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HYDROCARBONS MIGRATION IN TECTONIC ZONES OF THE WESTERN TATRA MOUNTAINS CRYSTALLINE BASEMENT (CENTRAL WESTERN CARPATHIANS)

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Abstract: In the Western Tatra Mountains crystalline basement a bituminous matter was found in tectonic zones (faults, shatter zones). The tectonic zones run NE-SW cutting both the Variscan crystalline basement and its sedimentary Mesozoic cover. Oxyreactive Thermal Analyses of whole rock samples and Gas Chromatography–Mass Spectroscopy analyses of extractable organic matter revealed that the bitumens in question are heavy fractions of crude oils. The source rocks of the bitumens were marine shales and lacustrine sediments, relatively poor in organic material, accumulated in suboxic shelf conditions. The thermal maturity of the bitumens was determined as the oil-window stage (R_{CS} = 0.74–0.82 %). The terrestrial organic matter admixture was negligibly small, so we can suggest the age of the source material may be older than Tertiary (by comparison with the other Carpathian oils). The comparison with the Outer Carpathian crude oils showed that the Western Tatra bitumens resemble Jurassic oils more than Paleogene ones. Jurassic and Upper Triassic carbonates and black shales from the overthrust Tatricum sequences seem to be a more plausible source rocks for the investigated bitumens. The tectonic zones, rejuvenated after or during Miocene uplift of the Tatra Block served as the paths for bitumens migration.

Key words: Tatra Mountains, crystalline basement, hydrocarbons, migration, source rocks, biomarkers, maturity.

Introduction

The presence of hydrocarbons *sensu lato* (crude oil, asphalt, ozokerite etc.) in fractured crystalline rocks (especially granites) has been reported from many localities in the world (Great Britain, Venezuela, Argentina, China, Egypt, Libya, USA). In all cases the basement reservoirs which usually form topographic highs on the basement paleosurface (Parnell 1988), are fed by the sedimentary cover. Hydrocarbons can migrate both downwards — as a result of squeezing during compaction, and laterally — to the fractured highs. The regional unconformities are of great significance, forming the pathways for the migration of both hydrocarbons and hydrothermal fluids.

There are several theories accounting for the presence of hydrocarbons in crystalline rocks. Most stress the role of granite intrusions and the thermal reactivation of the basement rocks as a source of heat and hydrothermal fluids (e.g. Parnell 1988). The heat could cause the transformation of organic matter while hydrothermal fluids penetrating the fractured portion of basement could facilitate the migration of newly formed hydrocarbons. Other sources of heat are the radioactive elements, although their activity tends to be connected directly or indirectly with granitic plutons.

In the Tatra Mountains crystalline basement the bituminous matter has not been described previously. The aim of this paper is to as certain whether the bitumens found in the crystalline basement are really genetically related to the basement or are formed by another process. The additional purpose of the presented work was to characterize the bitumen-bearing samples and, on the basis of their characteristic features, to determine their provenance, source rocks and the environmental conditions of hydrocarbons generation.

Geological setting and sampling

The Tatra Mountains form a rhomboidal massif, limited by regional faults: the Subtatra fault on the south, the Choč and Krowiarki faults on the west and north-west and the Drużbaki (Ružbachy) fault on the east and south-east (Bac-Moszaszwili 1993, 1996). The Tatra Mountains form the northernmost crystalline massif among the so-called internal massifs in the Central Western Carpathian belt, probably allochthonous and transported to the north during the Alpine orogenesis and Carpathian belt formation (Lefeld & Jankowski 1985; Wieczorek 1990).

The Western Tatra Mountains crystalline basement comprises a polygenetic granitoid pluton, of Variscan age (340–370 Ma, Gawęda 1995; Janák et al. 1998; Todt et al. 1998) and its pre-Variscan metamorphic envelope (380–405 Ma — Kohút et al. 1998; 395 Ma — Gawęda 1997). Among the metamorphic rocks two units could be distinguished, differing in metamorphic grade, petrographical features and geochemical character (Janák 1994; Gawęda & Kozłowski 1998; Kozłowski & Gawęda 1999). In the Lower Structural Unit (LSU) mica schists, interfoliated with minor amphibolites predominate, metamorphosed under upper greenschist to lower amphibolite facies conditions, whereas the Upper Structural Unit (USU) is composed of amphibolite facies migmatitic gneisses and amphibolites, graphitic quartzites and orthogneisses (Gawęda & Cebulak 1999; Kozłowski & Gawęda 1999, Fig. 1).

The crystalline rocks are covered by the parautochthonous Triassic succession and a series of nappes, containing Triassic, Jurassic and Cretaceous variegated sedimentary rocks, overthrust during the Alpine orogenesis. Faults and zones of shattering, trending NE-SW with a strike-slip displacement, discordantly cut both the crystalline basement and its sedimentary cover (Fig. 1) and are thought to be connected to the Miocene uplift of the Tatra Mountains crystalline basement (Burchart 1972).

Analytical methods

The dark-grey or black samples of rocks from tectonic zones, weighing 0.5–3 kg each were taken from the NE-SW trending fault-zones in the crystalline basement of the Western Tatra Mts (Fig. 1).

All microscopic observations were carried out in the Faculty of Earth Sciences, University of Silesia. Three selected samples were analysed by XRF for major and selected trace element at Keele University (GB) during the scholarship of the second author, using both international and internal Keele standards. For two samples detailed trace element analyses (including REE) were carried out in the Activation Laboratories Ltd (Canada) using ICP-MS method.

OTA — The thermal analyses of the whole-rock samples, carried out as the oxyreactive variety (OTA — Cebulak & Langer-Kuźniarova 1997) were conducted on the MOM Derivatograph (Faculty of Earth Sciences, University of Silesia) in an air atmosphere. The analytical conditions were: dynamic conditions for the air suction of 1.9 cm^3min^{-1}, inflation rate 1 cm^3min^{-1}, multiple sample holders (3–10 Pt plates). The total mass of each analysed sample was within the range of 600–800 mg. The Oxyreactive Thermal Analysis assumes free access of oxygen to the substance throughout the heating process, so the reaction is a function of the structure and composition of the sample. OTA has been used in many research works on organic matter as the standard method of analysis.

Fractionations — Dry powdered samples were washed up in distilled water, dried and crushed in a ball-mill to the fraction below 0.2 mm ∅ and extracted in dichloromethane in Soxhlet apparatus. The extractable organic matter (EOM) was fractionated by thin-layer chromatography (TLC Merck plates 20×20 cm covered by silica gel 60 H 0.25 mm thick) and developed in *n*-hexane. Before separation the TLC plates were activated for 3 hours at 105 °C.

GCMS — Gas Chromatography–Mass Spectroscopy (GC–MS) analyses were carried out for aliphatic and aromatic hydrocarbon fractions separately. GC–MS analyses were performed on a HP 5890 chromatograph with capillary columns coated with diphenylpolysiloxane phase (HP-5, 0.25 μm of the film thickness), 60 m in length. The GC oven was programmed to increase the temperature from 45 °C to 300 °C at a rate of 3 °C min^{-1}. Helium (1 ml per min) was a carrier gas. The mass quadrupole 5971 A, operating with an electron energy of 70 eV was a detector of separated constituents. Scanning was carried out within the mass interval 45–550 with a cycle time of 1 s. The solutions were prepared by diluting 1–3 mg of each fraction in 1 ml dichloromethane. Individual compounds were identified by mass chromatography on the basis of mass spectra, relative retention time (Lee et al. 1979; Yawanarajah & Kruge 1994; Radke et al. 1982, 1986, 2000; Chakhmakhchev et al. 1997; Peters & Moldowan 1993; Kruge 2000; Marynowski & Czechowski 1999; Mössner et al. 1999; Mössner & Wise 1999) and by co-chromatography with reference compounds.

Isotope analysis — Isotope analyses of separated aliphatic and aromatic fractions were performed at the Institute of Geological Sciences, Wrocław University, Laboratory of Isotope Geology and Biochemistry. About 3 mg of hydrocarbon material from each sample was combusted with CuO wire in a sealed quartz tube, under vacuum at 900 °C. The CO_2 gas was cryogenically purified and then introduced into a mass spectrometer (Finnigan Mat CH7 with a modified inlet and detection system). The carbon stable isotopes ratio ($\delta^{13}C$) was measured with a precision of 0.05 ‰. Values are quoted relative to the PDB international standard.

Results

Microscopic and geochemical data

Strongly tectonized rocks from the NE-SW trending fault-zones represent the predominant brittle deformation (crushing and displacing called here shattering). In some cases the older ductile shear-zones (probably early Variscan in age — Gawęda et al. 1998) were reactivated by younger brittle fault structures and there the remnants of metamorphic S-C fabric were preserved. The tectonic zones are located mainly in the metamorphic rocks, usually mechanically weaker than massive granitic intrusions. The metamorphic complex in question consists of metapelitic-metapsamitic gneisses and migmatites (Burda & Gawęda 1997), interleaved with amphibolites (metamorphosed tholeiitic basalts — Gawęda et al. 2000a). The metapelitic-metapsamitic gneisses and migmatites are characterized by the typical mineral assemblage Qtz+Pl±Kfs+Bt±Grt±Sil±Ky+Ap+Ms±Gph, while amphibolites are composed of the Hbl+Pl+Qtz+Ilm±Grt+Ap. Chondrite normalized REE diagrams for the metamorphic rocks show typical negative Eu anomaly and fall into one field presented in the Fig. 2 (shaded area). REE patterns of the selected bitumen-bearing rocks show a medium fractionation trend and fall in the same field of REE characteristics for the crystalline rocks of the Western Tatra Mts (Table 1, Fig. 2). This fact suggests that the chemistry of the original rocks was not changed dramatically and REE were not mobilized during bitumens migration. In three samples bituminous matter is mixed with goethite (Baniste 2, Ł6, Ł20).

