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Thermal maturity and depositional environments of organic matter in the post-Variscan succession of the Holy Cross Mountains

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The results of GC-MS investigations of biomarkers in organic matter from the epicontinental Permian and Triassic strata of the Holy Cross Mts. indicate generally suboxic (Permian) and oxic (Triassic, except for the Middle Muschelkalk) depositional environments with accompanying intensive bacterial reworking of organic remains. The biomarker spectra found in the Middle Muschelkalk and in the *Entolium discites* Beds (Upper Muschelkalk) show the presence of gammacerane, an increased concentration of C_{34} homohopanes and a Pr/Ph ratio not exceeding 1. All these observations suggest a hypersaline sedimentary environment with water column stratification and poorly oxygenated conditions. Thermal maturity investigations were based on both vitrinite reflectance and biomarker indices. The organic matter in the Triassic succession is slightly more mature along the northern margin of the Holy Cross Mts. than along their southern part, due probably to a regional increase in the maximum burial depth during the Mesozoic. The maturity of the Permian strata at Gałęzice (southern Holy Cross Mts.) is similar to that of the Triassic rocks whereas Kajetanów (in the north) is characterised by values significantly higher and comparable to those found in wells further north. The difference cannot be accounted for solely by differential burial depths, and implies the existence of a positive thermal anomaly active before the Middle Triassic. Our investigations generally confirmed the low thermal maturity of the Triassic. However, contrary to earlier interpretations, we suggest that the maximum burial depths based on a reconstructed thickness of the post-Triassic deposits may account for the observed maturity levels, assuming that geothermal gradients in the Mesozoic were similar to today's.

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Key words: Holy Cross Mountains, Permian, Triassic, biomarkers, depositional environment, thermal maturity.

INTRODUCTION

The thermal maturity of the Cambrian to Carboniferous succession of the Holy Cross Mts. has been recently investigated by Belka (1990), Marynowski (1997, 1999) and Szczepanik (1997), which contributed to better understanding of the thermal history of this area. Nevertheless, a more complete understanding of the maturity of the Palaeozoic rocks and an explanation of factors controlling heat flow require information concerning the maturity of younger strata. To date, CAI measurements of conodonts from nine exposures of the Triassic strata from the margin of the Holy Cross Mts. (including only one locality from the northern part — Belka, 1990), represent the only published data regarding these problems. In this paper, we provide the first organic maturity investigations of the Permian carbonates of this region. These complement the picture of thermal alteration based on measurements of vitrinite reflectance in the Permian of the Polish Lowlands (Grotek, 1998). Moreover, our investigations embraced 14 Triassic localities encompassing deposits from the Röt to the Keuper (Fig. 1). Particular attention was paid to the exposures from the northern margin of the Holy Cross Mts. (6 localities). The investigations were conducted using gas chromatography coupled with mass spectrometry (GC-MS) analysis which enabled analysis of biomarker spectra. These spectra were interpreted in terms of both thermal maturity and environmental importance.

OUTLINE OF STRATIGRAPHY AND FACIES DEVELOPMENT

The Permian and Triassic strata investigated surround outcrops of the pre-Permian rocks of the Holy Cross Mts. from the south-west and north (Fig. 1). They rest with an angular uncon-

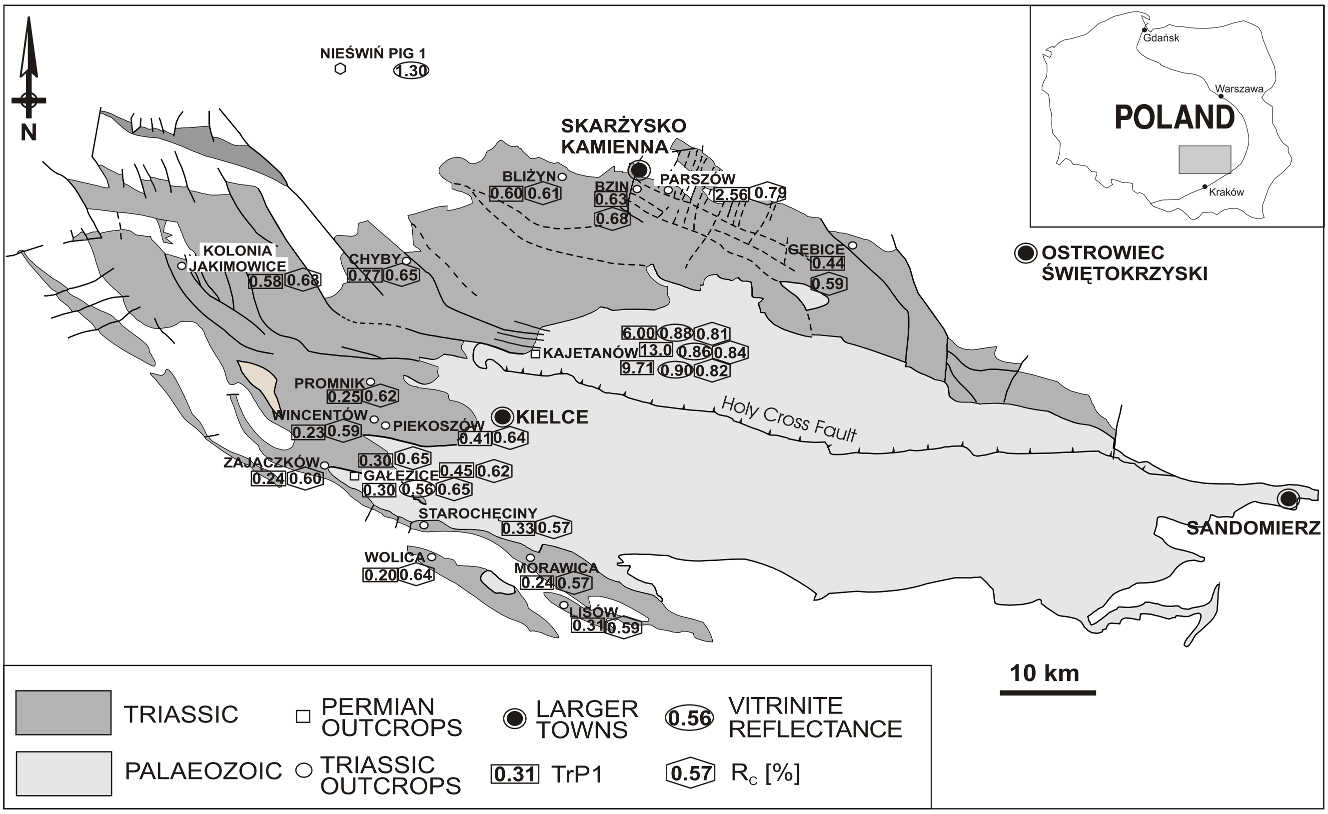

Fig. 1. Location of sampling sites with the measured values of vitrinite reflectance, theoretical values of vitrinite reflectance — R_C[%] after Radke and Welte (1983) and terphenyl parameter — TrP1 after Marynowski *et al*. (2001)

formity on different units of the Cambrian to Carboniferous. Structurally, they belong to the Mid-Polish Swell — a tectonic structure formed in the latest Cretaceous to earliest Tertiary due to inversion of the Mid-Polish Trough. The latter unit formed a depocenter of the polyphase Permian-Mesozoic Polish Basin, and extended along the SE-NW trending Trans-European Suture Zone between the Precambrian East European Craton and the Palaeozoic and Meso-Cenozoic terranes and orogens of Western Europe (e.g. Dadlez *et al*., 1995).

