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Oxyreactive Thermal Analysis of Dispersed Organic Matter - a Good Tool for Investigation of Geothermal Systems

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ABSTRACT

Data from the Oxyreactive Thermal Analysis (OTA) – a new method, introduced in the last years to geology – were used to document the indicative features of dispersed organic matter (DOM). DOM in rocks is a useful tool for investigations of thermal evolution of host rocks. The example of DOM features applicability in the investigations of geothermal Podhale system is presented in this paper. OTA results allow to distinguish the DOM transformation stages as well as the heating-up of the investigated rock-complexes. These results could form also the base for the better reconstruction of the thermal history of any rock-complexes, including paleothermal and current thermal regime. That could be applied especially to low-enthalpy geothermal sedimentary systems, rich in organic matter and hydrocarbons. In such systems a combination of mineralogical methods and DOM investigation methods (including thermal transformation of illite-smectite group serving as a geothermometer) to recognize the evolution and current state of the low-enthalpy systems, usually gives good results. The low-enthalpy systems were often potentially generating energy sources – geothermal waters and hydrocarbons – and at present they also contain both geothermal waters and hydrocarbons (i.e. gaseous hydrocarbons dissolved in water).

The obtained results point out a distinct differences of OTA features of organic matter from Mesozoic basement of Podhale system (containing geothermal aquifers) when compare to organic matter dispersed in impermeable Paleogene Flysch cover. The results point out also some convergences to tectonic processes in rock-complexes.

In the presented paper we also suggest the applicability of new OTA method to the investigations of the geothermal systems.

1. INTRODUCTION WITH A SHORT HISTORY OF INVESTIGATION AIM

Oxyreactive Thermal Analysis (OTA) is a new method of investigation of Dispersed Organic Matter (DOM) in rocks. It has been applied to this aim since the late 90-ies (Schnitzer and Skinner 1964, Domburg and Sergeeva 1969, Schnitzer and Kunal-Gosh 1982, Košik and all 1982, Reh and all 1990,Leinweber and all 1992). It is a good way to research these indicative features of DOM, which can help in the investigation of thermal evolution of rock masses.

OTA data enable to differentiate a transformation degree of this substance structure showing changes in its susceptibility to thermal destruction and in oxyreactivity of destruction products produced at different stages of the temperature increase. They also show variability in transformation results of genetically different organic matter.

This paper shows the example of such application of OTA data in geothermal investigation of the Podhale system (S Poland).

This new method of organic matter research has been well tested to record differences in oxyreactivity of organic matter from present sediments, as well as products of organic matter alteration caused by physical, chemical and biochemical factors of transformations (Cebulak and Schwed-Lorenz 1990, Cebulak 1992, Cebulak and Pliński 1996,Cebulak and all 1997,Cebulak and Langier-Kuźniarowa 1997, Cebulak and all 2002, Cebulak and all 2003, Cebulak and all 2004)). Such application has been also suggested by less precise methods of thermal analysis carried out since the late 60-ies in the static air.

Results of OTA-DOM in rocks indicate the particular usefulness of this method in two fields of geological work: in bitumen prospecting and geothermal system research.

2. BASICS OF THE OTA METHOD USEFULNESS IN THE GEOTHERMAL SYSTEM RESEARCH

The results of researches cited in the subchapter 3.1 indicate that during thermal decomposition of different organic substances present in rocks, the oxyrections always occur in four temperature ranges:

1. 290-360^{o}C

2. 360-420^{o}C

3.420-480^{o}C

4. above 480^{o}C

It is significant that for relatively young organic matter in rocks belonging to early stages of diagenesis oxyreactions of the first temperature range always dominate. It should be pointed out that if primary organic matter contained components with highly condensed structure fragments,, there are also present reactions of the next temperature ranges apart from the dominating first range reactions.

Transformation processes of the advanced diagenesis stage and early catagenesis result always in domination of oxyreactions belonging to the second and third temperature range. Advanced catagenesis stages and processes of metagenesis cause that the fourth reaction range dominates or occurs exclusively.

Higher maximum temperature of these reactions always indicates the increase of these processes intensity - the most often the higher maturity temperature of rock masses.