The cataclastic rocks are partly recrystallized and contain quartz, sericitized feldspars, muscovite, chlorites, sometimes remnants of biotite. Fine-grained quartz forms the mineral cement. Dark impregnations and patches concentrated along structural planes (preserved metamorphic foliation, fractures, etc.) were microscopically distinguishable (Figs. 3, 4).

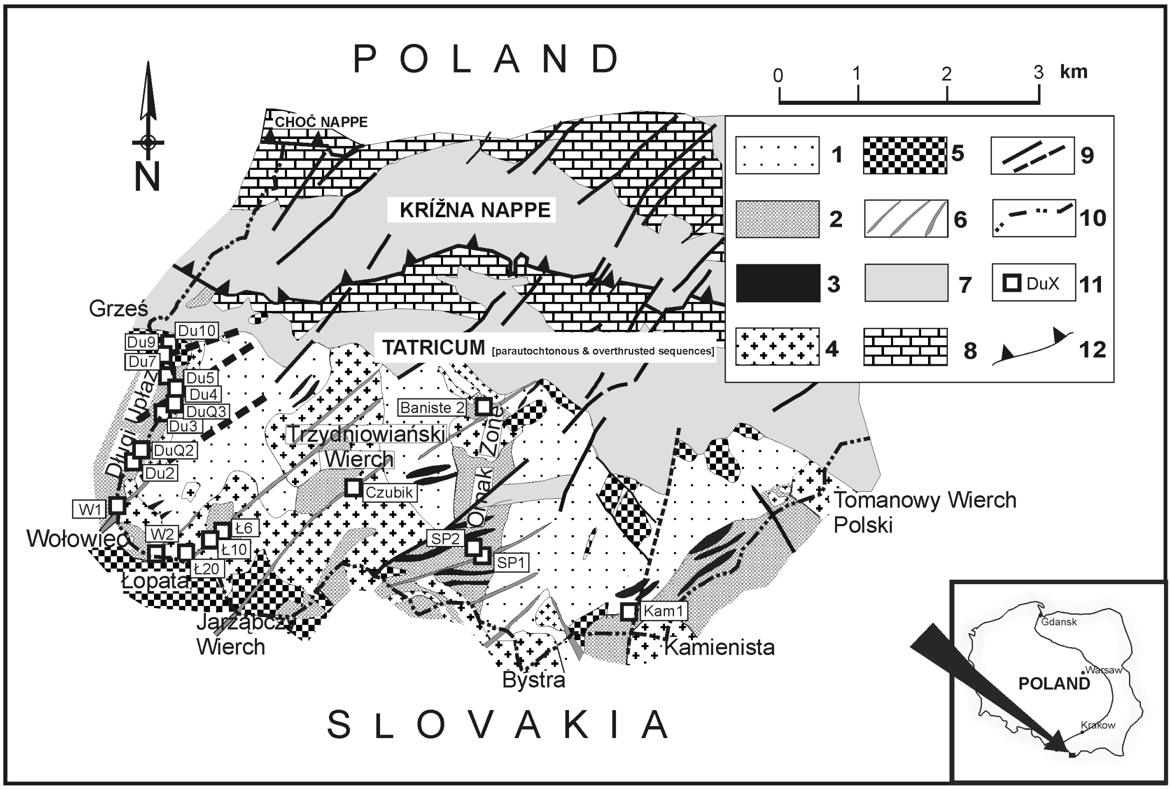

Fig. 1. Geological map of the Polish side of the Western Tatra Mountains with sample locations. *Explanations:* **1** — Lower Structural Complex; **2** — Upper Structural Complex; **3** — amphibolites; **4** — leucogranites (alaskites); **5** — biotitic granodiorite (Rohacze Granite); **6** — cataclastic rocks; **7** — Triassic sediments; **8** — Jurassic & Cretaceous sediments; **9** — faults; **10** — state boundary; **11** — sample locations; **12** — nappe boundary. ***1–6*** — Tatric basement complexes; ***7–8*** — Mesozoic cover and nappe complexes.

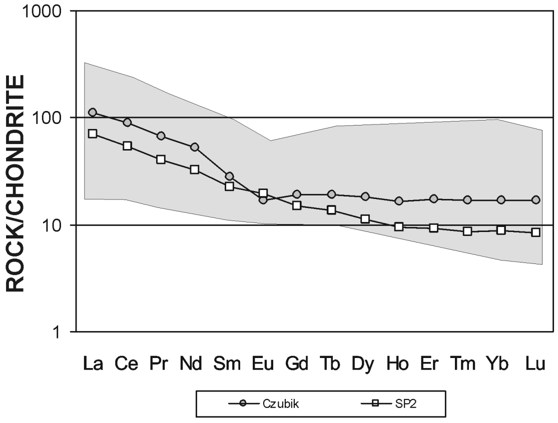

Fig. 2. Chondrite normalized REE concentrations in the bitumen-bearing rocks. The shaded area is the field of typical metamorphic rocks from the Western Tatra Mountains.

Table 1: Rare Earth Elements (REE) concentrations in the bitumen-bearing rocks.

Component	SP2	Czubik
La	16.6	26.5
Ce	32.9	55.4
Pr	3.86	6.32
Nd	15.3	24.4
Sm	3.24	4.32
Eu	1.13	0.97
Gd	3.10	3.94
Tb	0.51	0.72
Dy	2.82	4.58
Ho	0.53	0.93
Er	1.53	2.86
Tm	0.221	0.430
Yb	1.49	2.89
Lu	0.211	0.428
$(La)_N/(Yb)_N$	6.577	7.991

$(La)_N/(Yb)_N$ —— fractionation index

The low concentration of Na_2O (Table 2) is caused by the alkali leaching during alteration of plagioclase, while SiO_2 content exceeding 75 wt. % is usually the result of secondary quartz precipitation, which is a common matrix mineral for most of these mylonites. Reflected light microscopy shows the presence of small quantities of sulphide minerals (tetrahedrite, chalcopyrite) and — in some cases — barite and this is confirmed by enhanced concentrations of certain trace elements (Ba, Cu, Ag) in some samples from i.e. Ornak Ridge (SP2).

Mo (4–18 ppm), W (0.8–1.2 ppm), Be (3–4 ppm), U (4–9 ppm), Ni (17–31 ppm) are enriched in all analysed samples in relation to the other Tatra basement rocks (Mo is usually below 1 ppm, sporadically 2 ppm, W — below 1 ppm, Be — below 1, sporadically 1–2 ppm). The reference rock for the discrimination was the so-called "mean Tatra metamorphic rock" (MTR), created on the basis of the second author's whole-rock analyses (Table 1; Burda & Gawęda 1997; Gawęda & Kozłowski 1998; Kozłowski & Gawęda 1999). For the calculation of MTR composition about a hundred chemical analyses of metamorphic rocks were used assuming their volume proportion from the field studies.

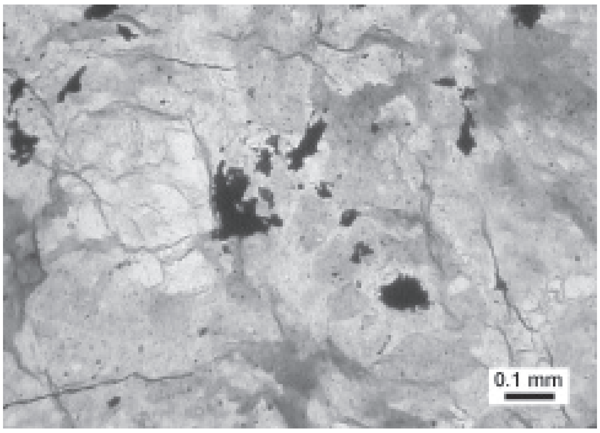

Fig. 3. Microphotograph of cataclasite with black patches of bitumens (Baniste 2). 1 polar.

Table 2: Chemical composition of the bitumen-bearing rocks and reference mean Tatra metamorphic rock (MTR). (Major elements given in [wt. %], selected trace elements in [ppm]).

