Acta Research Reports, No. 18, 53–58, 2009

ORGANIC MATTER DISPERSED IN ROCKS – OBJECTIVE CHARACTERIZATION, RELATION TO NATURAL AND ANTROPOGENIC PROCESSES

Grant project of the Grant Agency of the Academy of Science of the Czech Republic
No. IAA 300460510

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ABSTRACT

Organic matter is a common, though minor component of sediments and sedimentary rocks. Knowledge in rank and properties of carbonaceous substances number pivotal information at solving issues in geologic, environmental as well as soil science and archaeology. Purpose of the project was to specify the identification of organic matter, and assessment coalification degree by access based on the deal non-destructive methods optical and spectroscopic microscopy, chemical analysis, and CHNSO microanalysis in kerogens. The organic substances of different origin and rank, inclusive matter altered during thermal, tectonic and weathered processes. The main attention was aimed to characterization of high reflected carbonaceous particles particularly graphite, semigraphite and pyrobitumen dispersed in black shales. The properties and distribution of vitrinite, huminite, liptinite and inertinite macerals were studied in relation to paleoenvironment of fluvial sediments and coal seams. Results showed a great variety of fossil and modern forms of organic matter and close link its origin and properties with forming conditions and environment.

KEYWORDS: reflectance, micro-Raman spectra, dispersed organic matter, graphite, anthracite, coal, peat, thermal history, paleoenvironment

1. INTRODUCTION

Fossil organic matter comprises one of the more important and comprehensive records of environmental change on both local and global scales, extending over a time period from the present to at least three billion years ago. Organic matter in sedimentary sequences ranges from finally disseminated occurrence to concentrated organic matter in coals. We studied organic matter at its petrological and chemical levels and from diverse perspectives. The texture and variations of individual organic compounds and macerals are the important means of tracing organisms, subsequent diagenetic affects, and thermal history. Finally, and most significantly, the preserved geological record of bacterial microfossils, microbial materials, animal and plant materials isotopic anomaly and chemical composition tells about the timing of events and how construct evolutionary trees. The organic matter types was identified, determined and characterized by means of reflected and fluorescence light microscopy, combination of optical and spectroscopic methods (micro-Raman spectroscopy and micro-FTIR spectroscopy), and microprobe analysis.

2. PROJECT OBJECTIVES

Purpose of the project was to specify the identification of organic matter dispersed in sedimentary rocks and assessment coalification or maturation degree by access based on the deal non-destructive methods: optical and electron microscopy and Raman and FTIR spectroscopic analysis. The main attention was paid to the organic matter dispersed in shales and rocks of the Proterozoic, Silurian, Carboniferous and Tertiary age, and recent sediments.

Table 1 Characteristics of principle DOM types in sediments (Sýkorová et al., 2006).

DOM Type	Size (μm)	Morphology (shape)	Optical properties	R_{max} (%)	Maturation degree
I.	< 10	Elongated, irregular	Isotropic	2.9 – 8.8	Anthracite – meta-anthracite
II.	> 10		Isotropic to anisotropic		
III.		Irregular	Circular to lenticular anisotropy	9.0 – 10.8	Pyrobitumen
IV.		Elongated, lamella, rosette	Strong anisotropic	9.0 – 15.3	Graphite

3. RESULTS

1. The main part of the grant project solution was paid to the study of the oldest forms of dispersed organic matter in the sediments of the selected localities in the Czech Republic (Suchý et al., 2007), Burkina Faso in West Africa (Kříbek et al., 2008) and in South China (Kříbek et al., 2007; Pašava et al., 2008) in relation to palaeothermal and tectonic history.