Low differences in temperature maximums of each reaction indicate lower or higher energy of chemical bonds of structure fragments. They show variability in transformation processes. A type and transformation degree do not depend only on transformation factors (mainly temperature and pressure) but also on the presence of reactive chemical substances. They are related also to a primary composition and variability in structure of altered organic matter.

The given relationship depends on transformation reactions of a very complex organic matter substance leading to the increasing participation of fragments of higher energy bonds, both internal structural bonds of different structural fragments and external bonds between of them.

OTA results can help in better recognition of an investigated rock mass history, among them a paleothermal and current thermal regime. This note is especially valid in the case of low-enthalpy sedimentary systems rich in organic matter and hydrocarbons.

The basics of OTA interpretation results for identification of OM transformation stages, for finding differences in thermal maturity, were given in details in the work by Cebulak at al. (2002).

The basic data for differentiating DOM characteristics and identification of its transformation stage are relationships of oxyreaction heat expelled in three defined here temperature ranges:

I. up to 360^oC,

II. $360-460^oC$ (up to 480^oC in some samples),

III. above 460 or 480^oC.

These data are found calculating an peak area under a DTA curve, which represents the amount of received reaction heat in the defined temperature ranges. Percentage ratios of oxyreaction heat in three mentioned temperature ranges indicate well differences in DOM of investigated rock samples and its type and transformation degree. These differences are best shown in a ternary diagram.

Oxyreactions of the first temperature range (up to 360^oC) are characteristic for the processes of expelling and oxidation of components of low-energy chemical bonds, showing the lowest degree of structure condensation. Predomination of oxyreactions belonging to this temperature range indicates that DOM has been affected by transformation processes of the lowest maturation stages, i.e. early diagenesis. Vitrinite reflectance (R_o) values of such DOM are always lower than 0,50. It indicates that paleotemperature of rock masses was about 60ºC, within the stage called “oil window”.

The II temperature range falls into two sub-ranges, as it was shown above. There are two well-distinguished oxyreactions occurring in the relatively narrow temperature ranges: II a. $360-420^oC$ and II b. $420-460^oC$ (up to 480^oC in some cases).

The reaction of the II a temperature range includes oxidation of decomposition products of structural DOM fragments having higher energy bondings, which form as a result of advanced maturation. It indicates that DOM was transformed into a higher condensation structure formed during decomposition of fragments of low-energy bondings and expulsion of released gaseous decomposition products. The intensity of the I temperature rage oxyreactions decreases in a OTA curve and its maximum temperature increases up to value 320^oC or even above 330^oC. It testifies the intense generation of typical oil window components from structural fragments. The II a oxyreaction involves decomposition and oxidation of structural fragments typical for kerogen and hard brown coals and low rank hard bituminous coals with Ro = 0,90-1,00.

The reactions of the temperature range described as II b mainly comprise oxidation of these structural fragments, which are formed in the intermediate stages of coalification of terrigenous material occurring in DOM (Ro = 0,90-1,00). They may also result from reactions of decomposition and oxidation of rock bituminous fraction which were already coked. It indicates that DOM was affected by conditions typical for advanced stages of condensate generation called the wet gas zone.

The reactions of the III temperature range above 460^oC include oxidation of products of very advanced coalification stages from both humic DOM constituents and oxidation products of coking of heavy bitumen fractions. The Ro value is almost always higher than 1,60, which definitely indicates the dry gas stage.

Calculation of II a and II b parameters is not necessary to plot a ternary diagram. However, it is necessary for more detailed recognition of type and scale of transformation processes of the investigated rock masses.

To research properly these problems the suitable indeces should be calculated using basic OTA data. They enable to distinguish well the DOM transformation scale at all stages of its thermal evolution. Probably they will give also a possibility to find paleotemperatures of rock masses basing on OTA data.

The first of such indeces, showing the stage of decomposition of structural fragments of the lowest energy bondings and the generation of gaseous products of this decomposition, is a ratio of two basic parameters, i.e. a percentage of reaction heat in the total II temperature range to the I range reaction heat. A low value of this index helps to estimate the DOM evolution stage in its maturation processes. The index, called the A index, is defined by the (II a + II b)/I equation. High values of this index indicate highly advanced decomposition of structural fragments of low-energy bondings and generation of gaseous decomposition products.