Component	SP1	SP2	Czubik	MTR
SiO_2	74.47	76.46	71.16	62.06
TiO_2	0.58	0.31	0.71	0.97
Al_2O_3	13.11	8.96	16.87	15.64
$Fe_2O_3^T$	5.08	5.84	5.11	7.43
MnO	0.05	0.07	0.07	0.11
MgO	0.85	0.56	0.45	1.76
CaO	0.06	0.04	0.09	2.86
Na_2O	0.27	0.10	1.44	4.39
K_2O	2.92	3.08	4.16	2.66
P_2O_5	0.14	0.11	0.15	0.47
LOI	2.8	2.94	0.25	1.38
S	0.003	0.10	0.004	0.001
Total	100.333	98.55	100.464	99.731
Cs	7.0	7.9	8.4	2.0
Rb	104	132	118	767
Sr	41	163	67	212
Ba	273	9230	524	556
Be	4	4	3	1.89
U	8.9	9.13	4.65	2.3
Th	6.2	4.33	7.06	6.4
Zr	141	93	168	170
Hf	3.0	2.5	4.4	62
Y	19	16.3	27.6	28
Ga	16	16	20	15
Ge	3.0	2.9	1.1	nd
Cu	67	1680	79	19.7
Ag	78	84.6	5.9	25
V	143	53	130	107.5
Cr	80	30	48	16
Co	20	21	17	nd
Ni	23	31	17	8
Mo	15	18	4	<1
W	1.0	1.2	0.8	0.3
Nb	7	5.3	9.6	19
Ta	0.8	0.8	0.8	0.8

$Fe_2O_3^T$ — Fe_2O_3 as a total iron; nd — not determined concentration

Oxyreactive thermal analyses

The weight per cent of the bituminous matter, calculated from the loss of mass at characteristic reactions in the temperature range of 200–400 °C, is about 0.2–1.0 wt. %.

Oxyreactive thermal analyses of the whole-rock samples reveal the presence of endothermic peaks in the temperature range of 240–290 °C (after checking the mineral matrix thermal characteristics), and the exothermic reactions in the temperature range of 280–340 °C (Fig. 5). Where goethite is present in the analysed samples the exothermic peaks are homogenous and distinct, while in other samples the exothermic reactions are often non-homogenous, with subordinate "parasitic" peaks on both slopes of the main reaction peaks. Such thermal patterns are typical of heavy fractions of crude oil (Cebulak et al. 1999).

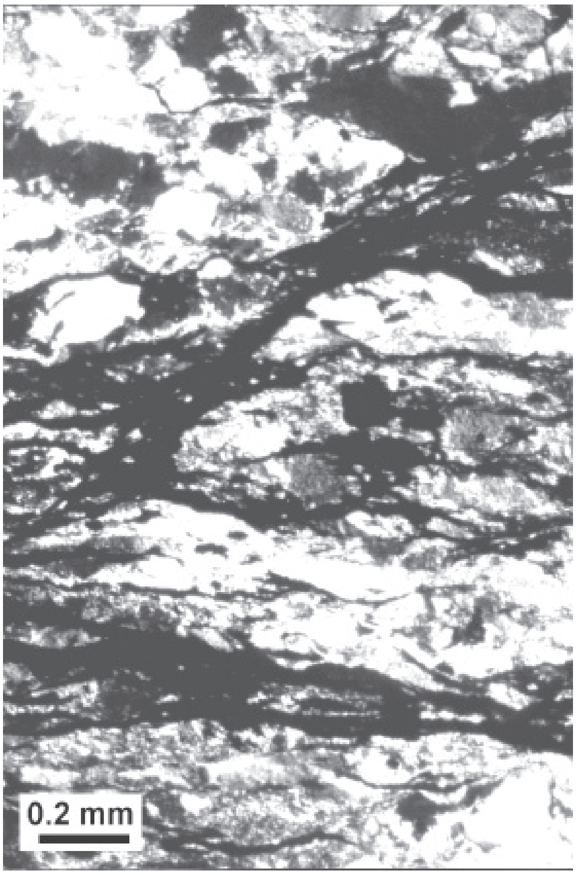

Fig. 4. Microphotograph of older S-C mylonite with bituminous impregnations on the shearing planes (Ł6). Crossed polars.

Carbon stable isotopes

Calculated values of $\delta^{13}C$ for aromatic fractions of extracted bituminous matter are within the range of –25.17 to –28.34 ‰ (Table 3). Such characteristics of unbiodegradated samples are

Table 3: Carbon isotope data of the extractable bituminous matter.

Sample No.	$\delta^{13}C$ AR	$\delta^{13}C$ AL	$\delta^{13}C$ POL
DU5	-25.87	-27.48	-27.07
DU7	-25.11	-25.17	-27.37
SP2	Nd.	-25.26	-27.13
Czubik	-26.02	-28.34	-26.82

AR — aromatic fraction; AL — aliphatic fration; POL — polar fraction

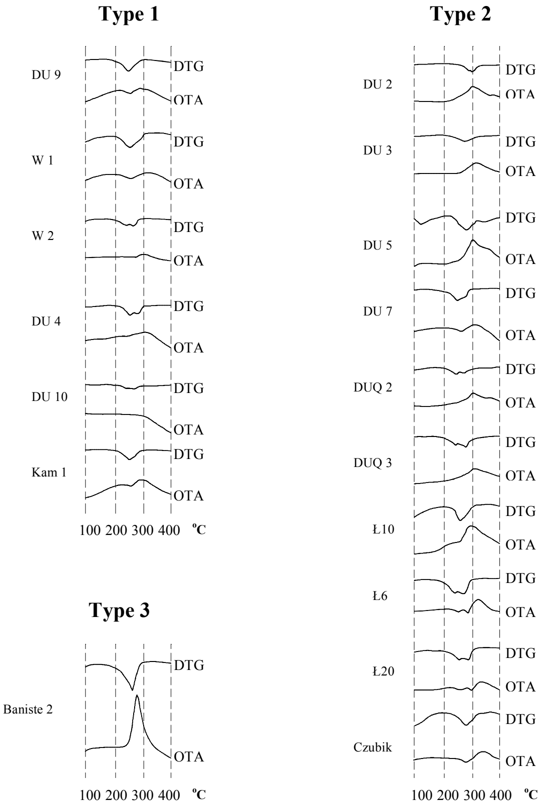

Fig. 5. OTA curves of the whole-rock bitumen-bearing samples from the tectonic zones of the Western Tatra Mountains. For location see Fig. 1.

typical of marine, algal or mixed marine and terrestrial source material (Sofer 1984), with dominant planctonic type of organic matter (Fig. 6).

GC–MS analyses

The extractable fraction forms 0.03–0.32 wt. % of the analysed samples. In the aliphatic fraction of analysed hydrocarbons the bimodal distribution of selected *n*-alkanes was observed with the first maximum in n-C_{18} or n-C_{17} and the second (smaller) maximum in n-C_{25} (Figs. 6, 7). Samples "Czubik" and DU5 contain a so-called "hump" that is unresolved compound mixture (Gough & Rowland 1990). All bitumen samples contain relatively high amounts of diasteranes (m/z 217; Fig. 7). The Pr/Ph ratio is about 1. The calculated values of vitrinite reflectance, based on the methyldibenzothiophene ratio (Radke & Willsch 1994) are in the range of R_{CS} = 0.75–0.82 %. The detailed characteristics of the parameters calculated from the GC–MS spectra are presented in Table 4 and the assignations of the identified compounds are in the appendix.

Discussion

The character and origin of bitumens

OTA — The OTA patterns of the analysed samples are typical of heavy fractions of rock-oil. The thermal analyses reveal the characteristics of both extractable (migratory) and non-extractable (unresolved in organic solvents) fractions. Non-extractable components are enriched in so-called pyrobitumens.

The results of oxyreactive thermal analysis (both DTG and DTA) show the diversification of the thermal reactivity of the analysed bituminous matter. We can distinguish three types of organic material.

Type 1. Organic matter characterized by the presence of endothermic reaction and lacking or only trace exothermic peaks (samples DU9, DU10, W1, W2, K1; Fig. 6). Endothermic reactions are observed at 240/250 °C and 280/290 °C. This type of sample lacks non-extractable components.

Type 2. Organic matter characterized by the presence of endothermic reactions, observed as the single peak at 290 °C or as two peaks at 240/250 °C and 280/290 °C and distinct exothermic reaction in the temperature range of 300–360 °C (samples DU2, DU3, DU5, DU6, Ł6, Ł10, Ł20, Czubik — Fig. 5). Such patterns are typical of samples enriched in the non-extractable components, showing the coking capacity.

Type 3. Sample Baniste 2 is characterized by the endothermic peak at 260 °C and distinct exothermic peak at 270/280 °C. The OTA patterns could suggest the susceptibility to catalytic transformations in the presence of Fe-compounds.

The differences in thermal features among the analysed bitumens (and consequently three distinguished types of organic matter) resulted mainly from the biodegradation and evaporation processes and transformation influenced by the Fe-rich fluids, stimulating maturation processes.

GC–MS — The distribution patterns of *n*-alkanes suggest a mixed (terrestrial-marine) character of the organic material primary for bitumen generation. It should be noted that in many cases biodegradation processes overprint the primary *n*-alkanes distribution patterns, causing the removal of short-chain *n*-alkanes. However, the samples Czubik and DU5 reveal features characteristic of small to moderate biodegradation degree (Fig. 6), manifested by the partial destruction of *n*-alkanes and isoprenoids: Pr/Ph Pr/n-C_{17} ratios are partly affected (Peters & Moldowan 1993). The thermograms of the samples with biodegradation show the shift in endothermic peaks to higher temperatures (see Fig. 5, sample DU5, Czubik), which is a direct effect of the short-chain *n*-alkanes removal/consumption.

