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OPTICAL, STRUCTURAL AND THERMAL CHARACTERIZATION OF META-ANTHRACITE FROM ZEMPLINICUM WEST CARPATHIANS

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Abstract: Carbonaceous material from several boreholes which penetrated the Carboniferous strata in the Zemplinicum block is according to reflectance and DTA characteristics at the meta-anthracitic stage. X-ray diffraction corresponds to a less ordered structure typical of anthracite what is supposed to be a result of high concentrations of intertinite in the samples. The analyses of carbonaceous material give evidence that the sedimentary rocks were exposed to very low-grade/low-grade metamorphism under high-temperature and low-pressure conditions, probably during the latest Paleozoic and the early Mesozoic periods. Discontinuities in graphitization with depth suggest postmetamorphic faulting and overthrusting of the partial blocks of the sequence.

Key words: meta-anthracite, reflectance, DTA, diffraction, thermal history, Paleozoic, West Carpathians.

Introduction

The carbonization and graphitization of coals and kerogens have been studied in relation to regional or contact metamorphism by numerous authors (French, 1964; Grifin, 1967; Izawa, 1968; Landis, 1971; Grew, 1974; Diessel and Offler, 1975; Oberlin and Terriere, 1975; Ragot, 1976; Diessel et al., 1978; Teichmüller et al., 1979; Kwiecińska, 1980; Molák et al., 1986; Okuyama-Kusunose and Itaya, 1987; Deurbergue et al., 1987; Rouzaud and Jehlička, 1988; Molák et al., 1989). In spite of certain differences in terminology and "rank" boundaries (e. g. meta-anthracite/semi-graphite) a general irreversible structural ordering of the carbonaceous matter in zones of progressive metamorphism has been described. Blyuman et al. (1972) proposed to use carbonaceous matter as a "geothermometer" sensitive especially to thermal and pressure conditions of the very low- and low-grade metamorphism.

In this paper different characteristics of highly altered seamcoals and kerogen disseminated in surrounding rocks are presented in order to estimate the metamorphic grade and possible thermal/burial history of the Paleozoic formation of the Zemlinicum.

Geological outline

The Zemplinicum is a tectonic unit outcropping at the southern margins of the Transcarpathian Basin in the southern part of East Slovakia (Fig. 1). It shows a genetic affinity to the Central West Carpathians (Vozárová and Vozár, 1988) and comprises Mesozoic, Late Paleozoic and older crystalline rock. The Permo-Carboniferous is divided into 6 partial lithostratigraphic formations from which the Veľká Tŕňa formation is rich in coal seams up to 160 cm thick (Grecula and Együd, 1982; Együd, 1982) and black shales and siltstones. From studies of mineralogical assemblages and degreee of recrystallization Vozárová and Vozár (1988) conculded that the regional metamorphism of the late Paleozoic rocks did not exceed the beginning of the chlorite zone of the greenschist facies and is of high-temperature low-pressure character. The high concentration of carbonaceous matter in sediments, however, makes it difficult to apply the microscopical methods effectively used for metamorphic zonation of carbon-lean rocks (Vozárová, 1989, personal com.). The metamorphic alteration is of regional character and does not show significant relationship to local ancient and Neogene volcanic bodies. According to isotopic analyses of Pb in galena (Ďuďa in Grecula et al., 1982) the peak metamorphism is of the Permo–Triassic age, more precise dating being still matter of discussion.

Geothermal conditions

Both outcrops of the Zemplinicum unit and its parts buried under the Neogene of the adjacent Transcarpathian Basin are situated in a region with a high heat flow (90–113 mW m^{-2})