Optical microscopic investigation of Neoproterozoic Barrandian black shales, Paleoproterozoic Birimian black shales of Kaya-Goren greenstone belt and black shales of Lower Cambrian Niutitang formation and slates showed that these rocks contain a mixture of various types of dispersed organic matter (DOM) that reveal varying thermal transformation. Both highly and partially graphitized particles of uncertain origin and different purity coexist, characteristically being mixed together in the samples (Sýkorová et al. 2006). Four principal DOM types differing in size, morphology, optical reflectance R_{max} and maturation degree were distinguished (Table 1). The parameters of organic matter dispersed in studied localities are summarized in Table 2. Very small particles of Type 1 DOM were dominant in all studied samples. Particles of Types 2 and 4 DOM were common in Birimian black shales and less common in samples from Barrandian Basin. Pyrobitumens (Type 3) with numerous internal pores and cracks filled small cleavages and fissures within host rocks in samples from Barrandian Basin and Niutitang Formation. Large graphite lamellae up to 50 μm long were common in selected samples. Micro-Raman spectra of carbonaceous particles display a wide band in the area of 1600 cm^{-1} (G-band) and approximately the same band in the area of 1350 cm^{-1} (D-band). The ratios of integrated areas of two bands [L_a = 4.4* (AG/AD)] corresponded to R_{max} values (Table 2). In the all samples, the L_a ratio of disordered carbon of Types 1 and 2 DOM varied between 1.9 and 2.15 and in the case of pure graphite increased La parameter of well ordered carbon L_a above 3.0.

The highly reflective carbonaceous particles resembling pyrobitumen and graphite were recognized as the main constituents in the Neoproterozoic sequence of the Barrandian area. Their parameters were used together with illite and chlorite crystallization, sediment microstructures, and results of apatite fission-track analysis in the evaluation of time and temperature evolution and tectonic strain influence in the Teplá-Barrandian unit (Suchý et al., 2007). In these samples were found a heterogenous assemblage of carbonaceous materials with different thermal maturities generally similar to those of sub-greenschist and greenschist-facies metamorphic rocks of the Birimian black shales studied by Kříbek et al. (2008). The chemical, optical and structural characteristics of carbonaceous matter show modal variations in several coexisting phases rather than a uniform transformation of the initial organic matter into graphite. In the carbonaceous rocks investigated, the process of graphitization is accompanied by the crystallization of graphite in situ or precipitation of graphite from external metamorphic or hydrothermal fluids at separate sites. Detailed optical studies of carbonaceous particles together with the results of micro-Raman spectroscopy enable the conditions governing their formation to be assessed and objective conclusions to be reached about the geological history of rocks in areas where index metamorphic minerals are rare or completely missing.

The morphology and relative abundance of organic particles in barren and mineralized shales of the Lower Cambrian Niutitang Formation in southern China were different (Kříbek et al., 2007; Pašava et al., 2008; Sýkorová et al., 2006). In barren black shales, organic particles comprised only fragments of Types 1 and 2 (Table 1) with reflectance ranged from 2.96 % to

Table 2 Composition and properties of DOM in studied sediments.
(Sýkorová et al., 2006; Suchý et al., 2007; Kříbek et al., 2007; Kříbek et al., 2008).

Locality	DOM Type	Range of R_{max} (%)	Range of R_{min} (%)	L_a = 4.4* (AG/AD)
Teplá-Barrandian Basin (Czech Republic)	I, II, III, IV	3.1 – 7.7 9.0 – 15.3	1.48 – 2.57 0.53 – 1.84	1.96 – 2.15 > 3.0
Birmian Greenstone Belts (Burkina Faso)	I, II, IV	6.0 – 8.8 9.0 – 15.0	0.98 – 1.83 0.51 – 0.75	1.55 – 2.4 > 4.0
Niutitang Formation (People´s Republic of China)	I, II, III	2.9 – 5.2 5.9 – 8.8	0.98 – 2.26 0.85 – 1.15	1.3 – 2.08 2.09 – 2.76

5.21 %. Mineralized black shales contained a complex mixture of Types 1 and 2 DOM with reflectance R_{max} = 2.96 – 4.57 % and Type 3 DOM of carbonaceous particles differing in their origin. Type 3 DOM solidified products or oil-derived material represented as small veinlets or irregular organic accumulation of pyrobitumen, that display weak to well develop circular and lenticular optical anisotropy and a variable reflectance ranged from 3.55 % to 8.65 %. The L_a values calculated from Raman spectra for individual types of organic particles from barren and mineralized rocks of the Niutitang Formation were correlated with their R_{max} values (Table 2). Type 1 and 2 particles were interpreted as remnants of *in situ* bacterially reworked organic matter of cyanobacteria-algal type in ore layer and barren shale, and particles as remnants of original organic matter in phosphatized or sulphidized algal-microbial oncolite-like bodies in ore clasts. Detailed characterization of organic particles by optical and electron micrsocopy and micro-Raman spectroscopy contributed to the understanding of the paleoenvironmental conditions of black shales and ore formation, and to specified the relationship between organic matter and the V-Ni-PGE ore accumulation.