The values of dibenzothiophene/phenanthrene (DBT/P), alkyldibenzothiophene/alkyldibezofurane (ADBT/ADBF) and pristane/phytane (Pr/Ph) ratios for the analysed samples are plotted on the genetic diagrams according to Hughes et al. (1995) and Radke et al. (2000) (Fig. 8a,b). Three samples plot in the field 3 (marine shales and lacustrine sediments) while two other samples plot in the field 2 (lacustrine, sulphate — poor sediments). However, the recent data from rocks of the Devonian carbonate platform and shelf basin show that marine, poor in organic matter samples also plot in field 2 (Marynowski et al. 2000). The GC–MS data are supported by the isotopic results showing the algae and terrestrial source (Fig. 6).

All bitumen samples are characterized by relatively high diasterane/sterane ratios (m/z 217 — Fig. 7, Table 4). High diasterane concentration depends on the clay minerals content relative to the organic matter content in the rock (clay/

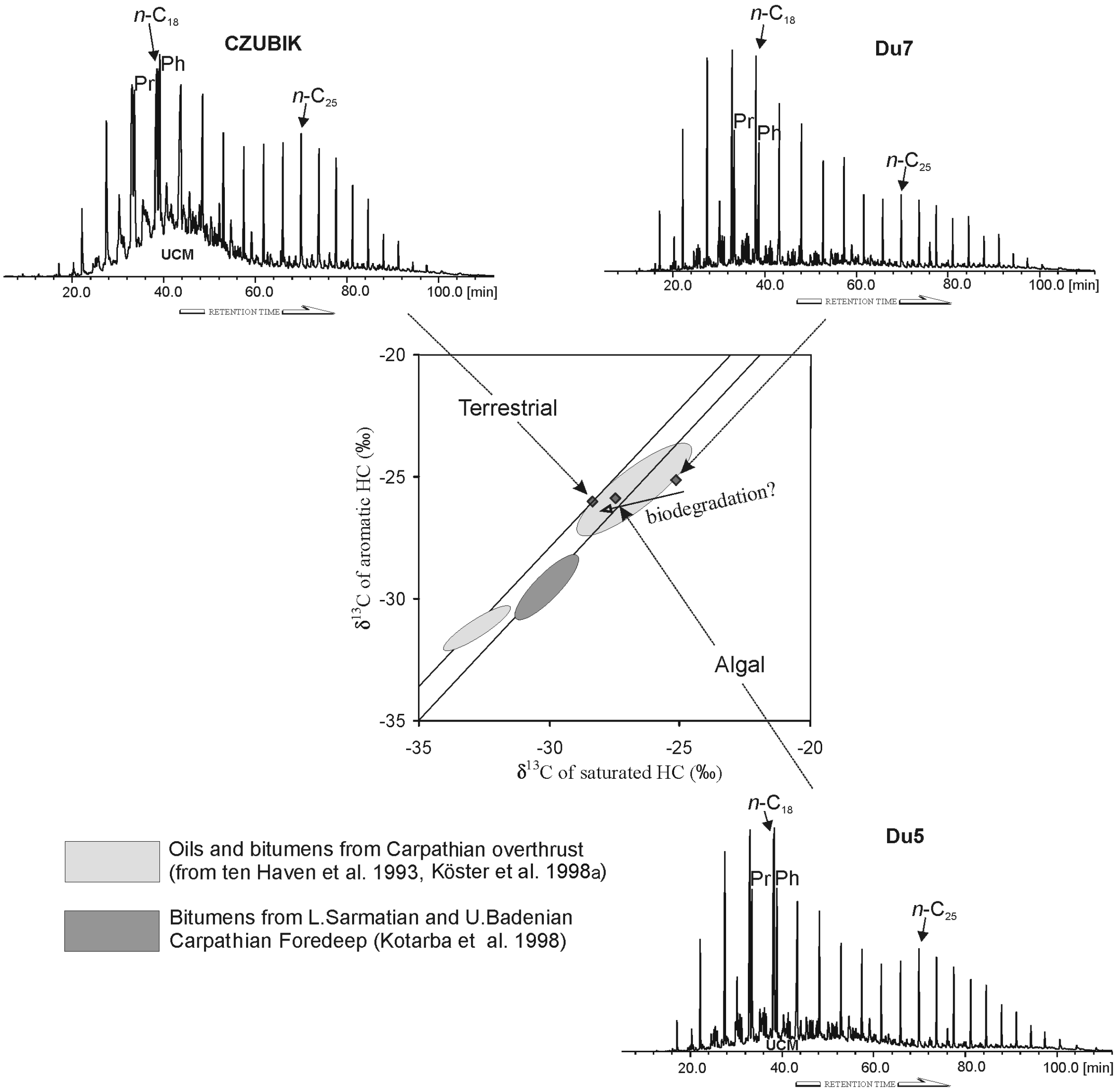

Fig. 6. Carbon isotope composition of saturated versus aromatic hydrocarbon fraction (after Sofer 1984) and distribution of saturated hydrocarbons fractions from the selected samples. **UCM** — unresolved compound mixture; **Pr** — pristane; **Ph** — phytane.

TOC ratio — van Kaam-Peters et al. 1998). High diasterane concentrations could be caused by the enrichment in clay minerals in the source rocks, which generate hydrocarbons (Peters & Moldowan 1993) and suggests a relatively low concentration of organic matter in the clayey source rocks, in which bitumens were generated. High hopane concentrations (ster/17α(H)-hop parameter, Table 4) and the presence of tetracyclic triterpanes (C_{24}tetra/C_{26}tri parameter, Table 4), described as microbial compounds (Hughes & Holba 1988; Wan Wasiah 1999) suggests that organic matter in the source rocks was subjected to the secondary bacterial reworking in the sedimentary basin after deposition.

Small amounts of cadalene and retene are present in the investigated rocks. They are the biomarkers indicating the former presence of higher plant material (van Aarsen et al. 2000). The presence of mentioned biomarkers, originated from higher plant material, could suggest a negligible small admixture of the terrestrial organic matter influence in the source, bitumen-generating rocks. However, there is a lack of oleanes, compounds typical of angiosperms and occurring commonly in Carpathian Tertiary oils and sediments (Kruge et al. 1996; Lafargue et al. 1994; Köster et al. 1998a,b; Picha & Peters 1998; Francŭ et al. 1996; ten Haven et al. 1993).

In the ternary diagrams (Fig. 9a,b) the relative concentrations of C_{27}, C_{28} and C_{29} steranes and C_{27}, C_{29}, C_{30}, and 17α(H)-hopanes are shown. The results indicate the uniform character of the investigated bitumens. Fig. 9a presents the difference in sterane concentrations in the presented Western Tatra bitumens from the sterane concentrations in samples of oils from the Outer Carpathians (Poland and Czech Republic), of Jurassic and Oligocene age.

The hopane distribution patterns (Fig. 7, m/z 191), including low values of the Homohopane Index (0.15–0.21, Table 4) as well as the presence of C_{30}*-17α(H)-diahopane suggest