Recently, the Permian of the Holy Cross Mts. has been studied in detail by Bełka (1978, 1991) (see also Skompski, 1995) and Kowalczewski and Rup (1989). The total thickness of these poorly exposed deposits ranges from 0 to 200 metres (Głazek and Kutek, 1976). The basal unit locally comprises irregularly distributed continental clastics questionably attributed to the Rotliegend or Lower Permian (e.g. Kowalczewski and Rup, 1989; Wagner, 1994). The bulk of the Permian succession represents a transgressive marine facies — from conglomerates and peritidal carbonates to marly subtidal deposits. According to Bełka (1991) and Wagner (1994) these deposits correspond mostly to the basal units of the earliest Zechstein cycle, in particular to the Ca1 (Zechstein Limestone) of the Werra Cyclothem.

The Gałęzice locality (Fig. 1) represents nearshore, peritidal and playa facies. The section comprises two conglomeratic horizons separated by relatively thick calcareous and subordinate silty deposits (Bełka, 1978, 1991). On the other hand, the Kajetanów section is composed of dark marly limestones with brachiopods and coalified plant remains, thus clearly representing open marine areas with a considerable terrigeneous clay and organic matter input. The sections are located on opposite flanks of an important structural line — the Holy Cross Fault (HCF — compare Fig. 1) dividing the Holy Cross Mts. into two distinct palaeotectonic-facies regions, a southern and northern one (e.g. Kutek and Głazek, 1972; Głazek and Kutek, 1976).

The Triassic deposits rest upon the Permian either conformably and with a gradual sedimentary transition or, in areas of synsedimentary elevations, with non-depositional and erosional gaps and a slight angular unconformity (Kowalczewski and Rup, 1989). In the Triassic, the present Holy Cross Mts. area formed part of the large epicontinental basin stretching from Poland to Germany and further west. A tripartite general lithostratigraphic division is typical of this basin comprising two terrigeneous units, a lower one — Bunter Sandstone (Buntsandstein), and an upper one — the Keuper and Rhaetian, separated by various carbonates of the Muschelkalk (see e.g.

Table 1

Geochemical characteristics of the Permian and Triassic organic matter from the Holy Cross Mountains

No	LOCALITY	LITHO-STRATIGRAPHY	CAI[a]	R_o [%]	Pr/Ph	Ts/(Ts+Tm)	ββ/(ββ+αα)	20S/(20S+20R)	MDR	MPI1	R_c [%]	TMN	TeMN	TrP1	PhNR	TMN2	TeMN2	PMN
						m/z 191	m/z 217	m/z 217	m/z 198	m/z 178+m/z 192		m/z 170	m/z 184	m/z 230	m/z 204	m/z 170	m/z 184	m/z 198
PERMIAN																		
1	Gałęzice 1	Zechstein-Werra	-	0.56	1.01	0.18	0.39	0.45	2.00	0.42	0.65	0.61	0.26	0.30	0.72	0.22	0.21	0.19
2	Gałęzice 2	Zechstein-Werra	-	-	0.84	0.24	0.44	0.40	2.00	0.27	0.56	0.45	0.15	0.30	0.73	0.17	0.13	0.20
3	Gałęzice 3	Zechstein-Werra	-	-	1.00	0.29	0.46	0.42	2.10	0.37	0.62	0.75	0.64	0.45	0.66	0.54	0.40	0.42
4	Kajetanów 1	Zechstein-Werra	-	0.90	1.64	0.60	0.58	0.54	4.40	0.70	0.82	0.93	5.13	9.71	0.93	0.77	0.84	0.75
5	Kajetanów 2	Zechstein-Werra	-	0.88	1.60	0.75	0.53	0.50	4.00	0.73	0.84	0.88	2.00	6.00	0.94	0.62	0.67	0.65
6	Kajetanów 3	Zechstein-Werra	-	0.86	2.15	0.59	0.55	0.51	5.60	0.68	0.81	0.93	2.00	13.0	0.95	0.79	0.66	0.59
TRIASSIC – southern and western margin																		
7	Starochęciny	Röt	1*	-	1.00	0.16	0.36	0.30	2.26	0.28	0.57	0.62	0.22	0.33	0.70	0.27	0.18	0.30
8	Piekoszów	Röt	-	-	0.86	0.35	0.48	0.36	2.27	0.40	0.64	0.72	0.63	0.25	0.75	0.36	0.39	0.42
9	Strawczynek	Middle Muschelkalk	1*	-	0.66	0.32	0.51	0.42	2.29	0.38	0.62	0.69	0.45	0.25	0.70	0.38	0.31	0.34
10	Lisów	Middle Muschelkalk	-	-	0.64	0.31	-	-	2.30	0.32	0.59	0.73	0.88	0.31	0.65	0.48	0.47	0.41
11	Wincentów	Łukowa Beds	1	-	0.89	0.25	0.49	0.31	2.40	0.32	0.59	0.69	0.56	0.23	0.71	0.34	0.36	0.34
12	Zajączków	*Plagiostoma striatum* Beds	-	-	1.00	0.37	0.55	0.42	3.00	0.33	0.60	0.76	0.91	0.24	0.67	0.46	0.48	0.40
13	Wolica 1	Wellenkalk	1	-	0.92	0.32	0.42	0.28	1.66	0.40	0.64	0.72	0.67	0.20	0.75	0.38	0.41	0.43
14	Morawica	Łukowa Beds	-	-	0.84	0.27	-	-	2.63	0.29	0.57	0.76	1.00	0.24	0.67	0.43	0.50	0.41
TRIASSIC – northern margin																		
15	Bliżyn	Wolica Beds	-	-	0.67	0.30	0.48	0.48	3.44	0.35	0.61	0.90	1.35	0.60	0.72	0.63	0.57	-
16	Kolonia Jakimowice	Middle Muschelkalk	-	-	0.86	0.40	0.47	0.42	2.20	0.46	0.68	0.75	0.77	0.58	0.65	0.39	0.44	0.50
17	Parszów	*Plagiostoma striatum* Beds	-	-	0.64	0.47	0.58	0.52	2.00	0.65	0.79	0.88	1.50	2.56	0.88	0.58	0.60	0.53
18	Bzin	*Entolium discites* Beds	-	-	0.97	0.33	0.40	0.42	2.27	0.46	0.68	-	0.66	0.63	0.80	-	0.40	-
19	Gębice	*Plagiostoma striatum* Beds	-	-	1.05	0.40	-	-	2.04	0.32	0.59	0.74	0.60	0.44	0.70	0.40	0.38	0.38
20	Chyby	Keuper	-	-	1.40	0.46	0.57	0.43	2.29	0.42	0.65	0.77	0.78	0.77	0.79	0.36	0.44	-