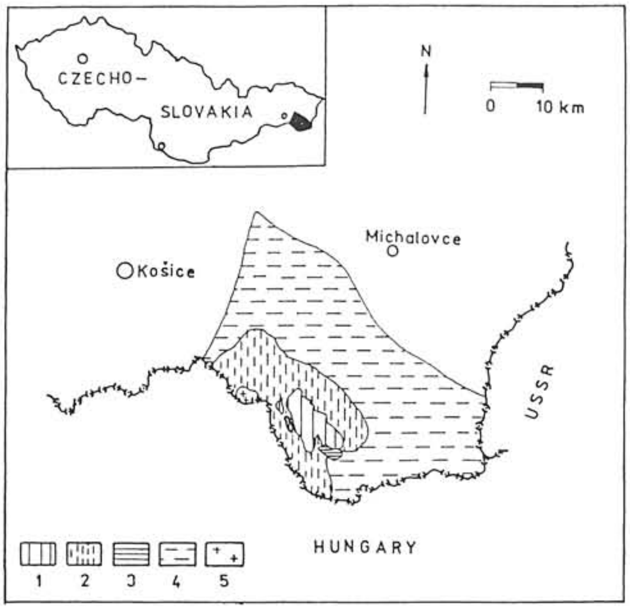

Fig. 1. Geographical position and geological characteristic of Zemplinicum.
1, 2 – Late Paleozoic; 3, 4 Mesozoic; 5 – crystalline rocks. 1 and 3 outcrops, 2 and 4 buried under the Tertiary of the Transcarpathian depression (adapted from Rudinec, 1980).

and geothermal gradient (50–60 K km^{-1} within the first 1000 m) (Čermák, 1979; Král et al., 1985). Due to high temperature at depth (200 °C at 4 km) the kerogen in the Neogene rocks is catagenically altered to dry gas stage corresponding to the beginning of the anthracitic rank (Francŭ and Milička, 1988; Francŭ et al., 1989).

Experimental

Polished section were prepared from pieces of seam coals and black shales and siltstones cut perpendiculary to bedding and fixed in synthetic resin. Reflectance in oil was measured using microscope-photometer Leitz Wetzlar MPV 2 under standard conditions (Stach et al., 1975): mean "vitrinite" reflectance R_m in non-polarized light, maximal and minimal reflectance R_{max} and R_{min} in polarized monochromatic light (546 nm).

Prior to XRD and DTA analyses the samples were crushed to less than 0.1 mm, extracted with $CHCl_3$ and repeatedly treated with HCl and HF at 60 °C until all carbonates and silicates were removed (Robinson, 1969; Durand and Nicaise, 1980).

The mineral free powder (less than 0.05 mm) with Si as an internal standard was both smeared with distilled water on glass slides (oriented samples) and pressed into an alumina holder (non-oriented samples). Diffractograms were measured using Philips PW 1050/25 from 16 to 60 °2Θ (CuK_α/Ni filter, 40 kV, 15 mA, slits 1–0, 1–1, goniometer 2 °2Θ/min, chart speed 20 mm/min).

The same powder was homogenized with Al_2O_3 (1 : 1) and analysed using Du Pont 990 thermoanalyser under static air, heating rate 20 °C/min from 100 to 1100 °C.

Results and discussion

General characteristics

The studied Paleozoic rocks are black shales and siltstones interbedded with coal layers with distinct bedding, fault polishes but without folding structures. The coal material is often coarse-grained of vitritic and glossy character, sometimes also dull and "porous" when composed exclusively of inertinite.

Total organic carbon (TOC) varies from 1.8 to 8 % in rocks an up to 75 % in coal layers.

Microscopic photometry

In Fig. 2 the published reflectance data (R_{max}, R_{min}) are summarized for a metamorphic sequence of anthracite, meta-anthracite, semi-graphite and graphite (ranks after Teichmüller et al., 1979) which occur at progressive metamorphic facies and zones: lawsonite, prehnite, chlorite, biotite, amphibolite and granulite (Diessel and Offler, 1975). It is evident from the general trend that maximal reflectance (R_{max}) is incresing with progressive metamorphism (maximal scatter occur at the semi-graphitic and graphitic stages). At the meta-anthracitic stage two types of constituents are often observed – one is more coaly (structured, inertinitic) and is more resistent to graphitization, the second type being more amorphous (liptinitic) and is distinctly more graphitized (Dg) due to its chemical structure with higher affinity to ordering (Diessel and Offler, 1975; Diessel at al., 1978).