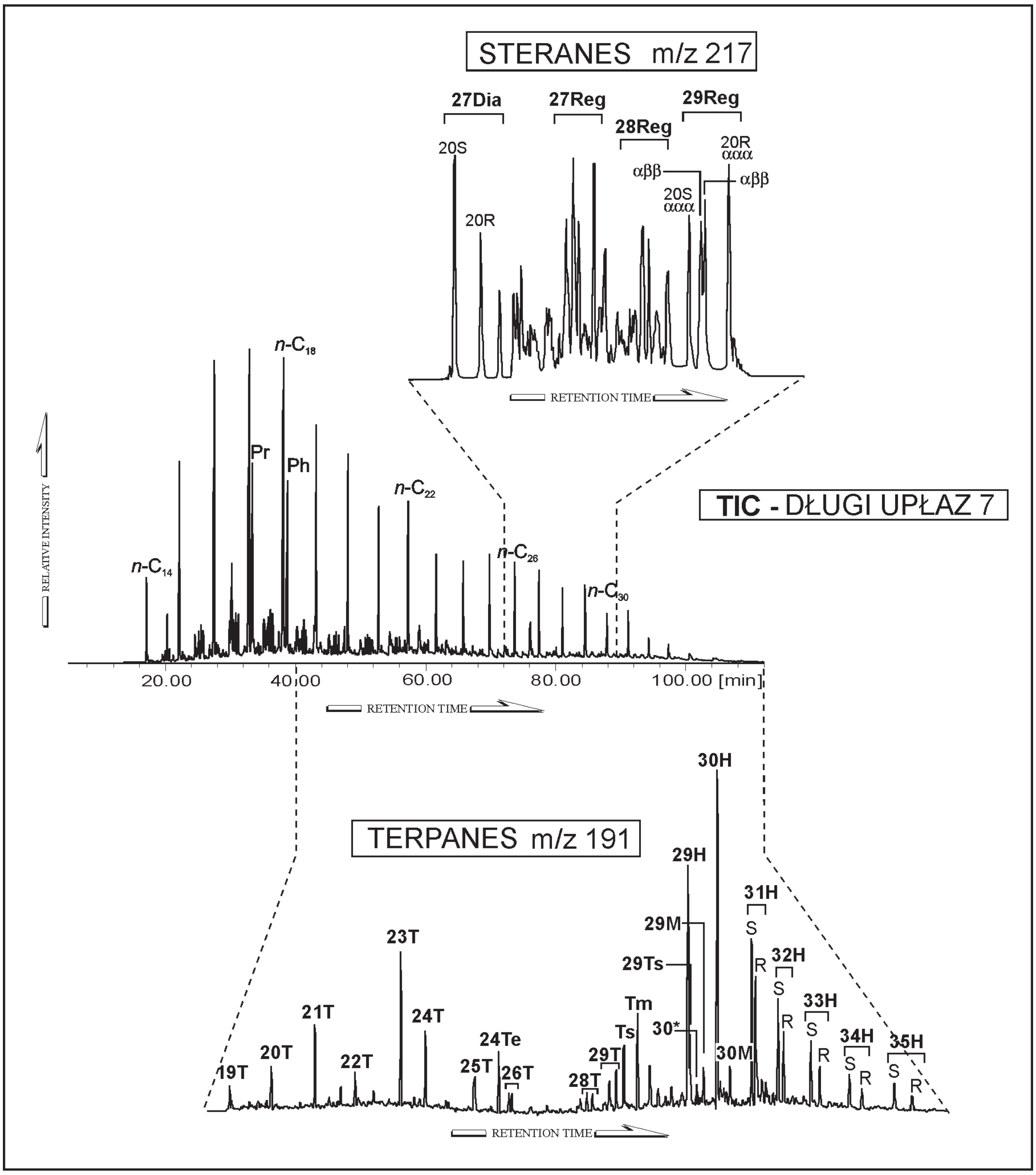

Fig. 7. Total ion chromatogram and fragmentograms of tricyclic, tetracyclic, pentacyclic triterpanes (m/z 191) and steranes (m/z 217) from sample Du7. The assigned peaks are listed in appendix.

that the parental organic matter was accumulated in the marine, suboxic shelf conditions.

Organic maturation

The thermal maturity of the investigated bitumens was determined on the basis of organic compounds in aliphatic and aromatic fractions. Parameters like Ts/(Ts+Tm), ββ/(ββ+αα), 20S/(20S+20R), MDR DMBT, TMDBT, MPI1 or TrP1 have almost equal values for specific samples of the Western Tatra bitumens (Fig. 10, Table in appendix). They are typical of mature organic matter at catagenetic stage of transformation (Horsfield & Rullkötter 1994). The MDR parameter value was recalculated to theoretical vitrinite reflectance (R_{CS} according to Radke & Willsch 1994). The R_{CS} = 0.74–0.82 % are typical of the oil-window stage of transformation. Note that the values of the popular metylphenanthrene 1 index (MPI1) are significantly lower than the other parameters (MPI1 = 0.19–0.23). It is widely known that this index does not work for the II type of kerogen (algae marine organic material — Peters 1986) that can be responsible for the lowered MPI1 index values (Radke et al. 1986).

Where are the source rocks for bitumens?

Due to high metamorphic alteration, the present host rocks of the investigated bitumens cannot be considered as their source rocks. Considering the above mentioned characteristics the most convenient source for the bitumens are the sedimentary overlying rocks. They were not metamorphosed during the Alpine overthrusting; the conodont alteration index (CAI) from the Triassic limestones from the Tatricum se-

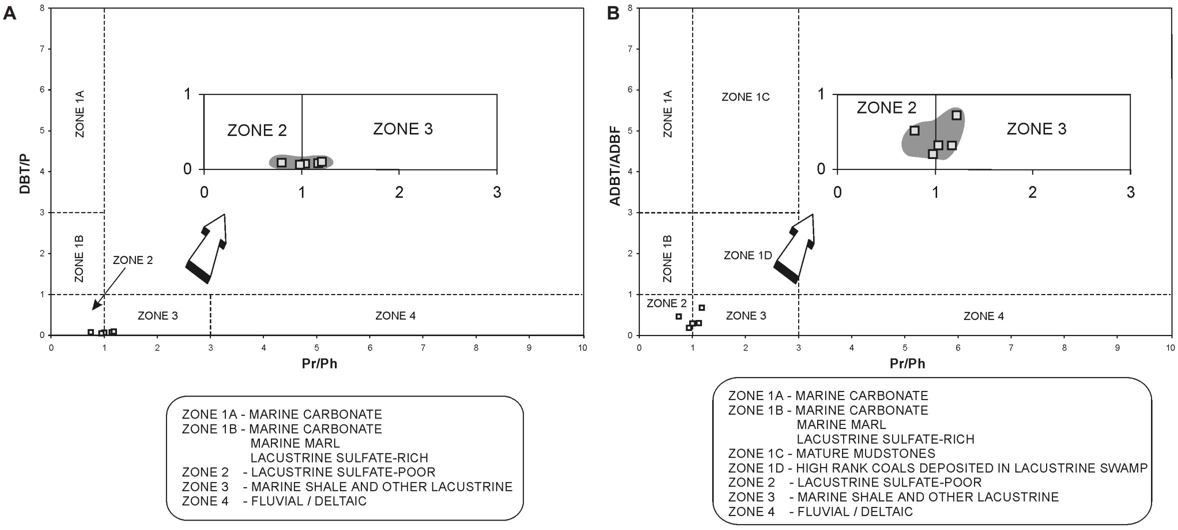

Fig. 8. Analysed samples from the Western Tatra Mountains in 2 cross plots: **A.** dibenzothiophene/phenanthrene (DBT/P) versus pristane/phytane (Pr/Ph) ratios (based on Hughes et al. 1995) **B.** alkyldibenzothiophene/alkyldibenzofuranes (ADBT/ADBF) versus pristane/phytane (Pr/Ph) ratios (after Radke et al. 2000).

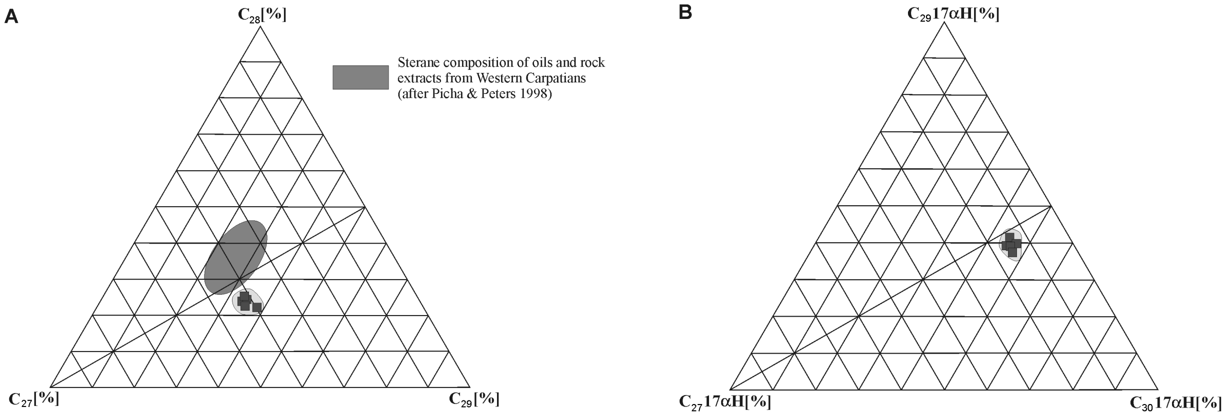

Fig. 9. Ternary diagram of C_{27}, C_{28} and C_{29} sterane composition [5α, 14α, 17α (H) 20S+20R and 5α, 14β, 17β (H) 20S+20R] for bitumens from the Western Tatra Mountains. For comparison see Picha & Peters (1998).

Table 4: Geochemical characteristics of the bitumens from the Tatra Mountains.

