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OXYREACTIVE THERMAL ANALYSIS OF DISPERSED ORGANIC MATTER, KEROGEN AND CARBONIZATION PRODUCTS
A tool for investigation of the heated rock masses

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Abstract

This paper presents the results of oxyreactive thermal analyses of organic matter in rocks, heated naturally during diagenetic to metamorphic processes. During the experiments we traced the reactions in the temperature range up to 900°C, it means from the very beginning of diagenetic transformations to the highest real temperatures acting in the Earth's crust as a solid phase. The results showed that TA could be a tool for the reconstruction of thermal regime in natural coal-bearing systems

Keywords: coal, DTA, graphite, kerogen

Introduction

Carbonaceous matter, found in many rocks, represents different stages of coalification and differ in physical-chemical properties depending on the temperature of diagenesis and/or metamorphism as well as on the nature of organic precursors. The temperature is the most important factor during the stages of coalification. Consequently, the aim of the presented paper is to show the possibility of reconstruction of the thermal regime in natural coal-bearing rocks using oxyreactive thermal analysis. Such variety of thermal analysis is a good way of identification of the transformation stages of organic matter starting from diagenesis through catagenesis and metagenesis to deep metamorphism.

The results obtained by this method are in agreement with data from routine geological investigations. Oxyreactive thermal analysis can be quite precisely used to differentiate the stages of deep catagenesis and metamorphism as well as the genetic features of the products of organic matter metamorphism.

Sampling and methods

As to the material for investigation we used three types of coal-bearing rocks:

1. Kerogen-rich samples from the boreholes drilled in Paleozoic rocks: Cambrian-Ordovician-Silurian shales from North Poland and Baltic Area and Permian

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rocks from drillings from the Polish Cechstein Basin. The temperature range – according to the geologically reasonable markers – are within the range typical of diagenesis-catagenesis of sediments (90–200°C).

2. Coals and anthracites showing different degrees of coalification from Upper Silesian Coal Basin, Ukraine and Ireland. Samples of coals and anthracites from Ukraine were taken at different distances from magma intrusions. The geologically estimated temperature ranges of Upper Silesia coals are from 100 to 190°C and from Ukraine: from 350 to above 650°C.

3. Semigraphites and graphites from metamorphic rocks, showing different degree of metamorphism: from greenschist facies (350–450°C) to upper amphibolite facies (700–800°C) metamorphism. They are characterised by different degrees of crystallinity and different parent material.

Consequently, all investigated samples are within the temperature interval from diagenesis/catagenesis (90–200°C and pressures below 1 kbar) to the high stages of metamorphism (approx. 800°C and pressures about 7–10 kbar).

Most of the samples were preliminary investigated using conventional geological and petrographic methods: Vitrinite Reflectance, T_{max} Rock Eval, Geochemical Ranks of Coalification and thermodynamic calculations of temperature for metamorphic rocks according to popular geothermometers suitable for specific mineral assemblages.

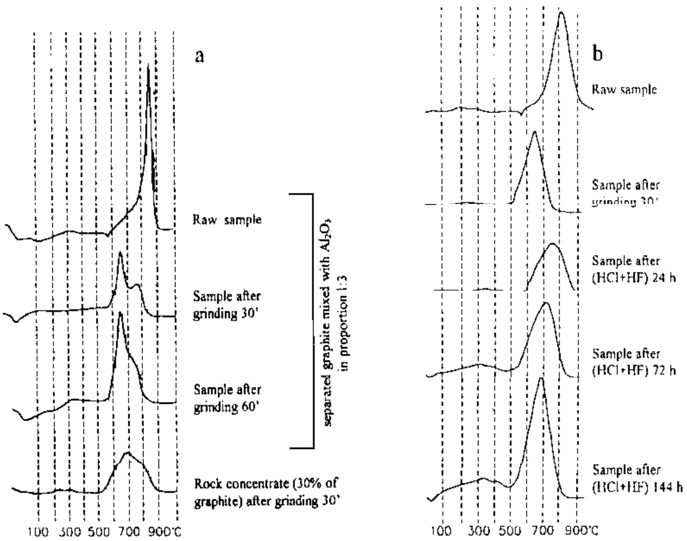

Fig. 1 DTA curves of graphite: a – sample Or. 17 – location: Ornak Ridge, Western Tatra Mts. S-Poland; raw and after grinding; b – sample SP – location: Siwa Pass, Western Tatra Mts., S-Poland; raw and after acid treatment

As the main tool for investigations we used the Oxyreactive Thermal Analysis. All analyses were performed in a MOM Derivatograph (Hungary) in an air atmosphere.