[a] Data from Belka (1990); asterisk marks the data from a stratigraphic unit other than sampled in the present study; **CAI** — colour alteration index; **R_o** — vitrinite reflectance [%]; **Pr/Ph** — pristane to phytane ratio; **Ts/(Ts + Tm)** — 18 -22, 29, 30-trisnorneohopane/(18 -22, 29, 30-trisnorneohopane + 17 (H)-22, 29, 30-trisnorhopane) (Seifert and Moldowan, 1978); /(+) — [5 (H), 14 (H), 17 (H) (20R + 20S) C_{29}steranes]/ [5 (H), 14 (H), 17 H) (20R + 20S) C_{29}steranes + 5 (H), 14 (H), 17 (H) (20R + 20S)] C_{29}steranes (Peters and Moldowan, 1993); **20S/(20S + 20R)** — C_{29}5 (H), 14 (H), 17 (H)20S/[C_{29}5 (H), 14 (H), 17 (H) 20(S + R)] (Peters and Moldowan, 1993); **MDR** — methyldibenzothiophene ratio [*4*-MDBT]/[*1*-MDBT] (Radke *et al.,* 1986; Radke and Willsch, 1994)); **MPI1** — methylphenanthrene index 1-MPI1 = 1.5([*2*-MP] + [*3*-MP])/([P] + [*1*-MP] + [*9*-MP]) (Radke and Welte, 1983); **R_c[%]** — calculated vitrinite reflectance: R_c[%] = 0.60 MPI1 + 0.40 (for R_o<1.35%) (Radke and Welte, 1983); **TMN** — trimethylnaphthalene ratio (1, 3, 7– + 1, 3, 6– + 2, 3, 6-TMN)/(1, 3, 7– + 1, 3, 6– + 2, 3, 6– 1, 2, 5-TMN) (Yawanarajah and Kruge, 1994); **TeMN** — tetramethylnaphthalene ratio (1, 3, 6, 7-/(1, 2, 5, 6– + 1, 2, 3, 5-TeMN)(Czechowski, 1995); **TrP1** — terphenyl ratio 1, [p-TrP]/[o-TrP] (Marynowski *et. al*., 2001); **PhNR** — phenylnaphthalene ratio, PhNR = 2-PhN/(1-PhN + 2-PhN) (Marynowski *et. al*., 2001); **TMN2** — trimethylnaphthalene ratio 2 (1, 3, 7-TMN)/(1, 3, 7– + 1, 2, 5-TMN) (van Aarsen *et al*., 1999); **TeMN2** — tetramethylnaphthalene ratio 2 (1, 3, 6, 7-TeMN/(1, 3, 6, 7– + 1, 2, 5, 6– + 1, 2, 3, 5-TeMN) (van Aarsen *et al*., 1999); **PMN** — pentamethylnaphthalene ratio (1, 2, 4, 6, 7-PMN/1, 2, 4, 6, 7– + 1, 2, 3, 5, 6-PMN) (van Aarsen *et al*., 1999)

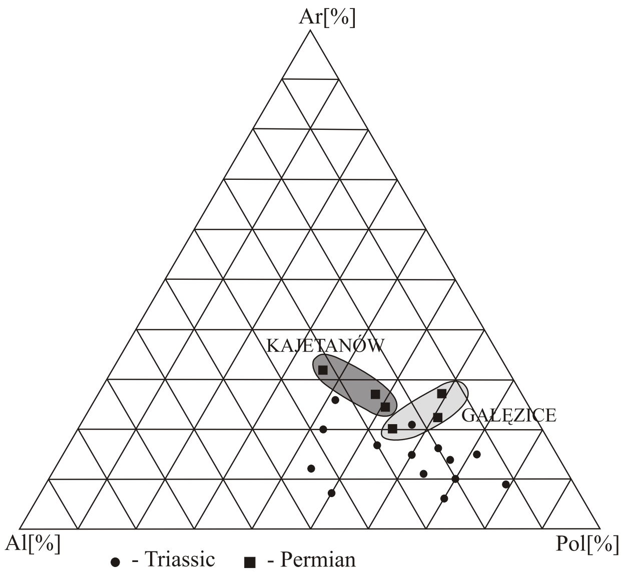

Fig. 2. Fractional composition of the studied samples

Al — aliphatic fraction, Ar — aromatic fraction, Pol — polar fraction

the reviews by Senkowiczowa, 1970, 1973). The Lower Triassic clastics are developed in their lower part as redbeds belonging to alluvial and aeolian depositional systems, with a total thickness from 0 to 400 m SW and 450–900 m N (Senkowiczowa, 1973).

The Upper Bunter Sandstone (Röt), is composed of extremely shallow-water marine carbonates and sulphates with marly and sandy intercalations, and an overall thickness of *ca.* 100 m SW and 80 to 200 m N (Senkowiczowa, 1973). These restricted facies are interpreted as analogues of the recent Persian Gulf shallow-water lagoons and sabkhas (Kostecka, 1978). They mark the onset of the major transgression which culminated in the development of a vast carbonate platform or ramp system in the Middle Triassic. The Muschelkalk sequence in the investigated area is 20 to 150 metres thick (Senkowiczowa, 1973). It has been subdivided into several lithostratigraphic units, in ascending order: Wolica Beds, Wellenkalk, Łukowa Beds, *Plagiostroma striatum* Beds (the four units collectively composing the Lower Muschelkalk), the Middle Muschelkalk, and the Upper Muschelkalk comprising the *Entolium discites* Beds and *Ceratites* Beds (Senkowiczowa, 1970; Trammer, 1975; chapter on the Middle Triassic in: Marek and Pajchlowa, 1997).

According to Kostecka (1978) the Wellenkalk and Lower Łukowa Beds are developed in open marine, subtidal facies, thus recording the maximum palaeo-water depths of the basin. These facies gradually pass upwards into more agitated shallow marine, and even partly restricted carbonate systems of the upper Lower Muschelkalk (Upper Łukowa Beds and *P. striatum* Beds). The overall regressive trend culminated in a development of restricted facies with elevated salinity recorded in partly dolomitic deposits of the Middle Muschelkalk (Trammer, 1975; Kostecka, 1978). The Upper Muschelkalk open marine calcareous sedimentation reflects the onset of the next transgressive cycle. In turn, the lithostratigraphic boundary between the Muschelkalk and Keuper marks a regressive phase and the development of a shallow-water intra-continental basin with mixed deltaic-lagoonal-fluvial sedimentation (Gajewska in: Marek and Pajchlowa, 1997). The Keuper deposits form erosional remnants (pre-Rhaetian erosion) up to 90 m thick (Senkowiczowa, 1973).

The samples investigated by the present authors were taken from the southwestern and northern margins of the Holy Cross Mts. (Fig. 1). The stratigraphic position of the samples as well as the general description of the sampled localities are given in Table 1 and in Appendix 2.

MATERIALS AND METHODS

The deposits investigated were sampled in inactive quarries and natural exposures. Unweathered samples were selected. In the laboratory, all samples were washed with methanol. GC-MS analysis of aliphatic fractions of the investigated samples reveals no effects of biodegradation (e.g. disappearance of low molecular weight *n*-alkanes and the occurrence of unresolved compound mixtures) or water washing (see also van Aarsen diagram below).

Vitrinite was not found in the organic-poor Triassic deposits. The measurements were carried out on vitrinite-rich samples from two Permian localities. In the sample from Kajetanów, 95 vitrinite grains were measured and in the Gałęzice sample, 62 measurements were taken. The vitrinite reflectance was measured using a *ZEISS* photomicroscope III, using reflected light, oil immersion and a magnification of about x 400. The value of vitrinite reflectance was estimated based on the prepared diagrams.

The total organic carbon (TOC) content was determined using an automated *LECO CR-12* analyser. After disintegration and grinding in a ball mill to a fraction below 0.2 millimetres, all investigated samples were extracted with dichloromethane in a *Soxhlet* apparatus. The extractable organic matter (EOM) was separated into aliphatic, aromatic and polar + asphaltenes fractions using thin-layer chromatography (TLC Merck plates 20 x 20 cm covered by silicagel 60 H 0.25 mm thick) and developed in *n*-hexane.