MOLECULAR PARAMETERS	BANISTE	Du5	Du7	CZUBIK	SP2
Isoprenoids					
Pr/Ph	0.71	0.95	1.09	0.91	1.10
Pr/*n*-C_{17}	0.40	0.74	0.63	0.97	0.61
Triterpanes					
Ts/(Ts + Tm)	0.42	0.44	0.42	0.45	0.42
Homohopane Index	0.17	0.18	0.21	0.15	0.21
C_{24}tetra/C_{26}tri	1.0	1.0	1.20	0.71	1.0
C_{23}tri/C_{30}hop	0.69	1.30	0.49	0.60	0.42
Steranes/17α(H)-hop	0.50	0.48	0.46	0.50	0.57
Steranes					
C_{27}-Sterane [%]	41	42	40	41	43
C_{28}-Sterane [%]	25	25	21	26	24
C_{29}-Sterane [%]	34	33	39	33	331
Dia/Ster	0.50	0.62	0.50	0.55	0.53
ββ/(ββ+αα)	0.52	0.49	0.47	0.50	0.53
20S/(20S + 20R)	0.47	0.49	0.44	0.48	0.51
Polycyclic Aromatic Compounds					
MDR	4.26	4.26	3.63	3.08	3.63
R_{CS}[%]	0.82	0.82	0.77	0.74	0.77
TA(I)/TA(I + II)	0.33	0.30	0.29	0.50	0.25
DMDBT	0.61	0.56	0.58	0.53	0.52
TMDBT	1.04	1.10	1.12	1.12	1.15
MPI1	0.21	0.22	0.19	0.21	0.23
TrP1	0.38	0.41	0.17	0.73	0.26

Pr/Ph — pristane/phytane;

Pr/*n*-C_{17} — pristane/*n*-heptadecane;

Ts/(Ts + Tm) — 18α-22,29,30-trisnorneohopane/(18α-22,29,30-trisnorneohopane + 17α(H)-22,29,30-trisnorhopane)(Peters & Moldowan 1993);

Steranes/17α(H)-hop. — regular steranes consist of the C_{27}, C_{28}, C_{29} ααα(20S + 20R) and αββ(20S + 20R), 17α(H)-hopanes consist of the C_{29} to C_{33} pseudohomologue (including 22S and 22R epimers) (Peters & Moldowan 1993);

Homohopane Index — $C_{35}/(C_{31}+C_{35})$ homohopanes (Peters & Moldowan 1993);

C_{24}tetra/C_{26}tri — C_{24} tetracyclic terpane/C_{26} tricyclic terpane (Wan Hasiah 1999);

ββ/(ββ+αα)—[5α(H),14β(H),17β(H)(20R+20S) C_{29}sterane]/ [5α(H),14β(H),17βH) (20R + 20S) C_{29}sterane + 5α(H),14α(H),17α(H)(20R + 20S)] C_{29}steranes (Peters & Moldowan 1993);

20S/(20S + 20R) — C_{29}5α(H),14α(H),17α(H)20S/[C_{29}5α(H),14α(H),17α(H)20(S +R)] (Peters & Moldowan 1993);

MDR — methyldibenzothiophene ratio [*4*-MDBT]/[*1*-MDBT] (Radke et al. 1986);

R_{cs}(%) = 0.073 MDR + 0.51 (Radke & Willsch 1994);

TA(I)/TA(I + II) — sum of C_{26}-C_{28}(20S + 20R) triaromatic steroids as TA(II) and the C_{20} and C_{21} triaromatic steroids as TA(I) (Peters & Moldowan 1993);

DMDBT — dimethyldibenzothiophene ratio, DMDBT = 2,4-DMDBT/1,4-DMDBT (Chakhmakhchev et al. 1997);

TMDBT — trimethyldibenzothiophene ratio, TMDBT = 2,4,7-TMDBT/1,4,7-TMDBT (Chakhmakhchev et al. 1997);

MPI1 — methylphenanthrene index 1, MPI1 = 1.5([2-MP] + [*3*-MP])/([P] + [*1*-MP] + [9-MP]) (Radke & Welte 1983);

TrP1 — terphenyl ratio 1, [*p*-TrP]/[*o*-TrP] (Marynowski & Czechowski 1999).

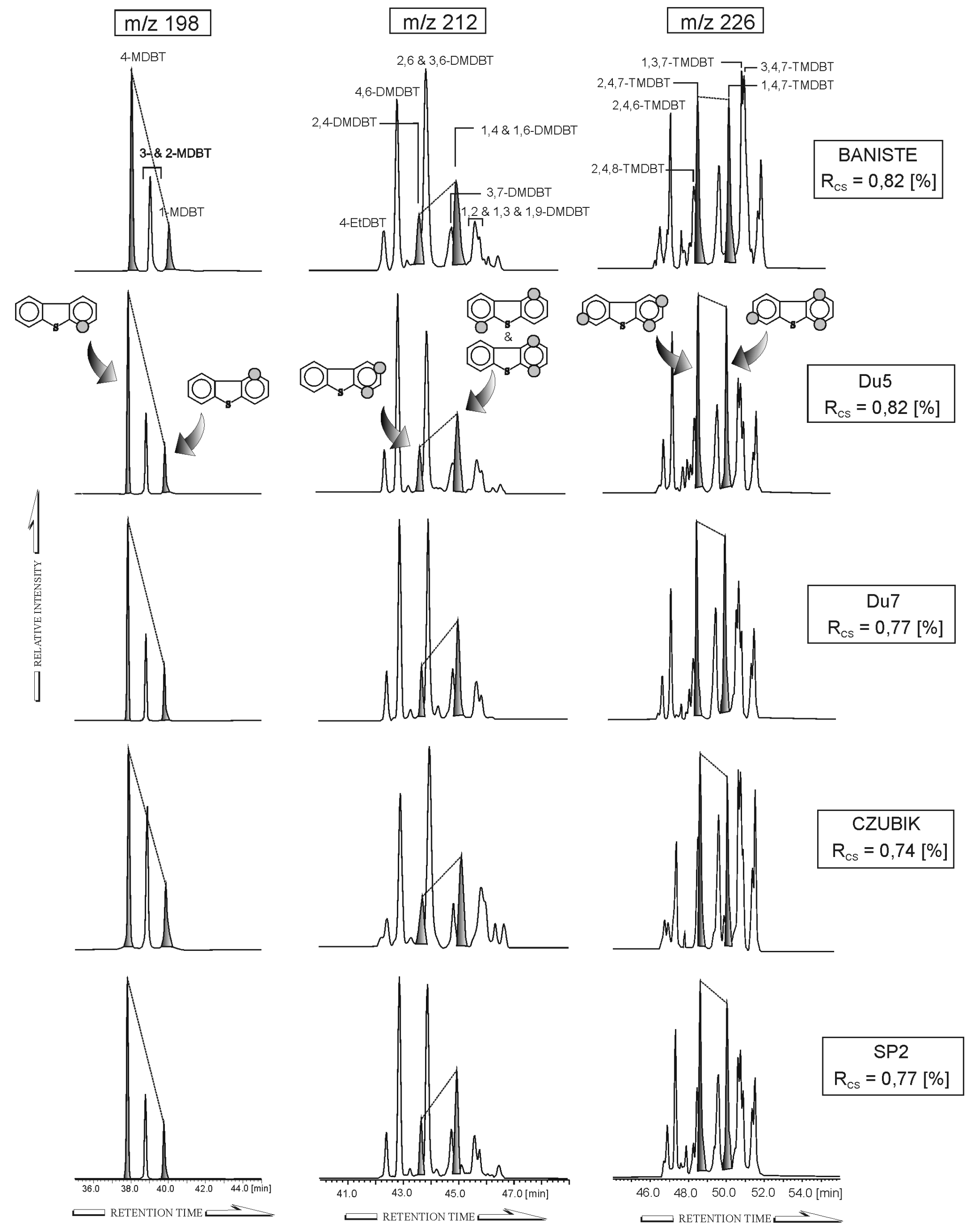

Fig. 10. A — Ternary diagram of C_{27}, C_{29}, C_{30} - 17α (H) hopanes. See Table 4 for detailed designations. **B** — Similar chromatographic distribution of metyldibenzothiophenes (m/z 198), dimetyldibenzothiophenes (m/z 212) and tentatively identified trimetyldibenzothiophenes (m/z 228) for bitumens from the Tatra Mountains with description of individual peaks (after Chakhmakchev et al. 1997; Mössner et al. 1999). Theoretical value of vitrinite reflectance (R_{CS} [%] = 0.073 MDR+0.51) MDR = (4-MBT)/(1-MBT) after Radke & Willsch (1994).

quence is about 1.5–2.0, which together with paleomagnetic studies, suggests that the whole complex was heated to 50–80 °C for about 10 Ma (Grabowski et al. 1999). The highest possible temperature of syntectonic heating was suggested for the lower parts of the parautochthonous and overthrust Tatricum sequences. It is 150–200 °C (Lefeld 1997a).

Comparison with the Outer Western Carpathian crude oils showed that the investigated bitumens resemble Jurassic rock-oils more than Paleogene ones. Jurassic marine sedimentary rocks in the Western Tatra Mts are present both in the Tatricum and in the Križna Nappe. However, the Krížna Nappe Triassic-Jurassic carbonate series were deposited in a deep sedimentary basin (i.e. Lefeld 1997b), which does not correspond to the suggested oxic marine shelf conditions needed for the source rocks of the bitumen. The Upper Triassic and/or Jurassic carbonate series of the parautochthonous Tatric successions Nappe seem to be more plausible source rocks.

Mechanism of migration

The NE-SW trending faults, probably active after the Alpine overthrusting, are likely paths for migration of bitumens. Some shear-zones could be rejuvenated earlier faults, which acted formerly as the paths for fluid circulation and contain abundant carbonate-quartz-sulphide-barite mineralization (Wątocki 1950; Paulo 1970; Gawęda et al. 2000). Microscopic observations show that the mineralization is older than the bituminous impregnations.

It is likely that the lighter fractions of the oils migrated (or were flushed through by circulating water), while the heavy fractions of crude oils were trapped in the tectonic zones. Migration of the hydrocarbons occurred most probably during or after overthrusting of the Mesozoic nappes.