The minimal reflectance (R_{min}) is of about 2/3 of (R_{max}) at the anthracitic stage. R_{min} is increasing up to the meta-anthracitic stage when it starts to decrease, i. e. the bireflectance ($R_{max}-R_{min}$) starts to increase significantly. This is atributed to the formation of three dimensionally ordered graphitic structural units (Ragot, 1976). The lowest values of R_{min} and the highest bireflectance has an ordered graphite.

For the Zemplinicum profile the range of the R_{min} and R_{max} data fall within the meta-anthracitic stage (Fig. 2). The R_{max} increases irregularly with depth (Fig. 3) from 4.5 to almost 8 %. The deepest and the most altered sample (1540 m) is of the lowest R_{min} (1.43 %) and highest R_{max} (7.80 %) and bireflectance (R_{max} – R_{min} = 6.37 %) The mean reflectance R_m increases slightly in the first kilometer of depth and then does not show any systematic change with depth. When comparing the data from the Zemplinicum with those from the Ruhr Carboniferous (Teichmüller et al., 1979) the former show in general lower R_{min} and higher bireflectance (Fig. 3) and thus ought to be of higher metamorphic grade. From partial resemblance of the Veľká Tŕňa 59 section with the lower part of the Münsterland 1 (below 4 km) it may be deduced, however, that the studied Paleozoic rocks of the Zemplinicum were exposed to similar or only slightly higher metamorphic conditions than the Ruhr Carboniferous. Similary to the Münsterland 1 section, the discontinuities in the R_m and R_{max} increase and R_{min} decrease with depth are interpreted as a result of tectonic displecements of the partial blocks and their postmetamorphic overthrusting.