GC-MS analysis was conducted on aliphatic and aromatic hydrocarbon fractions. Analyses of the hydrocarbons were performed on a *Hewlett Packard 5890* chromatograph with a *DP-5* capillary column (internal diameter 0.32 mm, thickness of an active-phase film 0.25 mm) 60 metres long. The GC oven was programmed from 35 to 300°C at a rate of 3°C min^{-1}. Helium was used as a carrier gas. Detection of separated constituents was conducted using a mass quadrupole 5971A operating with an electron energy of 70 eV. Scanning was done within a mass interval from 45 to 550 with a cycle time of 1 s.

Biomarker parameters are commonly used to assess a maturity of crude oil, coal and dispersed organic matter (Alexander *et al.*, 1985; Lu and Kaplan, 1992; Peters and Moldowan, 1993; Yawanarajah and Kruge, 1994; Li *et al.*, 1998; van Aarsen *et al.*, 1999), especially when simpler pyrolitic (RockEval), petrographic (vitrinite reflectance), and other (CAI, TAI, *etc.*) methods cannot be used. Some of the parameters have been empirically compared with the values of the vitrinite reflectance (R_o). In this work, the MPI1 parameter (methylphenanthrene index 1) (Radke and Welte, 1983; Radke *et al.*, 1986) was widely used. It was recalculated to a theoretical value of vitrinite according to the formula given by Radke and Willsch (1994) (Table 1).

PREVIOUS STUDIES

As regards the thermal maturity of the Holy Cross Mts. area, the Devonian deposits have been studied most. These studies showed that vitrinite reflectance varies considerably from 0.52 to 1.22%R_o across a distance of about 30 km. Generally, it increases towards the north-west and, at the same time, towards the HCF (Marynowski, 1999). Carboniferous deposits have a limited distribution in the Holy Cross Mts. and their maturity is similar to that of the neighbouring Devonian strata (Belka, 1990; Marynowski — unpub. materials).

Investigations of the conodont CAI in the Ordovician to Triassic (Belka, 1990) and data on changes of thermal maturity with depth (Janczyce I and Kowala 1 boreholes — Marynowski, 1999) show that the present organic maturity in the Devonian and Carboniferous developed mostly before the Late Carboniferous uplift (Belka, 1990). Maximum maturity levels are due to increased heat flow during Variscan tectonic activity (Belka, *op. cit.*) associated probably with a deep crustal fracture whose surface expression is the HCF (Marynowski, 1999).

Grotek (1998) investigated the %R_o distribution in Polish Zechstein rocks including data from the Nieświń PIG 1 borehole located close to the northern margin of the Holy Cross Mts. (Fig. 1). She explained the distributional pattern as generally reflecting maximum burial depths during the Mesozoic. However, in the case of i.a. the Nieświń PIG 1 borehole she was able to detect an additional thermal component attributed to extra heat flow due to tectonic activity in the basin.

Belka (1990) reported uniform CAI 1 values for the Muschelkalk carbonates in the Holy Cross Mts. area for both southwestern (8 locations) and northern margins (a single location). He concluded that the reconstructed thickness of the overlying Mesozoic deposits cannot account for the reported CAI values assuming a present-day geothermal gradient. Therefore he proposed that "...a very low heat flow is suggested for the Late Cretaceous...".

RESULTS

Values of total organic carbon (TOC) in the samples studied are small, in the range of 0.11–0.14% for the Zechstein deposits and less than 0.1% for the Triassic rocks. The content of extractable organic matter in the samples studied is also small, in the range of 0.02–0.05 % for the Permian and 0.002–0.004% for the Triassic sediments.

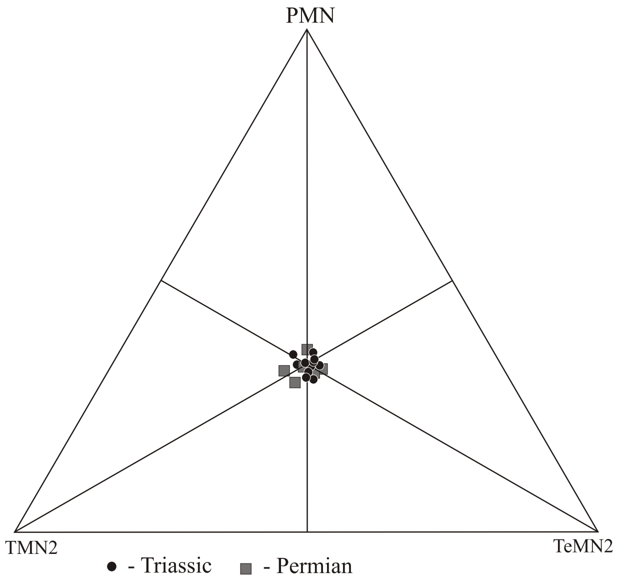

Fig. 3. Ternary plot of the extracts of Permian and Triassic samples, according to van Aarsen *et al.* (1999)

TMN2 — trimethylnaphthalene ratio 2, TeMN2 — tetramethylnaphthalene ratio 2, PMN — penthamethylnaphthalene ratio, for explanation of parameters see Table 1

The fractional composition of the extractable organic matter is a general and simplified measure of thermal maturity. A large proportion of polar compounds is usually typical of thermally immature samples (Tissot and Welte, 1984). There are, however, many exceptions related for example to processes of secondary biodegradation (Connan, 1984), water washing (Palmer, 1984) or resulting from the particular genetic character of the initial organic matter (Hunt, 1996). On the other hand, increased concentration of aliphatic and aromatic fractions is often associated with increased maturity of the non-biodegraded sedimentary organic matter (Tissot and Welte, 1984). On this basis, a low maturity for the Triassic deposits (large participation of polar fraction — Fig. 2) and a slightly higher maturity for the Permian deposits from Kajetanów (25 to 33% of the aliphatic fraction) can be suggested. The fractional distribution of Gałęzice (Permian) organic matter is similar to that found in the Triassic rocks. Moreover, in the four Triassic samples, an increased (30–45%) percentage of the aliphatic fraction was observed (Fig. 2) which may reflect the specific character of the original organic input.