The second index is a ratio of heat reaction parameters within the II temperature range. It is a good parameter informing about the advancement of transformation up to higher stages of DOM evolution pointing out the role of lower coalification stages and the occurrence of bitumen carbonisation. This index, called the B index, takes a form of a ratio of the II b reaction heat to the II a reaction heat (II b/ II a).

The third index is a ratio of the heat reaction parameters of the third temperature range ($>460/480^oC$) to the heat of both reactions of the II range. It indicates the advancement of transformation process of humic and heavy carbonised bituminous DOM being at a high coalification stage. This C_1 index takes a form of the following equation: III/(II a +II b).

The fourth index being a ratio of III/II b parameters complements the indications of the C_1 index. It distinguishes the role of a low coalification stage and higher maturation stages of DOM maturation in its transformation processes. It is called the C_2 index and has the following equation: III/II b.

Given here OTA indeces are good supplements of the basic parameters of the described method of thermal rock investigation. They are particularly useful for quick estimation of DOM transformation scale in rock mass profiles, enable to illustrate well a correlation between OTA results and results of other methods of DOM transformation assessment and evaluation of differences in paleotemperatures of rock masses.

The details of interpretation of OTA results and calculations of data for this analysis and their transposition to indicators of maturation and coalification can be compared with results of different methods and analytical techniques to define a degree of dia- and catagenetic processes of transformations of the researched rocks. A combination of the methods of organic matter investigation with mineralogical methods (among them i.e. thermal transformation of illite/smectite group serving as a geothermometer) gives good results in recognition of evolution and a present state of systems, which were in conditions enabling to generate the both types of energy raw materials - geothermal water and hydrocarbons, and at present they also contain both geothermal waters as well as hydrocarbons (for example, hydrocarbon gases dissolved in geothermal waters).

3. SAMPLING AND ANALYTICAL METHODS – MATERIAL

The detailed description of the methodology of OTA analyses to find differences in DOM caused both by its genetic and its evolution in the maturation and coalification processes was given in the work of Cebulak and Langier-Kuźniarowa (1997).

Largely simplifying the description, the basic rule of proper OTA research is a such selection of analytical conditions that thermodestruction reaction of DOM particles and oxidation of decomposition products are carried out rapidly and uniformly in the whole particle and with good agreement with this reaction thermodynamics. A sample should be disintegrated up to the maximal possible degree, the oxygen access to a oxidised particle should be maximally high, as well as the volatilisation of gaseous reaction products. The requirements of the proper course of reaction of decomposition and oxidation are sufficiently fulfilled when a sample grain diameter is lower than 0,2-0,3□m, and a sample is diluted in the 1:2 or 1:3 ratio at least with Al_2O_3 powdered to the similar grain size, and when a sample is spread as a thin layer on a set of plates. Combustion is carried out in air and a combustion chamber should be sufficiently aerated.

Rocks were sampled in seven boreholes and seven sample rock outcrops in the region of the Podhale Foredeep Clearly darker parts of a core were chosen for sampling since they contain higher DOM concentrations as well as core parts with a distinctive fine lamination of darker argillaceous material.

The particular attention was given to the presence of organic remains on rock bedding planes, and higher weight samples were taken in such places. Sides of rock zones showing tectonical features such as slickensides and sets of cutting carbonate veins were sampled particularly carefully.

Together 86 rock samples taken from boreholes and surface outcrops were used as basic material of various special selections and preparations to separate samples for particular researches and OTA analyses. After the initial macro- and microscopic (with hand lens) findings 37 samples were selected for the next preparation works.

The first problem was to achieve a proper evaluation base of OTA data for the chosen research aim related to different features of oxyreaction of organic substance of marine and terrestrial source. This research direction required a special sample preparation done under a binocular by manual separation of distinguishingly different aggregates of organic substance present in selected rock samples. The particular attention was given to receive a concentrate of terrigenous detritus from its laminated and bedded occurrences. Lamines of dark rock masses without terrigenous material and with fauna remains were also separated.