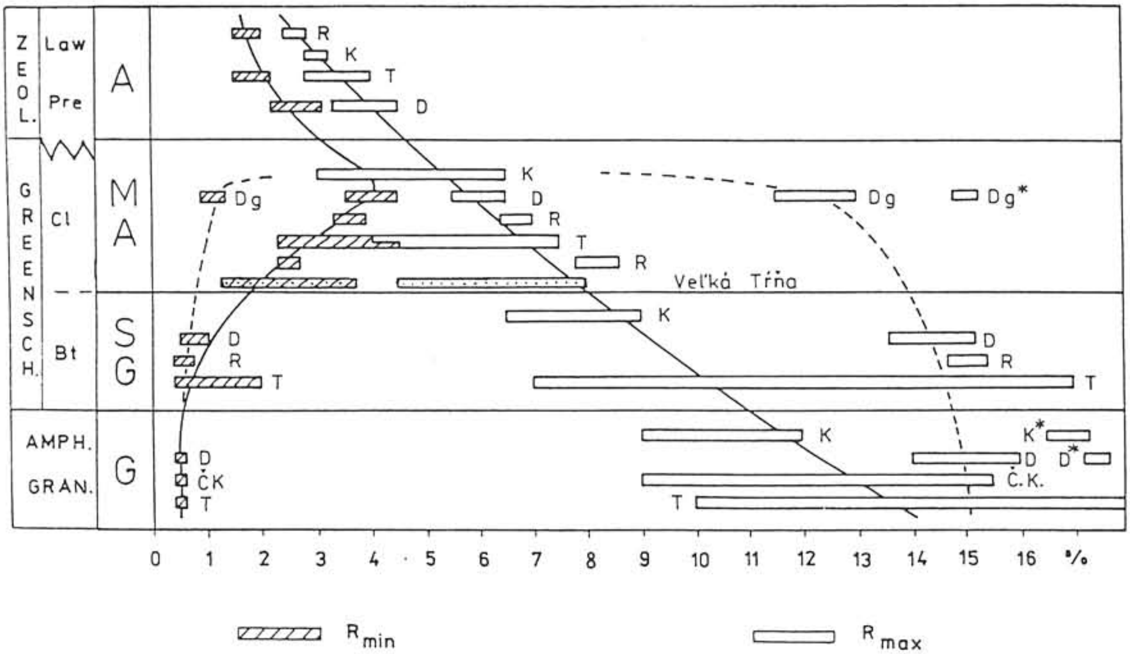

Fig. 2. Compiled data of maximal and minimal reflectance R_{max} and R_{min} of coal and dispersed carbonaceous matter in polarized light ordered according to increasing rank and metamorphic grade (D – Diessel and Offler, 1975; R – Ragot, 1976; T – Teichmüller at al., 1979; K – Kwiecińska, 1980; g – graphitic constituents, * – measured on natural cleavage surface, ČK – own data of graphite from the Český Krumlov deposit).
Since the meta-anthracitic stage the coal material accompanied with occurrence of "transitional matter" is observed, e.g. between D and Dg. Ranks A – anthracite, MA – meta-anthracite, SG – semi-graphite and G – graphite are after Teichmüller at al. (1979); metamorphic facies and zones after Diessel and Offler, (1975): Law – lawsonite, Pre – prehnite, Cl – chlorite, Bt – biotite (zones); AMPH – amphibolite and GRAN – granulite facies.

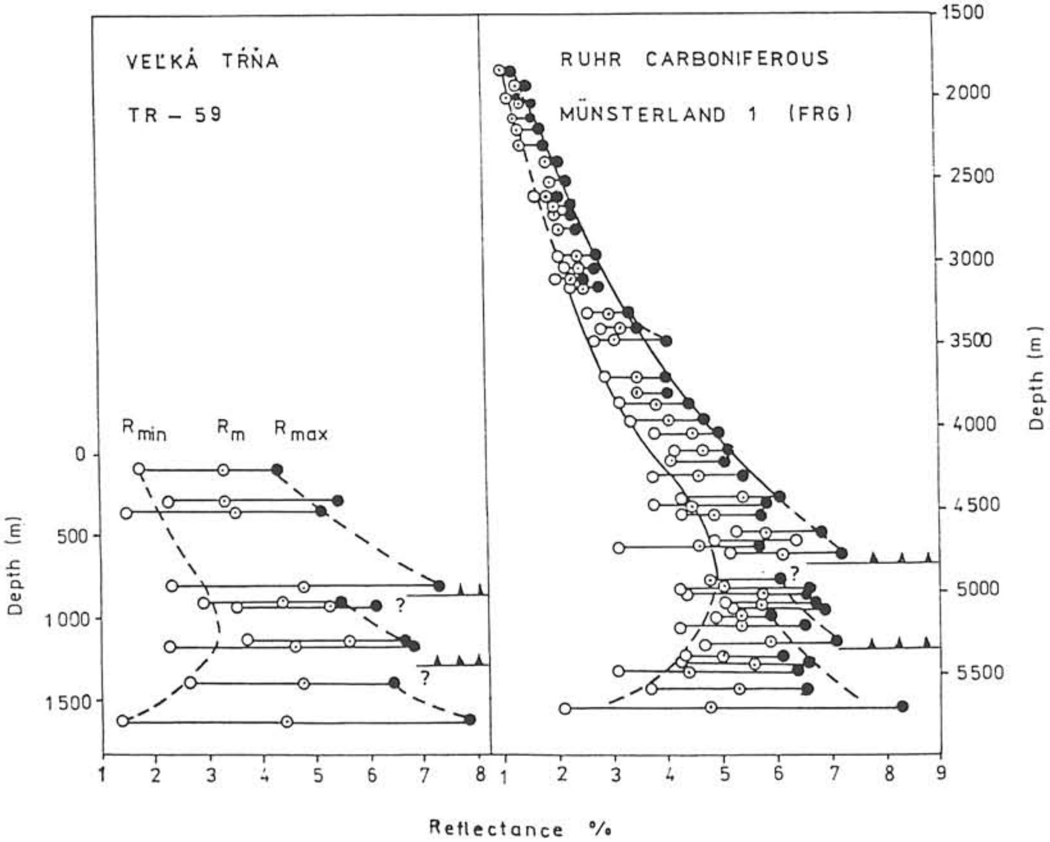

Fig. 3. Comparison of increase of coalification and graphitization with depth in Münsterland 1 (after Teichmüller et al., 1979) and TR-59 (Veľká Tŕňa, Zemplinicum) boreholes.