The possibility that the extractable organic matter investigated is allochthonous (has migrated) was tested using the distribution of methylnaphthalenes (van Aarsen *et al.*, 1999). Three methylnaphthalene parameters: TMN2, TeMN2 and PMN (for explanation see Table 1) were compared with each other using a ternary diagram (Fig. 3). When a crude oil or

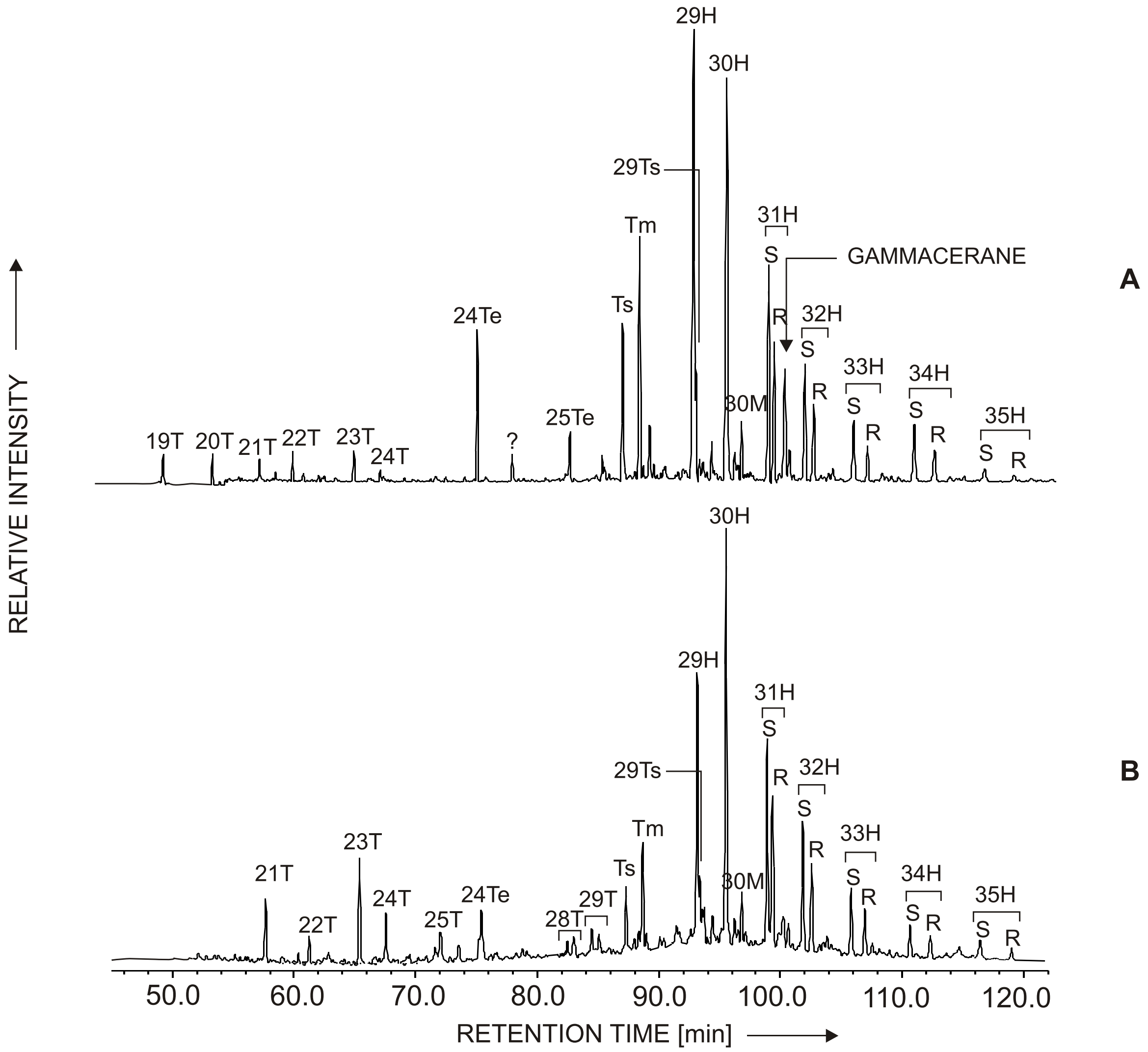

Fig. 4. Distribution of hopanes (m/z 191) derived from the aliphatic fraction of a typical sample of the Middle Muschelkalk from Kolonia Jakimowice (A) compared with the distribution in other Triassic carbonates examplified by the *Plagiostoma striatum* Beds at Zajączków (B)

For explanation of abbreviations see the Appendix 1

source rock extract plots in the centre of the diagram (the maturity centre) the value of any of the three parameters is an accurate indication of its thermal maturity. When an oil or bitumen plots outside the maturity centre, factors like mixing or biodegradation may be responsible for the distribution of methylated naphthalenes. Points representing all the analysed samples are located in the centre of the ternary diagram (Fig. 3), which clearly indicates (according to van Aarsen *et al.*, 1999, *op. cit.*) an autochtonous, non-biodegraded character of the extracted hydrocarbons.

BIOMARKERS AND DEPOSITIONAL ENVIRONMENTS OF THE ORGANIC MATTER

Based on previous interpretations, most of the samples studied represent marine facies — from restricted/marginal marine to open marine conditions. Only the Keuper fine-grained sandstone (Chyby locality) developed in lagoon-deltaic-fluvial environments (Senkowiczowa and Szyperko-Śliwczyńska, 1961). The organic matter present in all the deposits studied displays mixed terrestrial/marine characteristics, except for the purely terrestrial attributes of the Chyby sample. These mixed characteristics are shown by a bimodal distribution of *n*-alkanes with a maximum at *n*-C_{18} and *n*-C_{27} (Bzin, Promnik, Piekoszów, Gębice, Parszów, Kolonia Jakimowice, Gałęzice, Kajetanów) and the presence of typical organic compounds genetically associated with higher plants, such as cadelene, retene, or tricyclic and tetraciclic diterpanes (Noble *et al.*, 1985, 1986; van Aarssen *et al.*, 1996, 2000). The mixed character of kerogene considerably enhances the diagnostic value of the MPI1 index (Table 1), which precisely describes a level of thermal maturity for a III type kerogene, i.e. a kerogene with a considerable content of terrestrial organic matter (Radke *et al.*, 1986).

The organic matter was deposited in suboxic (Permian) and oxic conditions (Triassic, except for the Middle Muschelkalk, see below). This is shown by a relatively small content of TOC in the Permian sedimentary rocks studied and very small content in the Triassic, as well as the pattern of hopane distribution, typical of the above-mentioned sedimentary environments

