used for the construction of the diagrams (Fig. 3) have been based on the measurements of exothermic peaks area occurring in particular 4 temperature intervals corresponding to the following processes:

I up to 360°C liberation and oxidation of the compounds having the lowest bond energy and lowest structure condensation,

II a $360–420^{\circ}$C oxidation of the structural elements or compounds of higher bond energy,

II b $420–460^{\circ}$C or slightly above, oxidation of heavy bitumen fractions, as well as coking material and compounds susceptible to coalification,

III above 460°C oxidation of coalification products.

The location of the samples on the diagrams results from the reactions intensities (i.e. measured as the area of exothermic peks in distinquished OTA stages) as the effect of all transformation processes running during the rockmass heating.

There have been constructed two such diagrams containing different arrangements with very specifically variable parameter II.

Conclusions

The way of the evaluation of the results obtained as presented above allowed us to recognize a very clear sequence of the gradual disappearance of the kerogen constituents occurring in the temperature interval I and variable relations between the constituents showing OTA peaks in intervals II and III in both systems of proposed parameters arrangements.

Recently a similar way of the evaluation of OTA results was employed as the basis for the studies of different oils and oil-containing Zechstein rocks of NW Poland

[3]. It has been suggested that the peaks of temperature interval II b are due to the oxidation of the heavy bitumen fractions, particularly of coking ones. But probably in this interval there appears the coincidence of these peaks with the peaks resulting from the oxidation of the products of kerogen coalification.

Thus it may be assumed that both variants of the proposed systems will show the results of the influence of rockmass heating on kerogen transformation.

The mutual relations of parameters employed differentiate 4 particular parts of the area under consideration, i.e. comprising the following boreholes:

1. Gołdap IG 1, Kętrzyn IG 1 and Olsztyn IG 2,
2. Hel IG 1 and Gdańsk IG 1
3. Prabuty IG 1, Kościerzyna IG 1 and Lębork IG 1
4. Słupsk IG 1

These results indicate that there are still further possibilities for the employment of the OTA method for the studies of kerogen transformation caused by rockmass heating. This statement confirms earlier suggestions [5] dealing with the significance of kerogen transformation, also using thermal analysis (TG) for the geological investigations of buried rocks complexes submitted to the natural heating.

These investigations should be carried out on the natural and HCl treated samples with evaluation of the mutual relations between their OTA results. The results presented indicate that the oxyreactive thermal analysis applied for the OM/kerogen investigation is a successful method which may serve not only for the geochemical characterization of OM but also for the studies of some other aspects of geosciences, such as oil and gas prospecting and exploration of rockmass thermal history. It can also be used as the complementary method for the Rock Eval examinations [6, 7] because it records the course of the oxidation reactions enabling the evaluation the differences in the OM composition, which is not to be detected by means of the pyrolytic methods. The relationship between the research possibilities of the OTA and Rock Eval (including RE II and RE III) methods will be the subject of a separate paper (in preparation).

Further investigation of the applications of OTA in these studies will be carried out in the near future, dealing with problems connected with thermal influence of magmatic intrusions as well as of thermal waters on rocks complexes.

References

1 S. Cebulak and A. Langier-Kuźniarowa, J. Thermal, Anal., 50 (1997) 175.
2 S. Cebulak, A. Karczewska, A. Mazurek and A. Langier-Kuźniarowa, J. Thermal. Anal., 48 (1997) 163.
3 S. Cebulak and A. Langier-Kuźniarowa, ICTAC 12 Int. Congress, Copenhagen, Abstracts 2000 PIII-19.
4 F. Paulik, Special Trends in Thermal Analysis, John Wiley & Sons, 1995.
5 B. Tissot, B. Durand, J. Espitalie and A. Combaz, Am. Assoc. Petroleum Geologists Bull, 58 (1974) 499.
6 J. Espitalie, G. Deroo and F. Marquis, Rev. IFP 40 (1985) 563, 755.
7 J. Espitalie, G. Deroo and F. Marquis, Rev. IFP 41 (1986) 73.