The original chemistry of host rocks was not significantly changed during bitumen migration, but the enhanced concentration of U, W, Ni and Cr [forming the positive anomalies in the shattered (fractured) rocks] could be connected with the presence of bitumens. All these elements can form the metal-organic components and are usually enriched in the bitumens deposits. Especially uranium mobility should be considered with care — in the Białego Valley a small uranium anomaly was noted by the Russian IVth Prospecting Group in the tectonic zone running NE-SW. In the report of 1952 the concentration of U between 0.05 wt. % and 0.3 wt. % was mentioned, correlated with the presence of strongly shattered upper Triassic black shales (Wołkowicz — pers. commun.).

The original bitumen-bearing source rocks are unlikely to be found because bitumen removal would have been induced by the extensive tectonic movements. Nevertheless, this paper is the first step in understanding of the migration processes within the tectonic zones in the Tatra Mountains.

Conclusions

1. Bitumens found in the NE-SW trending tectonic zones of the Western Tatra Mountains belong to the heavy fractions of crude oil. They were trapped in the mineral pores and locally deposited on the tectonic planes during migration of rock-oils and fluids along the tectonic zones, cutting both basement rocks and the sedimentary cover rocks.

2. The source rocks of the bitumens were enriched in clay minerals, relatively poor in organic matter and were accumulated in marine, suboxic shelf conditions. The secondary bacterial reworking of the primary hydrocarbons took place in the sedimentary basin after deposition.

3. Organic maturation of the investigated bitumens reached the catagenetic stage of transformation (oil-window).

4. The source rocks of the migrated hydrocarbons could be the Upper Triassic and/or Jurassic sedimentary series of the Tatricum sequence. The younger (Tertiary) source was excluded on the basis of biomarkers analysis.

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References

Bac-Moszaszwili M. 1993: Structure of the western ending of the Tatra Massif. *Ann. Soc. Geol. Pol.* 63, 167–193 (in Polish, English abstract).

Bac-Moszaszwili M. 1996: Tertiary-Quaternary uplift of the Tatra massif. The Tatra National Park — Nature and Man. *Proc.* T.1, 68–70.

Burchart J. 1972: Fission-track age determination of accessory apatite from the Tatra Mts., Poland. *Earth Planet. Sci. Lett.* 15, 418–422.

Burda J. & Gawęda A. 1997: Mass-balance calculations in migmatites from the Upper Kościeliska Valley (the Western Tatra Mts., S-Poland). *Miner. Pol.* 28, 1, 53–68.

Cebulak S. & Langer-Kuźniarowa A. 1997: Application of oxyreactive thermal analysis to the examination of organic matter associated with rocks. *J. Thermal Analysis and Calorymetry* 50, 175–190.

Cebulak S., Gawęda A. & Langer-Kuźniarowa A. 1999: Oxyreactive thermal analysis of dispersed organic matter, kerogene and carbonization products. A tool for investigation of the heated rock masses. *J. Thermal Analysis and Calorymetry* 56, 917–924.

Chakhmakhchev A., Suzuki M. & Takayama K. 1997: Distribution of alkylated dibenzothiophenes in petroleum as a tool for maturity assessments. *Org. Geochem.* 26, 483–490.

Francŭ J., Radke M., Schaefer R.G., Poelchau H.S., Čáslavský J. & Boháček Z. 1996: Oil-oil and oil-source rock correlation in the northern Vienna Basin and adjacent Carpathian Flysch Zone (Czech and Slovak area). In: Wessely G. & Liebl W. (Eds.): Oil and Gas in Alpidic Thrustbelts and Basins of Central and Eastern Europe. *EAGE Spec. Publ.* 5, 343–353.

Gawęda A. 1995: Geochemistry and Rb/Sr isochron age of pegmatites from the Western Tatra Mts., (S-Poland). *Geol. Carpathica* 46, 95–99.

Gawęda A. 1997: Rb-Sr isochron age of metamorphism in the Polish part of the Western Tatra Mts. — preliminary data. *PTMin – Prace Spec.* 7, 65–67.

Gawęda A. & Kozłowski K. 1998: Magmatic and metamorphic evolution of the Western Tatra crystalline basement (S-Poland, W-Carpathians). *CBGA XVI Congress — Abstracts* 177.

Gawęda A., Kozłowski K. & Piotrowska K. 1998: Tectonic development of the crystalline basement of the Polish part of the Western Tatra Mts. *Acta Univ. Carolinae — Geol.* 42, 2, 252–253.

Gawęda A. & Cebulak S. 1999: The origin of graphite in the crystalline basement of the Western Tatra Mts. *Geol. Carpathica*

50, 295–304.

Gawęda A., Goławska B., Piwkowski R., Jędrysek M., Leichman J. & Paulo A. 2000: Carbonate mineralization in the Western Tatra crystalline basement, Poland. *Acta Mineral. Petrogr., Szeged, XLI, Suppl.* 46.

Gough M.A. & Rowland S.J. 1990: Characterisation of unresolved complex mixture of hydrocarbons in petroleum. *Nature* 344, 648–650.

Grabowski J., Narkiewicz K. & Poprawa P. 1999: First results of paleomagnetic and paleothermal (CAI) of the highest Sub-Tatric units in the Polish Tatra Mts. *Przegl. Geol.* 47, 153–158.

Horsfield B. & Rullkötter J. 1994: Diagenesis, Catagenesis, and Metagenesis of Organic Matter. In: Magoon L.B. & Dow W.G. (Eds.): The petroleum system — from source to trap. *AAPG Memoir* 60, 189–199.

Hughes W.B. & Holba A.G. 1988: Relationship between crude oil quality and biomarker patterns. In: Mattavelli L. & Novelli L. (Eds.): Advances in Organic Geochemistry 1987. *Org. Geochem.* 13, 15–30.

Hughes W.B., Holba A.G. & Dzou L.I.P. 1995: The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. *Geochim. Cosmochim. Acta* 59, 3581–3598.

Janák M. 1994: Variscan uplift of the crystalline basement, Tatra Mts., Central Western Carpathians: evidence from ^{40}Ar/^{39}Ar laser probe dating of biotite and P-T-t paths. *Geol. Carpathica* 45, 293–300.

Janák M., Poller U., Hurai V., Kohút M., Ludhová L., Spišiak J. & Todt W. 1998: Metamorphic evolution of the Variscan basement in the Western Carpathians; the Tatric Unit. *Acta Univ. Carolinae — Geol.* 42, 2, 272.

Kohút M., Poller U., Todt W. & Janák M. 1998: The crustal growth of the Pre-Mesozoic basement of the Western Carpathians (Slovakia). *XVI Congress CBGA, Book of Abstracts, Vienna, August 30th September 2nd 1998*, 271.

Köster J., Kotarba M., Lafargue E. & Kosakowski P. 1998: Source rock habitat and hydrocarbon potential of Oligocene Menilite Formation (Flysch Carpathians, Southeast Poland): an organic geochemical and isotope approach. In: Horsfield B., Radke M., Schaefer R.G. & Wilkes H. (Eds.): Advances in Organic Geochemistry 1997. *Org. Geochem.* 29, 543–558.

Köster J., Rospondek M., Schouten S., Kotarba M., Zubrzycki A. & Sinninghe Damsté J.S. 1998: Biomarker geochemistry of a foreland basin: Oligocene Menilite Formation in the Flysch Carpathians of Southeast Poland. In: Horsfield B., Radke M., Schaefer R.G. & Wilkes H. (Eds.): Advances in Organic Geochemistry 1997. *Org. Geochem.* 29, 649–669.

Kotarba M.J., Wilczek T., Kosakowski P., Kowalski A. & Więcław D. 1998: A study of organic matter and habitat of gaseous hydrocarbons in the Miocene strata of the Polish part of the Carpathian Foredeep. *Przegl. Geol.* 46, 742–750.

Kozłowski K. & Gawęda A. 1999: Pre-Variscan metamorphic evolution of the crystalline basement of the Polish part of the Western Tatra Mountains. *25 years of Geographical Faculty at the University of Silesia: memorial of professor Jan Trembaczowski. Eart Science series, Sosnowiec 1999*, 91–99 (in Polish, English abstract).

Kruge M.A., Mastalerz M., Solecki A. & Stankiewicz B.A. 1996: Organic geochemistry and petrology of oil source rocks, Carpathian Overthrust region, southeastern Poland — implications for petroleum generation. *Org. Geochem.* 24, 897–912.

Kruge M.A. 2000: Determination of thermal maturity and organic matter type by principal components analysis of the distributions of polycyclic aromatic compounds. *Int. J. Coal Geol.* 43, 27–51.

Lafargue E., Ellouz N. & Roure F. 1994: Thrust-controlled exploration plays in the Outer Carpathians and their foreland (Poland, Ukraine and Romania). *First Break* 12, 69–79.

Lee M.L., Vassilaros D.L., White C.M. & Novotný M. 1979: Retention indices for programmed-temperature capillary-column gas chromatography of polycyclic aromatic hydrocarbons. *Analyt. Chem.* 51, 768–773.