2. A representative vein-filling sequences developed in fractured basalt sills hosted in Silurian sediments in the Barrandian Basin were examined in the study. By using a combination of analytical techniques, including fluid inclusion microthermometry, organic petrology, gas chromatography-mass spectrometry, FTIR spectrometry and structural petrographic observations, were characterized basic forms of bitumens. The dominant vein bitumen was the amorphous substance having dark brown to black colour with carbon content higher than 80 % and random reflectance values ranged between 0.8 and 2.0 % R_r. Relatively younger was probably waxy materials with strong yellow fluorescence colour and random reflectance values lower than 0.80% R_r. These characteristics contributed to the explanation of fluid and hydrocarbon migration throughout the geological history of the linear zones (Suchý et al., 2007).

3. The reflected and fluorescence light microscopy, combination techniques should be used for detailed evaluation of the organic matter in Carboniferous and Tertiary basins in relation to organic facies and source potential of sedimentary section, reconstruction of depositional environments.

Petrographic changes observed in the studied section were interpreted in term of hydrological changes during the mire history the Prokop Coal in the Czech part of the Upper Silesian Basin. The Prokop Coal started to develop in planar (rheotrophic) mire as indicated by mineral matter (clastic-derived) and ash content over 10 % in basal 2 m of coal as well as predominance of vitrinite (mainly telovitrinite) over inertinite. Decrease in clastic mineral matter introduced into mire by water-courses and increase in inertinite content most probably indicate domed (ombrotrophic) mire development in about 9 m thick remaining part of the studied section. However, alternation of vitrinite- (mostly detrovitrinite) and inertinite-dominated benches can indicate alternation of relatively wetter and drier periods operating in millennia scale. Recognition of type of mire has implication for interpretation of climate in sense of annual rainfall and its distribution through the year (Opluštil et al., 2006).

The detailed composition of vitrinite, liptinite and inertinite maceral found in coal seam, sapropelic coal, carbonaceous claystone and "bělka" tuff bed contributed to the finding of pioneer plant assemblages in the Lower Radnice Coal and tuff and volcanic beds above coal of the Štílec opencast (Libertín et al., 2009).

Paleoecological and sedimentary model of the Jan Šverma group of coal seam formation in the Žacléř deposit in the Intra Sudetic Basin was originated from lithotype, microlithotype, maceral and mineral composition and chemical parameters. Results of microlithotype and maceral analysis demonstrated the prevalence of arborescent vegetation and the telmatic environment over limno-telmatic and limnic environment in studied profiles Combine results from trimodal reflectograms and sub-hydrous coal character detected zones of oxidation formed during the periods where water table can drop below the peat surface (Edress et al., 2005 and 2006; Edress and Sýkorová, 2007). The relationship between the actual anatomy of silicified wood remains from the Krkonoše Piedmont basin and Intrasudetic Basin, and the nature of their permineralization was summarized by Matysová et al. (2008).

The paleoenvironment of the seams in Miocene Merit Pila Basin (Malaysia) was defined as a mangrove swamp, which was affected by distributary channels and their flood plains in the western and eastern part of the pit on the base of results of the palynological, petrological and chemical research. The detailed maceral composition and structural parameters determined using FTIR spectrometry were used to the characterization of the basic facies (Osvald and Sýkorová, 2006).

4. The last part of project solution was aimed to investigation of early diagenetic processes, assessment of thermal maturity of host sediments, investigation of carbon fluxes, and assessment of anthropogenic impacts on carbon fluxes.