The method was previously used for kerogen analysis [1, 2]. The analytical conditions were as follows: dynamic conditions for the air suction of 1.9 cm^3 min^{-1} and inflations rate 1 cm^3 min^{-1}; multiple sample holders (3–10 Pt plates) [3]. The mass of each sample depended on the carbon content and was in the range of 40 to 1500 mg.

All samples with high carbon or organic matter content were ground with Al_2O_3 powder in proportion 1:2 to 1:3 to increase porosity of the samples and to enable the reactions between the oxygen and the sample components. For different kind of coal- and kerogen-rich rocks the grinding was diversified:

1. Kerogen-rich samples were ground for about 15 min.
2. Coals and anthracites were ground for 30 min.
3. For semigraphites and graphites grinding time is a very important factor. Grinding may change the polytype of graphite (from 3R to 2H) and apparent temperature of structure decomposition. The example of the peak shift caused by grinding is demonstrated in Fig. 1a. Despite the non-organic components (silicate and aluminosilicate minerals) are of great mass percentage (from some % mass to over 98% mass of the rock), we tried to avoid the acid treatment to make a C-rich concentrate. During the experiments we stated that even in the case of high temperature modifications as graphite there is an influence of HF+HCl mixture on the graphite crystallinity index and unit-cell parameters as well as on the peak temperature on the OTA curves (Fig. 1b) [4]. In the case of coals/anthracites the influence of acid treatment is even higher and the highest – is for the non-metamorphosed kerogen substance. When the use of concentrate was really necessary from analytical point of view (i.e. low graphite concentrations), we preferred the mechanical concentration by sedimentation in distilled water.

Results

1. Weakly transformed samples from North Poland (+Baltic Area) and Polish Zechstein Basin show the transition features from diagenetic to catagenetic transformation degree.

Three different types of thermal patterns can be distinguished in the samples from both sedimentation basins.

A) The first type is characterised by the distinct exothermic reaction in the temperature range of 280–330°C and moderately intensive reactions in the range of 370–480°C (Fig. 2a). It is manifested by the presence of several close maxima. The large variability of intensity and shape of the reaction peaks prove that the composition and structure of kerogen in that group of samples is very diversified. Apart from samples with the predominance of the reaction at about 300°C, the group with sharp peaks at the higher temperatures can be observed. Predominance of the high temperature reactions is a result of diagenetic and early catagenetic transformations.

B) The second group of samples shows the typical reaction interval of 360–480°C; the exothermic peak in the range of 280–330°C can be still seen but with low intensity. The lowering of peak intensity in relation to the increase of peaks of 360–480°C is a marker of increase in rockmass heating and generation of low temperature

Fig. 2a DTA curves of different types of dispersed organic matter and kerogen at the diagenetic stage of transformation. Symbols explanation: Gd – Gdańsk; Hl – Hel; Ol – Olsztyn; Kt – Kętrzyn; Gp – Gołdap. (All locations are boreholes in North Poland)

fractions. That group of samples shows the kerogen transformation at the higher diagenetic to catagenetic stages. It is demonstrated by the set of OTA-curves from Polish Cechstein Basin from one borehole arranged according to the increased depth in the rock complex (Fig. 2a).

2. In rock samples with kerogen at the catagenetic stage of transformation, for coals and anthracites a very slight peak or no reaction up to 350–360°C is observed, but the distinct peaks at the higher temperatures, also at 500–600°, are present (Figs 2b, 2c). Such oxyreactive patterns indicate that kerogen was subjected to catagenetic transformation, and when peaks in the range of 500–600°C occur – metagenesis process (anthracitization), either.