Differential thermal analysis

The oxidation exotherm curve of the studied rocks has a distinct maximum at 640–670 °C with a shoulder ending sharply at 800–1000 °C (Fig. 4.). Meta-anthracites from Donetsk basin (C^{daf} = 95.4 %, R_m = 5.2 %) analysed under the same conditions are of very similar maximum temperature range close to the end of the DTA curves of the Zempienicum samples and support the microscopic observations that the carbonaceous matter consists of two groups of "macerals" with lower and higher degree of graphitization.

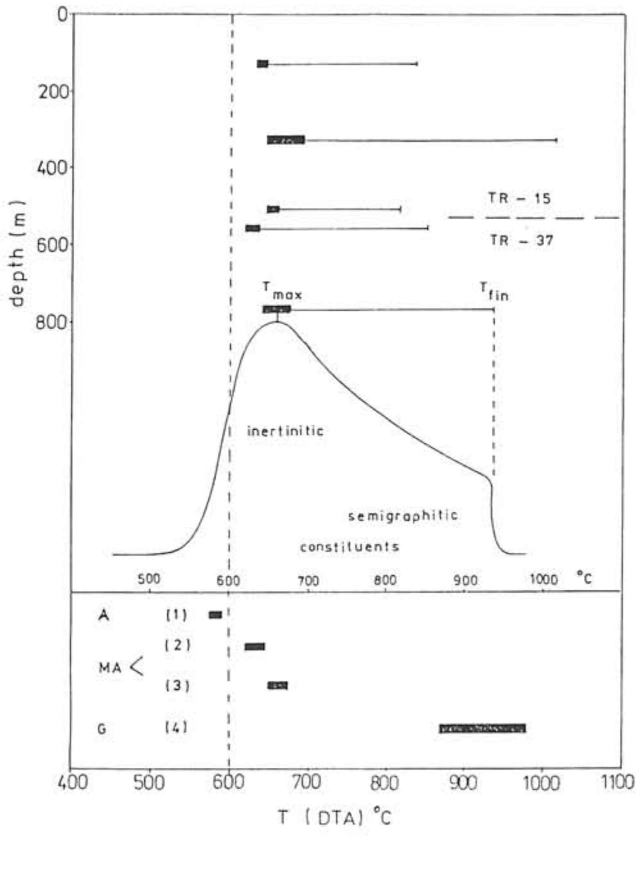

Fig. 4. Differential thermal analyses of meta-anthracitic material from Veľká tŕňa (TR-15 and TR-37 boreholes). Data show the maximal (T_{max}) and final (T_{fin}) temperatures of the oxidation exotherm in air.
Most of the samples have a similar shape to the representative curve (TR-37/771 m) which shows a "bimodal" character. Reference materials A (1) – anthracite; MA (2) and (3) – meta-anthracite from Donetsk basin, USSR; G (4) – graphite from Český Krumlov, Czechoslovakia (amphibolite facies).

X-ray diffraction

A characteristic diffraction pattern of the studied samples is shownin Fig. 5. From series of ordered graphite diffractions (see the reference sample-ČK) only a broad 002 and a weak 100 are developed. The 002 maximum ranges from 3.43 to 3.52 Å and does not show any significant change with depth.

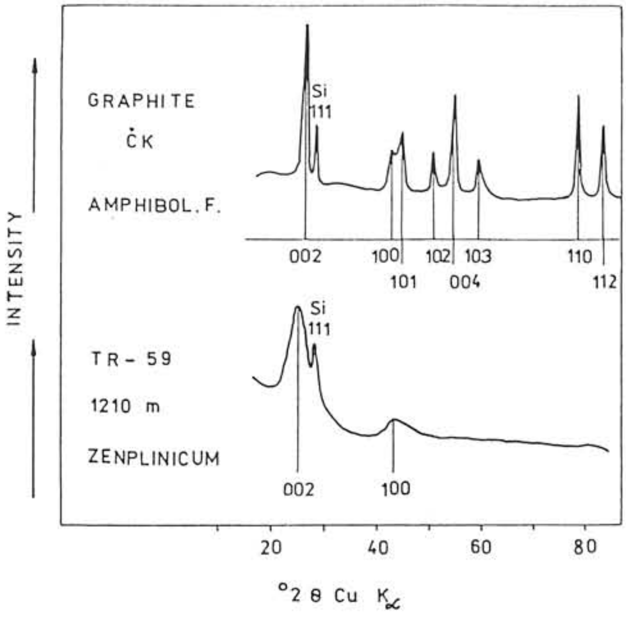

Fig. 5. X-ray diffraction patterns of carbonaceous matter of Zemplinicum (TR-59/1210 m) and graphite (ČK).