4. RESULTS AND DISCUSSION

Variations of oxyreactive DOM characteristics in rock masses profiles of the Podhale geothermal systems are shown by DTA curves of rock samples from one of the investigated boreholes - Biały Dunajec PAN-1 (Fig 1).

Variations in the shape and peak heights of these curves in the selected temperature ranges (deriving form oxyreactions) reflect well changes in DOM oxyreactivity, described above in chapter2. It can be seen that the temperature increase with higher depth of rocks causes diminishing of the I temperature range reactions and participation of the II range reactions increases, mainly these of the IIa range, corresponding to the first peak of this range. DOM oxyreactivity of rock samples reflects the temperature increase up to the level where reactions of the IIb temperature range predominate causing the almost complete (samples of 2177 – 2186 m) and complete (samples of 2216 – 2217 m) disappearance of the I and II a range reactions. They belong to calcareous rock masses of the Mesozoic part with distinctive tectonic features and the occurrence of thermal groundwater.

A DTA curve tends to bend in the III temperature range indicating the advanced reaction of DOM coalification, possible low input of terrestrial matter in these rock samples.

The ternary diagram of three basic parameters I, II and III, calculated using DTA curves (Fig 2) of all analysed rock samples of Podhale enables to show in details the usefulness of OTA analysis of DOM in investigations of geothermal systems. They clearly demonstrate the possibility to show differences in DOM transformation scale calculating the basic OTA parameters as it was described in section 2.

The diagram shows at which stage of decomposition and a stage of reactive components generation in the I temperature range analysed DOM is in the particular researched boreholes and which transformation processes it was submitted.

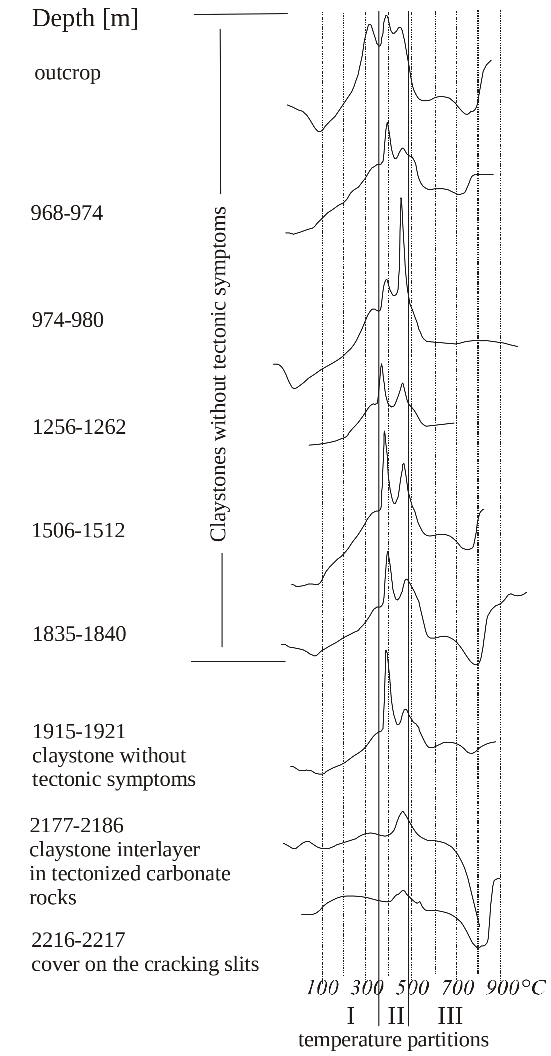

Fig-1: Bore hole Biały Dunajec PAN-1 and outcropes in Biały Dunajec area .Example DTA curves of rock samples mass with DOM

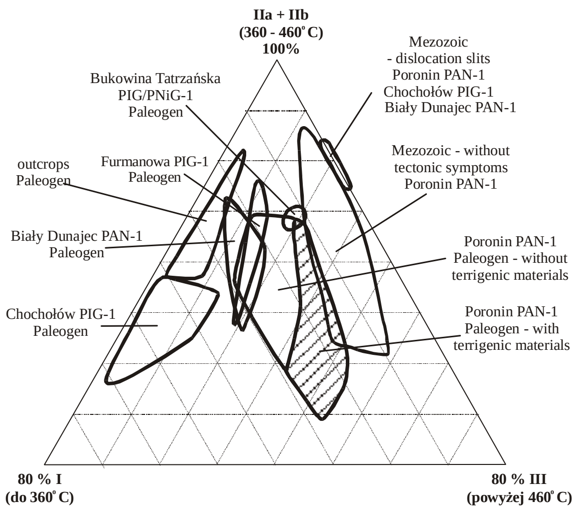

Fig 2: Diagramme of oxyreactive variability of DOM in rock samples from all analysed bore holes and outcropes in Podhale Geothermal Systeme