The humification and weathering processes were studied in selected profile in the western part of the Holocene Krásno peat deposit in the Krušné Hory Mountains. Three main strata were recognized in the profile: i) thick light brown layer of non-decomposed or slightly decomposed moss peat, ii) dark brown mineralized and highly decomposed peat with woody remains, and iii) grey brown mineralized and highly decomposed peat layer. The sharp transition from highly decomposed to non-decomposed peat was related to the increasing of TPI index, C/N and O/C atomic ratio, and decrease of GI index, ash yield, carbon and sulphur contents, amounts of carbonyl and carboxyl functional groups, and yields of humic acids. The base of the profile was formed by abundant quartz, K feldspars, biotite, amphiboles and accessory minerals. Kaolinite, carbonates and Fe compounds were very fine dispersed in both mineral and organic phases. Compared to slightly decomposed peat, mineralized peat appeared to be enriched in Cd, Co, Cu, Ge, Ga, Hf, Se, Th, U and Zn. The highest concentration of As, Ba, Cr, Fe, K, Mo, Na, Rb, Sr, Ta was found in the deepest layer of the peat bog profile probably due to the influence of the basal sediments and/or ground water. It was found that the upper layer of peat was weathered and enriched in particles of charcoals and chars with reflectance values ranged from 0.50 % to 3.2 % (Sýkorová et al., 2006). The optical properties of hese particles were studied in relation to the modern, ancient and artificial woody materials, xylite and charcoal fragments from Tertiary coal basins. They were investigated in order to discuss a range of optical and chemical variations that occur as a result of coalification and thermal alteration. The changes in original wood, buried wood and their samples from heating experiments were studied by a petrographic analysis, ultimate analysis and FTIR spectroscopy. Under reflected light, the wood fragments showed various degree of tissue preservation, from very well-preserved textinite in the non- and/or low degraded wood to almost lacking of cell structure of ulminite in the degraded wood and coal samples. Short-term thermal alteration of wood samples at temperature up to 200 °C led to the increase of reflectance values, carbon contents, and a cellular deformation and degradation. The similar chemical and optical properties were found out Tertiary xylite. It was reflected by a marked decrease in intensities of IR bands assigned to –OH deformation and aliphatic C-O-C and –OH stretching vibrations. The similar chemical and optical properties were found in xylite samples from the Czech Tertiary basins. Increased temperature, such as 480 °C and longer duration warming-up results in a charred wood with reflectance about 2.0 % R_r and carbon content higher than 75 % C^{daf}. The composition and properties of such a charred wood are consistent with properties of fusite from Czech Tertiary basins.

4. CONCLUSIONS

The above described forms of organic matter as are huminite, vitrinite, liptinite, inertinite macerals, dispersed plant tissue fragments, amorphous humic particles or discrete elements including zooclasts, bitumens, graphite, and weathered and thermal altered forms were studied in coal seams, shales, and peat bogs in relation to environment, deposition and source. Attention was paid to xylite-rich coal, charcoal and chars due to the study on impact to carbon fluxes. Images of macerals and other components in peat, low- medium- and high rank coal and anthracite and dispersed organic matter accompanied information on reflectance value and other basic characteristics were collected and presented by Sýkorová et al. (2007). The study emphasized that the monitoring and better understanding of organic matter during peatification,

humification, weathering and thermal and tectonic processes can be required in the various areas of geology, archaeology, and ecology.

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ORGANICKÁ HMOTA DISPERGOVANÁ V HORNINÁCH - OBJEKTIVNÍ CHARAKTERIZACE, SOUVISLOSTI S PŘÍRODNÍMI DĚJI A ANTROPOGENNÍ ČINNOSTÍ

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ABSTRAKT:

Organická hmota je běžnou, i když minoritní složkou sedimentů a sedimentárních hornin. Znalost prouhelnění a vlastností organických částic patří mezi klíčové informace při řešení problémů v geologii, ekologii, ale i v pedologii a archeologii. Cílem projektu bylo zpřesnění identifikace organické hmoty a stanovení stupně prouhelnění multidisciplinárním přístupem založeném na spojení nedestruktivních metod optické a spektrometrické mikroskopie a metod chemické analýzy a CHNSO mikroanalýzy v kerogenu. Studována byla organická hmota různého původu a prouhelnění, včetně hmoty postižené tepelnými, tektonickými a zvětrávacími procesy. Mimořádná pozornost byla věnována vysoce odrazným uhlíkatým látkám, především grafitu, semigrafitu a pyrobitumenu, dispergovaných v černých břidlicích. Vlastnosti a distribuce macerálů vitrinitu, huminitu, liptinitu a inertinitu byly studovány v souvislosti s paleoprostředím sedimentů a uhelných slojí. Výsledky projektu ukázaly značnou rozmanitost fosilních a moderních forem organické hmoty a těsné spojení jejich vzniku a vlastností s podmínkami a s prostředím jejich vzniku.