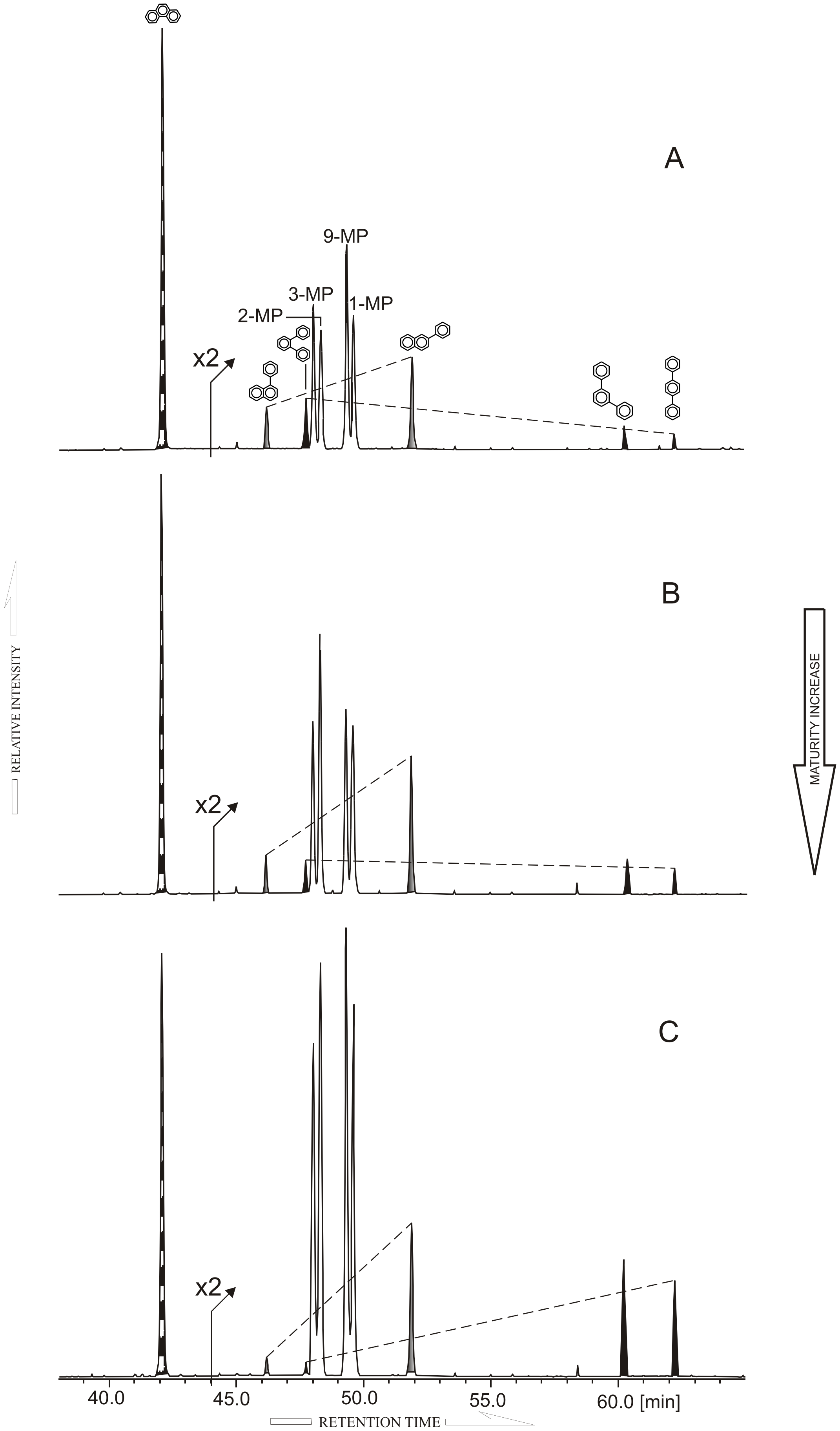

Fig. 5. Change in distribution of phenanthrene, methylphenanthrene, (1–, 2–, 3–, 9-MP), phenylnaphthalenes and terphenyls (m/z 178 + m/z 192 + m/z 204 + m/z 230) with the increasing thermal maturity; A — Lisów, B — Chyby, C — Kajetanów; note clearly different distribution for the Kajetanów locality reflecting its significantly higher maturity level

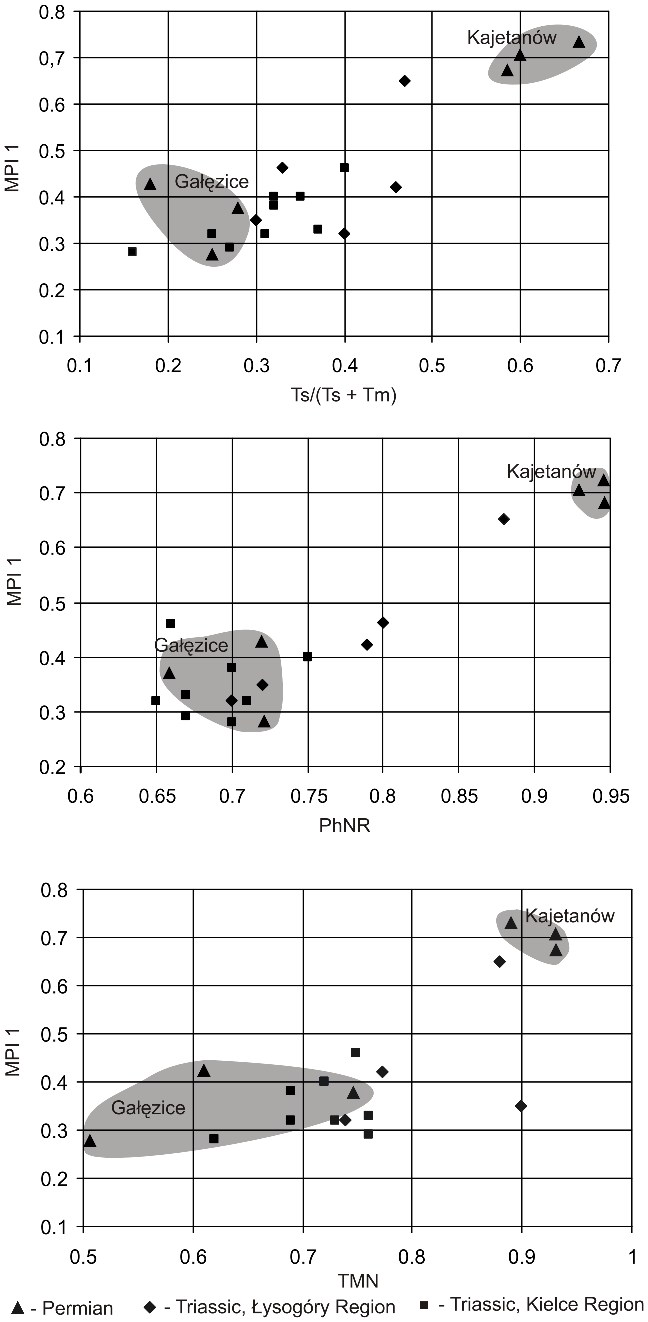

Fig. 6. Correlation of the values of more important maturity parameters for the samples of the Triassic and Permian sediments of the Holy Cross Mts.

For explanation of abbreviations see Table 1

(Fig. 4; compare Peters and Moldowan, 1993, figs. 3 and 11). In our samples, a clear predominance of relative concentrations of hopanes over steranes (about 20 times) was observed as well as the presence of tetracyclic triterpanes — Fig. 4, 24Te, 25Te), which indicate intensive bacterial decay of the deposited organic matter. Bacterial reworking is a typical process during carbonate deposition (relevant examples of biomarker interpretation in e.g. Wan Hasiah, 1999; Marynowski *et al*., 2000).

In the samples of the Middle Muschelkalk deposits (Strawczynek, Lisów and Kolonia Jakimowice), gammacerane was determined. For many years this compound has been regarded as an indicator of hypersaline conditions (ten Haven *et al*., 1985, 1988; Brassell *et al*., 1988; Peters and Moldowan, 1993). Recently, however, it has been considered as an indicator of water column stratification (Sinninghe Damsté *et al*., 1995) which, of course, is not always caused by increased salinity in a sedimentary basin. However, the presence of gammacerane in the samples studied together with the increased concentration of C_{34} homohopanes (Fig. 4) and a pristane to phytane ratio of less than one (ten Haven *et al*., 1987, 1988) may indeed indicate hypersaline conditions which occurred in a suboxic to anoxic stratified basin during Middle Muschelkalk sedimentation. A similar biomarker composition was determined in the sample from Bzin, which was initially ascribed to the Middle Muschelkalk (Senkowiczowa, 1956) and later to the lowermost Upper Muschelkalk (*E. discites* Beds — Senkowiczowa, 1957*a*). Our results suggest that either increased salinity persisted until the earliest Upper Muschelkalk times or the sampled interval belongs to the Middle Muschelkalk. On the other hand, a lack of gammacerane in the samples from the Röt and *P. striatum* Beds may suggest that the interpreted peritidal and/or restricted environment of their deposition (Kostecka, 1978; see above) did not involve water-column stratification.