Results of the research carried out in the Poronin PAN-1 borehole demonstrate how many different aspects of research OTA analyses of DOM can be applied to. A suitable selection of samples and separation of material for analyses handpicked in a very reproducible but not complicated way enable manifold interpretation of analytical data. It also shows differences in transformation processes of genetically different organic material since its differences in composition and structure. They demonstrate how to differentiate rock series of the Paleogene and Mesozoic.

Results of analyses for three boreholes: Poronin PAN-1,Biały Dunajec PAN-1 i Chochołów PIG-1 show that zones of rock masses with strong tectonic features and with circulating geothermal water can be distinguished well.

The calculation method of the suitable indices for DOM using the basic OTA parameters, presented in chapter 2, enables to define the detail variations in oxyreactive characteristics of this substance – detail variations in transformation processes. It is well shown by results of such calculations of OTA data done for the Poronin PAN-1 borehole (Fig 3).

The A index is a very good indicator of an advancement of decomposition stage and generation of components of I temperature range. It shows not only tectonic zones of rocks and circulation of thermal groundwater in the investigated borehole but also a generally higher degree of organic matter transformation in the Mesozoic than in the Paleogene rocks. Its values vary in the borehole profile in a very significant way.

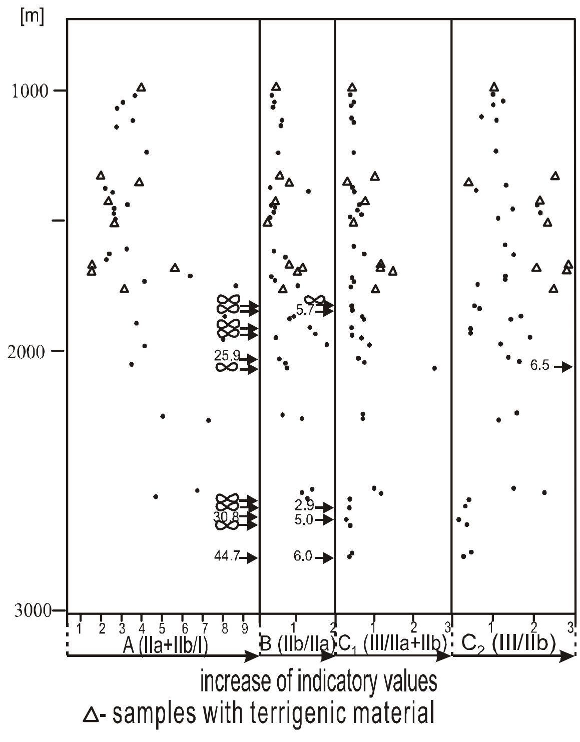

Fig 3. Borehole Poronin PAN-1: the variability of OTA indices for transformation process differences of DOM to estimation.

In the Paleogene rock masses they are in the range from 2 up to slightly above 4, the slow temperature increase in greater deepness range. At the contact of the underlying Mesozoic strata its values gradually increase up to slightly above 8,rapidly temperature increase. In the Mesozoic rocks without tectonic features they are between 4 and 8, similarly as in the floor Paleogene layers contacting with them-similarly temperatures. In the case of rocks showing tectonic features, at levels of thermal groundwater their values are extremely high, from 26 up to infinity-extremely temperature increasing in low deepness ranges to the boundary temperature for rapid DOM transformation.

The B index confirms the variability of transformation stage of the Paleogene and Mesozoic systems found by the A index. It also shows that a type of this transformation causes the gradual increase of reactions of the II b temperature range directed to the borehole floor. The domination of these reactions are also found in single sides in the roof part of the higher level of rocks with strong tectonic features and thermal water circulation, also in the lower level. It suggests the highest temperatures in the roof part of the high zone.