Degree of graphitization

The measured spacings d_{002} are bigger than the boundary value between anthracite and meta-anthracie (3.44 Å, Ragot, 1976). The d-values together with the overall shape of the obtained diffraction curves are typical of two-dimensionally ordered anthracitic structure (French, 1964; Landis, 1970; Ragot, 1976; Bonijoly et al., 1982). This is in discrepancy with reflectance and DTA results which give evidence of the meta-anthracite stage.

It may be caused partly by lack of unity in terminology (meta-anthracite vs. disordered graphite etc.) used by different authors but also by the complex character of the reflectance histogram interpretations. Relationship between R_{max} of different carbonacous constituents coaly material (C), transitional matter (TM) and ordered graphite (G) and decreasing bulk sample XRD spacings is in Fig. 6 based on data given by Okuyama-Kusunose and Itaya (1987). Our data fit fairly well in his sequence of gradually graphitited carbonaceous matter, and consist of two populations: R_1 of more isotropic inertinite and R_x of more bireflectant vitrinite. The more graphitized constituents are considered representative.

Inertinite has a "rigid" structure resistant to graphitization (Diessel et al., 1978; Bonijoly et al., 1982; Ouyama-Kusunose and Itaya, 1987). Being in higher concentration it influences the bulk diffraction towards a lower degree of ordering.

In this paper it is preferred to determine the metamorphic grade from those constituents which are not resistant, but which react to the influence of temperature and pressure even if they are not dominant fraction of carbonaceous rocks. The stage of alteration of the Paleozoic of the Zemplinicum is considered to be meta-anthracitic corresponding to anchimetamorphism (Teichmüller et al., 1979) or transition from the very low-grade to low-grade metamorphism (Diessel

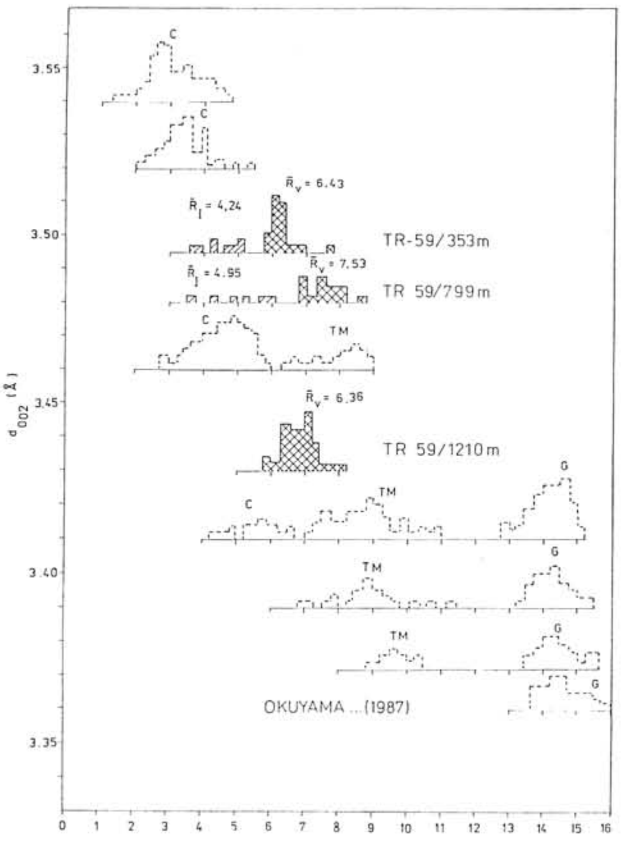

Fig. 6. Relationship between the interplanar spacing d_{002} (bulk sample) and the histograms of the maximal reflectance R_{max} of carbonaceous matter after Okuyama-Kusunose and Itaya (1987 – dashed line).
C – coaly material, TM – transition matter, G – ordered graphite. TR 59 – samples from the borehole in the Zemplinicum: R_I – intertinite, R_V – vitrinite.