VITRINITE REFLECTANCE

The results obtained (Table 1) indicate a large variability of $\%R_o$ values for the Permian samples. In the case of Kajetanów (Fig. 1) located in the northern region of the Holy Cross Mts., the value of R_o was 0.86–0.90%. This is compatible with the vitrinite reflectance (1.30%) measured by Grotek (1998) in the Zechstein from the Nieświń PIG 1 borehole situated about 30 km north of Kajetanów (Fig. 1). In view of the $\%R_o$ distribution shown by Grotek (1998) the $\%R_o$ increases towards the depocenter of the Zechstein basin, i.e. towards the north-west. The maturity at Kajetanów is only slightly lower than the maturity of the adjacent Devonian deposits (Zachełmie — R_{CS} = 1.12%, Bukowa Góra — R_{CS} = 1.15%) (Marynowski, 1999).

At Gałęzice in the southern Holy Cross Mts. the vitrinite reflectance is much lower (0.56%), similar to the $\%R_o$ of the Devonian deposits measured for the southwestern part of the study area (*op. cit.*) and also to the R_C values (Table 1) recalculated from the MP1 index (Radke and Welte, 1983) for the Triassic of this area.

MOLECULAR MATURITY PARAMETERS

The more important maturity parameters calculated from the results of the GC-MS analysis are shown in Table 1. Gas chromatography coupled with mass spectrometry appear to be a precise analytic method in the case of organic-poor Triassic carbonate rocks of the Holy Cross Mts. The results obtained, apart from some deviations discussed below, are considered to be reliable.

Triassic. Our investigations showed a slight variability in the organic matter maturity of the Triassic deposits. Table 1 shows the values of the more important biomarker indices which are based on ratios of relative concentrations of thermally more stable to less stable compounds. On average, most of the parameters show higher values for the Triassic samples from the northern margin of the Holy Cross Mts. than for those from the south-west (Table 1, Figs. 5 and 6). Figure 6 presents a graphical correlation of the selected indices showing that the array of points denoting samples from the northern area is shifted towards higher values relative to the respective points characterising the southwestern area.

It is interesting to note that a MDR index (Table 1) which proved correct as a maturity parameter of the Devonian deposits (Marynowski, 1999) does not seem adequate in the case of the Triassic rocks and does not correlate well with other parameters. Only for Kajetanów, the MDR value is much higher and thus in agreement with other indices. Recently Huang and Pearson (1999) showed that the values of MDR index in certain situations may be influenced by sedimentary conditions and the character of the primary organic matter.

Permian. The two Permian localities investigated display contrasting values of all the measured maturity indices (Table 1, Fig. 6). Extractable organic matter from Kajetanów showed the highest values of all the maturity parameters calculated in this study (Table 1, Figs. 5 and 6). High values of the parameters based on the distribution of the organic compounds closely correspond to the values of vitrinite reflectance measured at that locality (discussed above). The maturity indices for the Gałęzice locality are considerably smaller than the comparable values measured at Kajetanów and they correspond approximately to the values representative of the Triassic deposits (Table 1, Fig. 6).

THERMAL MATURITY — A DISCUSSION

The thermal maturity results allow us to refine the thermal history of the study area presented by Belka (1990). That study did not include the Permian deposits. Our results obtained for the Kajetanów locality and the data presented by Grotek (1998) indicate a relatively high degree of thermal alteration of the Permian rocks in the northern and northwestern margin of the Holy Cross Mts. Moreover, there is a significant difference in the level of maturity of the Permian rocks on either side of the HCF.

The distribution of thermal maturity in the Triassic rocks seems more uniform than in the Permian (Fig. 1), as already observed by Belka (1990). Our results, however, show that the northern area displays slightly increased maturity as reflected in values of respective indices (Table 1). This small difference can be easily explained by increased maximum burial depths in the northern area related to overall higher Mesozoic subsidence north of the HCF (Głazek and Kutek, 1976; Dadlez *et al.*, 1998). For example, the thickness of the Lower Triassic in the southern area is on average 200 to 300 m whereas in the north it can exceed 1000 m. Also the Lower and Middle Jurassic deposits, which are weakly developed in the south, can attain a thickness of more than 1000 m in the northern part of the Holy Cross Mts. (Głazek and Kutek, 1976). It seems significant that increased values of the maturity parameters (MP1, TrP1, TMN — Table 1) are observed at Kolonia Jakimowice, which occupies a westernmost location in the study area (Fig. 1). This is in agreement with the increased thickness of the post-Triassic sediments towards the west (Głazek and Kutek, 1976).

On the other hand, however, in view of the uniformly low maturity of the Triassic rocks, and also taking into account the possible variability in the thickness of the Lower Triassic, it would be difficult to explain the considerable difference in maturity observed in the Permian solely or even predominantly by differential burial by the end of the Early Triassic. It seems probable that, as in the Nieświń PIG 1 borehole (Grotek, 1998), the Permian in Kajetanów (and probably also in the entire northern Holy Cross Mts. area) has been affected by an increased heat flow which presumably ceased before the Middle Triassic. This could have been associated with a prolonged "syn-Variscan" thermal anomaly interpreted already by Belka (1990). Alternatively, it could represent a later thermal event, e.g. the one which started in the Early Permian as revealed by palaeomagnetic studies of the Devonian carbonates (Grabowski *et al.*, 2002).

According to Belka (1990) the low maturity of the Muschelkalk deposits is not compatible with the reconstructed thickness of the overlying Mesozoic sediments, assuming a geothermal gradient similar to the present. However, the reconstruction by Kutek and Głazek (1972; see also Głazek and Kutek, 1976) illustrated by Belka (1990, fig. 4) apparently shows thicknesses of post-Muschelkalk deposits considerably less than the 3 000 to 5 000 metres quoted by Belka. The respective thicknesses range from 2 000 to 3 500 metres which implies that it is not necessary to invoke a considerably lower thermal regime during Mesozoic to explain the maturity observed in the Triassic deposits. In fact, a geothermal gradient similar to today's (17.2–29.6°C Km^{-1} according to Belka, *op. cit.*) can account for these observations, particularly if values closer to the lower limit are assumed.

CONCLUSIONS

1. The results of our geochemical investigations of organic matter from the epicontinental Permian and Triassic deposits in the Holy Cross Mts. suggest suboxic (in the case of the investigated Permian units) and oxic depositional environments (most of the Triassic units, except for lower-oxygen conditions during Middle Muschelkalk deposition). Moreover, relative concentrations of hopanes as well as the presence of tetracyclic triterpanes indicate intensive bacterial reworking of the deposited organic matter.

2. The biomarker analysis of the aliphatic fraction of the Middle Muschelkalk and the *Entolium discites* Beds revealed

the presence of gammacerane, an increased concentration of C_{34} homohopanes and a Pr/Ph ratio not exceeding 1. All these observations suggest a hypersaline sedimentary environment with water column stratification and generally low oxygen conditions.

3. The thermal maturity of organic matter in the Triassic rocks is slightly higher in the northern margin of the Holy Cross Mts. than in their southern part. This small difference is probably associated with the regional variability of the maximum burial depth during the Mesozoic.

4. Considerable differences in maturity level were found between two investigated Permian localities. The maturity at Gałęzice (southern Holy Cross Mts.) is similar to that of the Triassic rocks whereas Kajetanów (north) is characterised by values significantly higher and comparable to those found further north, in the Nieświń PIG 1 borehole (Grotek, 1998). The difference cannot be accounted for solely by differential burial depths, instead it implies the existence of a positive thermal anomaly extending north of the Holy Cross Fault before the Middle Triassic.