A) In rock samples with kerogen subjected to catagenetic transformations the fading of the reactions at the temperatures up to 340°C can be observed (Fig. 2b). In the general TA image the reactions in the temperature range of 370–480°C dominate with the typical evolution to higher temperatures. In cases of the weakly advanced transformation process the intensities of peaks at the lower temperatures are higher. In opposite cases – when the rocks subjected the higher stages of catagenesis – the peaks at higher temperatures become more intensive (Fig. 2b – 1). Transition to

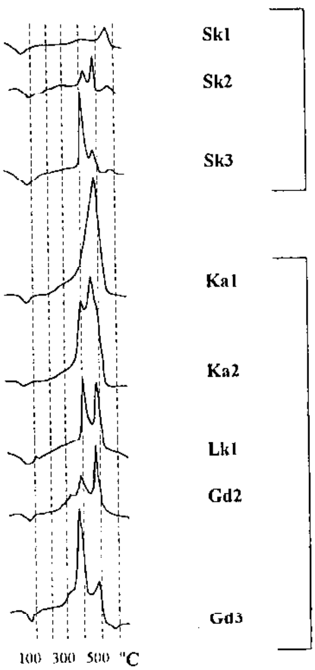

Fig. 2b DTA curves of kerogen at different stages of transformation: 1 – catagenetic stage; 2 – late catagenetic to early metagenetic stage. Symbols explanation: Gd – Gdańsk; Lk – Lębork; Ka – Kościerzyna; Sk – Słupsk. (All locations are boreholes in North Poland)

metagenesis is manifested by the presence of reaction in the temperature range of 500–600°C (Fig. 2b – 2).

B) Natural coals from the Polish, Venezuelian and Irish coal mines show the features of typical catagenetic transformations, characterized by the predominance of the single peak with T_{max} of exothermic reaction of aromatic core of coal structure at 350–590°C. The increasing degree of coalification up to anthracites is supported by the increasing maximum temperature of the oxyreaction (Fig. 2c). Semianthracites and anthracites are characterized by the steep, distinct peak with the beginning of the exothermic reaction at 500–520°C and the T_{max} at 590–600°C. Metamorphosed algae matter (including boghead) shows so peculiar thermal features, so they are not discussed here.

3. Metamorphic processes, especially high temperature metamorphism, strongly influence the coal matter, forming anthracites, semigraphites and graphites differing in their thermal characteristics.

A) A good example of coincidence of the OTA maxima and natural thermal effects are the cokes from Ukraine, influenced by magmatic intrusions. Cokes sampled at different distances from the contact with magmatic rock show the shift in the ther-

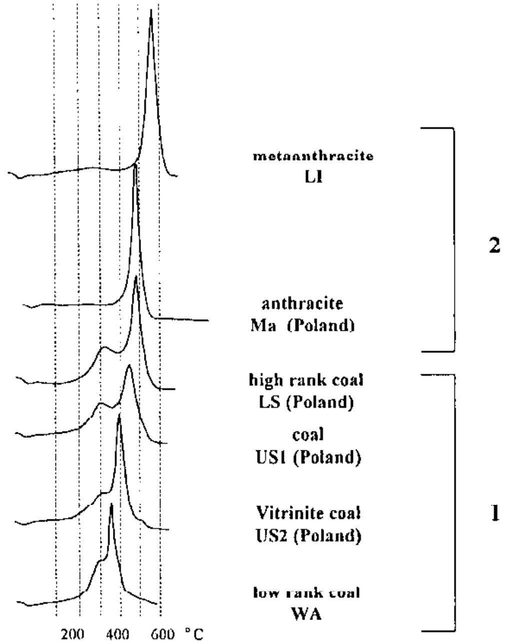

Fig. 2c DTA curves of coals and anthracites: 1 – catagenetic stage; 2 – early metagenetic to late metagenetic stage. WA – Wałbrzych Coal Basin (SW-Poland); US – Upper Silesia Coal Basin (S-Poland); LS – Lower Silesia Coal Basin (SW-Poland); LI – Leinster (SE-Ireland)

mal characteristics of T_{max} with the proximity to the intrusive body (Fig. 2d – 1). That is in agreement with the geologically determined temperatures ranged from 350 to over 650°C (possibly up to 800°C) at the contact [5]. OT analyses of coals from the Donieck Basin (Ukraine) prove the suitability of the presented method to the investigation of the higher stages of coal transformations - up to metamorphic stage.

B) Graphites from Kletno are characterized by the presence of the single steep peak with the beginning of exothermal reaction at 500–520°C and the T_{max} in the range of 640–650°C (Fig. 2d). Sampling was done in the Lądek-Snieżnik metamorphic complex, metamorphosed under the lower amphibolite facies conditions (T= 550–700°C and P=5–7 kbar [6]).