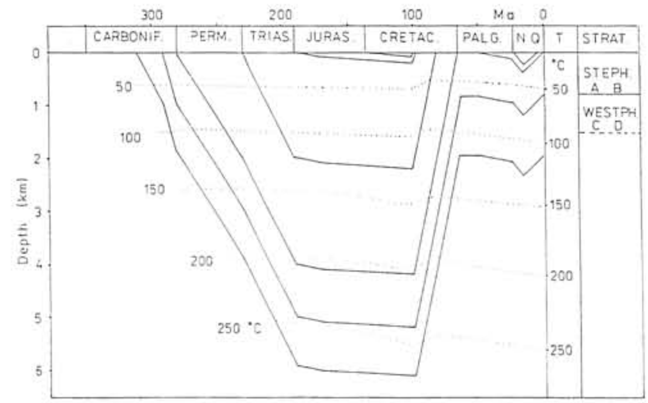

Fig. 7. Simplified approximation of burial/thermal history of the Paleozoic rocks of Zemplinicum (TR-59 borehole): horizontal axis – age in mil. years.

and Offler, 1975; Kwiecińska, 1980; Kisch, 1986) what is in agreement with the mineralogical and petrological studies of Vozárová and Vozár (1988) and palynological studies (Planderová, 1989; personal comunication).

Burial and thermal history

From a simple geometrical comparison of the Veľká Tŕňa TR-59 section with the Münsterland 1 section (Fig. 3) it may be deduced that the Carboniferous section of the Zemplinicum was buried 4 km deeper than at present.

Lopatin (1971) made an approximate reconstruction of the burial and thermal history of the Münsterland 1 profile and correlated the time-temperature index (TTI) with measured vitrinite reflectance. He concluded that the deepest layer of Münsterland 1 was buried to 5.7 km and exposed to maximal temperature over 210 °C.

The Lopatin method and the plot of Bostick et al. (1979 in Teichmüller, 1986) showed. the relation between time, temperature and reflectance R_{max}. Even less reliable in metamorphic than in diagenetic sequences his method was used for the reconstruction of burial and thermal history of the studied rocks (Fig. 7). According to the first approximation the Carboniferous section of the Zemplinicum was buried to 4–6 km and exposed to 210–270 °C during the Mesozoic period. During the Late Cretaceous the Alpine thrusting was active and the Zemplinicum block was uplifted and eroded. The mild Tertiary burial did not effect the meta-anthracitic stage of metamorphic alteration.

The maximal depth is bigger than it is admitted at present by majority of the geologists working in the region. Only a large intrusion could cause a higher geothermal gradient during the Late Paleozoic than it is considered in Fig. 7 (50 °C/km) and thus compensate the deep burial. The relatively long duration of the heating (90 Ma) and temperatures of 210–270 °C could result to R_{max} of 5–8 % while in the adjacent Transcarpathian Neogene basin at depth of 4 km (200 °C) kerogen enters only the anthracitic rank with R_m = 2.6 % (Francu and Milička, 1988).

Conclusion

The coal-rich rocks of the Carboniferous of the Zemplinicum correspond according to microscopic photometry and DTA to meta-anthracite. XRD does not support this conclusion and gives evidence of the presence of less-ordered carbonaceous structure (turbostratic, anthracitic). This may be caused by higher content of inertinite in the coal material.

The meta-anthracitic stage corresponds to transition from the very low-grade to low-grade metamorphic conditions which could have been reached under burial to 4–6 km and temperature of 210–270 °C during the Mesozoic period. The absence of signifiacant increase of metamorphic alteration with depth suggests a postmetamorphic thrusting of partial sheets of the Carboniferous sequence.

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