Lefeld J. 1997a: Tectogenesis of the Tatra Mts — Alpine cycle. In: *Polish Geological Association Meeting, Zakopane 1997,* 16–22 (in Polish).

Lefeld J. 1997b: Tatra Mts. sedimentary cover: Wierchy Nappe and Regle Nappe. In: *Polish Geological Association Meeting, Zakopane 1997,* 48–55, 61–64 (in Polish).

Lefeld J. & Jankowski J. 1985: Model of deep structure of the Polish Inner Carpathians. *Publs. Inst. Geophys. Pol. Acad. Sci.* A-16, 175, 71–100.

Marynowski L. & Czechowski F. 1999: Terphenyls — a novel group of biomarkers from Palaeozoic deposits of the Holy Cross Mountains (Central Poland). *Przegl. Geol.* 47, 87–92 (in Polish with English summary).

Marynowski L., Narkiewicz M. & Grelowski C. 2000: Biomarkers as environmental indicators in a carbonate complex, example from the Middle to Upper Devonian, Holy Cross Mts., Poland. *Sed. Geol.* 137, 187–212.

Mössner S.G., Lopez De Alda M.J., Sander L.C., Lee M.L. & Wise S.A. 1999: Gas chromatographic retention behaviour of polycyclic aromatic sulfur heterocyclic compounds, (dibenzothiophene, naphtho[b]thiophene, benzo[b]naphthothiophenes and alkyl-substituted derivatives on stationary phases of different selectivity. *J. Chromatography A* 841, 207–228.

Mössner S.G. & Wise S.A. 1999: Determination of polycyclic aromatic sulfur heterocycles in Fossil Fuel-Related samples. *Analyt. Chem.* 71, 58–69.

Parnell J. 1988: Migration of biogenic hydrocarbons into granites: a review of hydrocarbons in British plutons. *Mar. Petrol. Geol.* 5, 385–396.

Paulo A. 1970: The barite-quartz-sulphide mineralization in the Tatra Mountains in the light of new data. *Prace IG, T.* 59, 255–270 (in Polish, English abstract).

Peters K.E. 1986: Guidelines for evaluating petroleum source rock using programmed pyrolysis. *AAPG Bull.* 70, 318–329.

Peters K.E. & Moldowan J.M. 1993: The Biomarker Guide. *Prentise Hall,* New Jersey, 1–363.

Picha F.J. & Peters K.E. 1998: Biomarker oil-to-source rock correlation in the Western Carpatians and their foreland, Czech Republic. *Petrol. Geosci.* 4, 289–302.

Radke M. & Welte D.H. 1983: The Methylphenanthrene Index (MPI): a Maturity Parameter based on aromatic hydrocarbons. In: Bjøroy M. (Ed.): Advances in Organic Geochemistry 1981. 504–512.

Radke M., Welte D.H. & Willsch H. 1986: Maturity parameters based on aromatic hydrocarbons: influence of the organic matter type. *Org. Geochem.* 10, 51–63.

Radke M. & Willsch H. 1994: Extractable alkyldibenzothiophenes in Posidonia shale (Toarcian) source rocks: Relationship of yields to petroleum formation and expulsion. *Geochim. Cosmochim. Acta* 58, 5223–5244.

Radke M., Vriend S.P. & Ramanampisoa L.R. 2000: Alkyldibenzofurans in terrestrial rocks: Influence of organic facies and maturation. *Geochim. Cosmochim. Acta* 64, 275–286.

Radke M., Willsch H., Leythaeuser D. & Teichmüller M. 1982: Aromatic components in coal: relation of distribution pattern to rank. *Geochim. Cosmochim. Acta* 46, 1831–1848.

Sofer Z. 1984: Stable carbon isotope compositions of crude oils: Application of the source depositional environments and petroleum alteration. *AAPG Bull.* 68, 31–49.

ten Haven H.L., Lafargue E. & Kotarba M. 1993: Oil/oil and oil/

source rock correlations in the Carpatian Foredeep and overthrust, south-east Poland. *Org. Geochem.* 20, 935–959.

Todt W., Poller U., Kohút M. & Janák M. 1998: U-Pb zircon dating of metamorphic rocks from the West Tatra using single zircon grains under catodoluminescence control. Abstracts of ICOG 9, 1998, Beijing, *Chin. Sci. Bull.* 43, 130.

van Aarssen B.G.K., Alexander R. & Kagi R.I. 2000: Higher plant biomarkers reflect palaeovegetation changes during Jurassic times. *Geochim. Cosmochim. Acta* 64, 1417–1424.

van Kaam Peters H.M.N., Köster J., Van Der Gaast S.J., Dekker M., De Leeuw J.W. & Sinninghe Damsté J.S. 1998: The effect of clay minerals on diasterane/sterane ratio. *Geochim. Cosmochim. Acta* 62, 2923–2929.

Wan Hasiah A. 1999: Organic facies variation in the Triassic shallow marine and deep marine shales of central Spitsbergen, Svalbard. *Mar. Petrol. Geol.* 16, 467–481.

Wątocki W. 1950: Mineral veins at Ornak in the Western Tatra Mts. *Rocznik PTG, XX* 1–2, 11–60 (in Polish).

Wieczorek J. 1990: The main stages of geological evolution of the Western Tethys — the outline. *Kwart. Geol.* 33, 401–412.

Yawanarajah S.R. & Kruge M.A. 1994: Lacustrine shales and oil shales from Stellarton Basin, Nova Scotia, Canada: organofacies variations and use of polyaromatic hydrocarbons as maturity indicators. *Org. Geochem.* 21, 153–170.

Appendix

Assignation of compounds in the TIC, m/z 191, m/z 217 mass fragmentograms shown in Fig. 8.

Peak number	**Compound assignation**
TIC	
Pr	Pristane
Ph	Phytane
n-C_{14}	*n*-Tetradecane
n-C_{18}	*n*-Octadecane
n-C_{22}	*n*-Docosane
n-C_{26}	*n*-Hexacosane
n-C_{30}	*n*-Triacontane
m/z 191	
Ts	18α(H)-22,29,30-Trisnorneohopane,
Tm	17α(H)-22,29,30-Trisnorhopane,
29H	C_{29} - 17α,21β(H)-30-norhopane,
29Ts	C_{29}Ts - 18α(H)-30-norneohopane,
C_{30}*	C_{30}* - 17α(H)-diahopane,
30H	C_{30} - 17α,21β(H)-hopane,
29M	C_{30} -17β,21α(H)-hopane (moretane),
31H-S	C_{31} - 17α,21β(H)-29-homohopane 22S,
31H-R	C_{31} - 17α,21β(H)-29-homohopane 22R,
32H-S	C_{32} -17α,21β(H)-29-bishomohopane 22S,
32H-R	C_{32} -17α,21β(H)-29-bishomohopane 22R,
33H-S	C_{33} -17α,21β(H)-29-trishomohopane 22S,
33H-R	C_{33} -17α,21β(H)-29-trishomohopane 22R,
34H-S	C_{34} -17α,21β(H)-29-tetrakishomohopane 22S,
34H-R	C_{34} -17α,21β(H)-29-tetrakishomohopane 22R,
35H-S	C_{35} -17α,21β(H)-29-pentakishomohopane 22S,
35H-R	C_{35} -17α,21β(H)-29-pentakishomohopane 22R,
19T	C_{19} – Tricyclic terpane (Cheilanthane),
20T	C_{20} – Tricyclic terpane (Cheilanthane),
21T	C_{21} – Tricyclic terpane (Cheilanthane),
22T	C_{22} – Tricyclic terpane (Cheilanthane),
23T	C_{23} – Tricyclic terpane (Cheilanthane),
24T	C_{24} – Tricyclic terpane (Cheilanthane),
24Te	C_{24} – Tetracyclic terpane,
25T	C_{25} – Tricyclic terpane (Cheilanthane),
26T	C_{26} – Tricyclic terpane (Cheilanthane),
28T	C_{28} – Tricyclic terpane (Cheilanthane),
29T	C_{29} – Tricyclic terpane (Cheilanthane),
m/z 217	
27Dia-20S	C_{27} - 13β,17α(H)-diacholestane 20S,
27Dia-20R	C_{27} - 13β,17α(H)-diacholestane 20R,
27 Reg	C_{27} - 5α,14α,17α(H)-cholestane 20S,
	C_{27} - 5α,14β,17β(H)-cholestane 20R,
	C_{27} - 5α,14β,17β(H)-cholestane 20S,
	C_{27} - 5α,14α,17α(H)-cholestane 20R,
28 Reg	C_{28} - 5α,14α,17α(H)-ergostane 20S,
	C_{28} - 5α,14β,17β(H)-ergostane 20R,
	C_{28} - 5α,14β,17β(H)-ergostane 20S,
	C_{28} - 5α,14α,17α(H)-ergostane 20R,
29 Reg	C_{29} - 5α,14α,17α(H)-stigmastane 20S,
	C_{29} - 5α,14β,17β(H)-stigmastane 20R,
	C_{29} - 5α,14β,17β(H)-stigmastane 20S,
	C_{29} - 5α,14α,17α(H)-stigmastane 20R,