The C index values indicate the poor advancement of the coalification process of DOM in the investigated borehole; there are not the III temperature range reactions. Distinctive coalification is found only at levels with high terrestrial matter input and in the case of one sample of organic matter from dislocation fissure. The other samples of this matter are characterised by domination of the II b or even II a temperature range reactions. It indicates the presence of bitumens in DOM which are easily (carbonised) coked.

There are seen variations in values of the C2 index at both levels of rocks with tectonic features. Its very low values at the lower level probably result from water washing of these DOM constituents which are easily carbonised, possibly the mentioned above bitumen fractions susceptible to coking.

Presented results of OTA analyses of the Podhale geothermal system DOM correspond well with results of investigations of this substance done by other methods. There is a complete agreement between OTA and GC-MS results and petrological analysis concerning differentiation of the transformation scale of DOM in Paleogene rock samples. Similarly as it was shown in the ternary diagram of the basic OTA data (Fig 2), GC-MS data and Ro values for vitrinite present the identical degree of changes in organic matter a transformation stage in rock samples of the particular investigated boreholes. The lowest stage was found for the Chochołów borehole, the intermediate one for the Biały Dunajec and Furmanowa boreholes and the higher for the Poronin and Bukowina Tarzańska boreholes. There is also a complete agreement concerning a degree of transformation scale in the profiles of the investigated boreholes found by data coming from these three methods.

Data of terrestrial matter input assessed by these methods are also in a complete agreement.

However, such agreement could not be seen in the analytical results of the Mesozoic rock samples. Differences found by the OTA method data conform the petrological investigation results only. Results of these two methods show well the higher DOM transformation stage and also they differentiate particularly well strata with tectonic features in the Mesozoic rock masses and the occurrence of thermal groundwater.

GC-MS data and also mineralogical investigations do not confirm such differentiation. It results from a temperature increase over 160ºC in the Mesozoic strata, what caused decomposition and almost total generation of the extractable fraction of organic matter. Conditions typical for the more advanced catagenesis stage occurred, including the higher stage of wet gas generation.

However, the OTA data suggesting bitumen presence in the Mesozoic rock masses correspond well with GC-MS analysis data. Results of GC-MS indicate the occurrence of bitumen in some samples of the Mesozoic rocks of the higher level of rocks with strong tectonic features in the Poronin PAN-1 borehole. They also suggest high similarity of these bitumens to migrabitumens of the Tatra surroundings.
The good agreement if the OTA data with the measurements of Ro of vitrinite was also found in investigations of the Lower Paleozoic sedimentary basins of NE Poland (Cebulak et al. 2002), as well as in the Zechstein basins of Poland. Evaluation of paleotemperatures based on Ro measurements has been a commonly applied technique for many years (Tissot and Welte, 1984).

The comparisons presented above justify the evaluation of paleotemperatures (PT) of the investigated Podhale rock masses using the results of OTA research.

For the Paleogene rock mass

The Chochołów PIG-1 borehole PT- 90ºC up to about 100ºC

The Biały Dunajec PAN-1

and Furmanowa PIG-1 boreholes PT slightly over 100ºC up to about 160ºC

The Poronin PAN-1 borehole PT slightly over 100ºC up to slightly over 160ºC

The Bukowina Tatrzańska PIG-1 PT slightly over 160ºC

For the Mesozoic rock mass

The Poronin PAN-1 borehole

rocks without tectonic features PT slightly over 160ºC up to 180ºC

rocks with tectonic features PT slightly over 180ºC up to slightly over 200ºC

5. CONCLUSIONS

The presented results of investigations demonstrated the validity to apply DOM as an indicator in the research of thermal evolution of rock mass.

The whole presented here material of the DOM research results by OTA method in the Podhale geothermal system verifies the usefulness of this method in investigation of geothermal systems. The good applicability of this method was demonstrated in the case of investigation of thermal evolution of rock masses in the wide range of temperatures.

Its particular usefulness was shown in the higher temperature range, where commonly used methods have failed up to now.

Research should be undertaken to recognise its other applicability, particularly concerning parameters based on OTA data for paleotemperature estimation.

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