C) Graphite-bearing rocks from the shear-zones from the crystalline basement of the Western Tatra Mts. show the thermal characteristics which could be grouped in two sets:

1. primary graphites – metamorphosed organic substance – with the beginning of the reaction at 690–700°C and T_{max} in the temperature range of 698–780°C and

2. secondary (hydrothermally precipitated) graphites with the beginning of the reaction in the range of 550–650°C and T_{max} usually below 700°C (sporadically at 730°C). The temperatures of crystallization are supported by the so-called 'graphitic

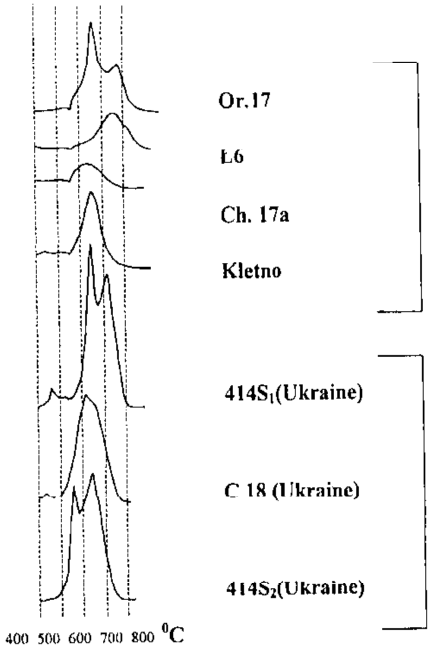

Fig. 2d DTA curves of cokes and graphites at the metamorphic stage of transformation: 1 – late metagenesis ($414S_2$) to metamorphism (C_{18}); 2 – different degree of regional metamorphism: Kletno – Sudety Mts., SW-Poland; Ch.17a, L6, Or.17 – Western Tatra Mts., S-Poland

geothermometer' [7] which gives the similar results: 730–625°C for the hydrothermal graphite. In one sample (Or. 17) the presence of two generations of graphites was observed: both primary and hydrothermal [4] and consequently the OTA curve shows the presence of two exothermic effects: at 650 and 790°C (Fig. 2d). The Western Tatra metamorphic complex was metamorphosed under the upper amphibolite facies conditions. In the metamorphic evolution of the upper (graphite-bearing) unit of the W-Tatra crystalline basement two stages can be distinguished:

1. maximum of metamorphism: T=690–780°C and P=7.5–10 kbar;
2. retrogression and hydrothermal precipitation: T=700–550°C and P=4–2 kbar [8].

Observed peak temperatures of the analysed graphites clearly correlate with the metamorphic temperatures cited above.

Conclusions

1. Oxyreactive Thermal Analysis (OTA) is a useful tool for the discrimination of the composition and structure of transformed organic matter. These features are the

results of both the type of parental organic substance and the thermal regime in the coal-bearing rockmasses.

2. Thermal analysis can trace the transitions between the geological processes in the whole range of the temperature in the crustal regimes:

A) the transition between diagenesis and catagenesis (coalification of organic matter) is marked by the loss of the peak with T_{max} around 300°C and the presence of the distinct peak in the temperature range of 360–480°C;

B) the beginning of anthracitization of coals is marked by the presence of peaks with T_{max} at 460–480°C;

C) metamorphic graphitization can be based on peaks with T_{max} above 640°C and up to over 800°C.

3. The thermal analysis of dispersed organic matter and kerogen can be used as an indicator of the diagenesis/catagenesis border what is important for oil, gas and coal exploration and recovery.

4. Anthracitization (catagenesis/metagenesis) marks the transition from the disordered coal-matter to the ordered structures (up to graphitic highly ordered structure) it means, to minerals sensu stricte. Such a mineralogical transition can be visible in thermal patterns as the formation of the single steep peak with the diagnostic reaction temperature.

5. Peak temperatures observed in metamorphosed coal matter (from anthracite to graphite) show the similarity to the calculated temperatures of metamorphism. This observation suggests the possibility of the new geothermometer calibration, based on the OT analyses of metamorphosed organic matter, in the temperature range of approx. 400–900°C.

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