5. The present investigations generally confirmed low thermal maturity in the Triassic as reported by Belka (1990). However, contrary to the interpretation by the latter author it is here suggested that the maximum burial depths based on the reconstructed thickness of the post-Triassic deposits can account for the observed maturity levels assuming that geothermal gradients in the Mesozoic were comparable to presently measured values.

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REFERENCES

ALEXANDER R., KAGI R. I., ROWLAND S. J., SHEPPERD P. N. and CHIRILA T. V. (1985) — The effect of thermal maturity on distribution of dimethylnaphthalenes and trimethylnaphthalenes in some ancient sediments and petroleums. Geochim. Cosmochim. Acta, **49**: 385–395.

BELKA Z. (1990) — Thermal maturation and burial history from conodont colour alteration data, Holy Cross Mountains, Poland. Cour. Forsch. Inst. Senckenberg, **118**: 241–251.

BEŁKA Z. (1978) — Stop Gałęzice. In: Symposium on Central European Permian (eds. T. Piątkowski and R. Wagner). Excursion Guide, **2**: 49–55.

BEŁKA Z. (1991) — Permian. In: Field-guide of the Geological Excursion to Poland (eds. Z. Bełka, A. Matyja and A. Radwański): 54–61. Univ. Warsaw.

BRASSELL S. C., SHENG GUOYING, FU JIAMO and EGLINTON G. (1988) — Biological markers in lacustrine Chinese oil shale. In: Lacustrine Petroleum Source Rocks Geological Society Special Publication (eds. A. J. Fleet *et al.*). Geol. Soc. Spec. Publ., **40**: 299–308. Blackwell Sc. Publ., Oxford.

CONNAN J. (1984) — Biodegradation of crude oils in reservoirs. In: Advances in Petroleum Geochemistry (eds. J. Brooks and D. Welte). Academic Press, London, **1**: 299–335.

CZECHOWSKI F. (1995) — Biomarkers assemblage in relation to coal rank (eds. J. A Pajares and J. M. D Tascon). Coal Sc. Technol., **24**: 291–294.

DADLEZ R., MAREK S. and POKORSKI J. (eds) (1998) — Atlas paleogeograficzny epikontynentalnego permu i mezozoiku w Polsce 1:2 500 000. Państw. Inst. Geol., Warszawa.

DADLEZ R., NARKIEWICZ M., STEPHENSON R. A., VISSER M. T. M. and VAN WEES J.-D. (1995) — Tectonic evolution of the Mid-Polish Trough: modelling implications and significance for central European geology. Tectonophysics, **252** (1–4): 179–195.

GŁAZEK J. and KUTEK J. (1976) — Powaryscyjski rozwój geotektoniczny obszaru świętokrzyskiego. Przew. 48 Zjazdu PTG: 14–51, Wyd. Geol. Warszawa.

GRABOWSKI J., NARKIEWICZ M., NAWROCKI J., WAKSMUNDZKA M. I. (2002) — Permian diagenetic event in the Devonian carbonates in southern Poland — palaeomagnetic evidence (in Polish with English summary). Prz. Geol., **50** (1): 78–86.

GROTEK I. (1998) — Thermal maturity of organic matter in the Zechstein deposits of the Polish Lowlands area (in Polish with English summary). Pr. Państw. Inst. Geol., **165**: 255–259.

HUANG H. and PEARSON M. J. (1999) — Source rock palaeoenvironments and controls on the distribution of dibenzothiophenes in lacustrine crude oils, Bohai Bay Basin, eastern China. Org. Geochem., **30**: 1455–1470.

HUNT J. M. (1996) — Petroleum geochemistry and geology. W. H. Freeman and Company, New York.

KLECZKOWSKI A. (1959) — The Muschelkalk on the northern border of the Holy Cross Mts. west of Skarżysko-Kamienna (in Polish with English summary). Rocz. Pol. Tow. Geol., **29** (1): 3–59.

KOSTECKA A. (1978) — The Lower Muschelkalk carbonate rocks of the south-western margin of the Holy Cross Mountains (central Poland). Rocz. Pol. Tow. Geol., **48** (2): 211–243.

KOWALCZEWSKI Z. and RUP M. (1989) — Zechstein rocks of the Góry Świętokrzyskie. Biul. Inst. Geol., **362**: 5–39.

KUTEK J. and GŁAZEK J. (1972) — The Holy Cross Area, Central Poland, in the Alpine cycle. Acta Geol. Pol., **22** (4): 603–653.

LI M., OSADETZ K. G., HUANXIN Y., OBERMAJER M., FOWLER M. G., SNOWDON L. R. and CHRISTENSEN R. (1998) — Unusual crude oils in the Canadian Williston Basin, southeastern Saskatchewan. Org. Geochem., **28** (7–8): 477–488.

LU S. T. and KAPLAN I. R. (1992) — Diterpanes, triterpanes, steranes, and aromatic hydrocarbons in natural bitumens and pyrolysates from different humic coals. Geochim. Cosmochim. Acta, **56**: 2761–2788.

MAREK S. and PAJCHLOWA M. (eds.) (1997) — The epicontinental Permian and Mesozoic in Poland. Prace Państw. Inst. Geol., **153**.

MARYNOWSKI L. (1997) — Maturity level of the organic matter from the carbonate Devonian rocks in the Holy Cross Mountains (in Polish). Prz. Geol., **45** (9): 899–904.

MARYNOWSKI L. (1999) — Thermal maturity of organic matter in Devonian rocks of the Holy Cross Mountains (in Polish with English summary). Prz. Geol., **47** (12): 1125–1129.

MARYNOWSKI L., NARKIEWICZ M. and GRELOWSKI C. (2000) — Biomarkers as environmental indicators in a carbonate complex, example from the Middle to Upper Devonian, Holy Cross Mts., Poland. Sediment. Geol., **137** (3–4): 187–212.

MARYNOWSKI L., CZECHOWSKI F. and SIMONEIT B. R. T. (2001) — Phenylnaphthalenes and polyphenyls in Palaeozoic source rocks of the Holy Cross Mountains, Poland. Organic Geochem., **32** (1): 69–85.

NOBLE R. A., ALEXANDER R., KAGI R. I. and KNOX J. (1985) — Tetracyclic diterpenoid hydrocarbons in some Australian coals, sediments and crude oils. Geochim. Cosmochim. Acta, **49**: 2141–2147.

NOBLE R. A., ALEXANDER R. and KAGI R. I. (1986) — Identification of some diterpenoid hydrocarbons in petroleum. Org. Geochem., **10**: 825–829.

PALMER S. E. (1984) — Effect of water washing on C_{15+} hydrocarbon fraction of crude oils from northwest Palawan, Philippines. AAPG Bull., **68**: 137–149.

PETERS K. E. and MOLDOWAN J. M. (1993) — The biomarker guide. Prentice Hall, New Jersey.

RADKE M. and WELTE D. H. (1983) — The Methylphenanthrene Index (MPI): a maturity parameter based on aromatic hydrocarbons. Advances in Organic Geochemistry 1981 (ed. M. Bjrroy): 504–512.

RADKE M. and WILLSCH H. (1994) — Extractable alkyldibenzothiophenes in Posidonia shale (Toarcian) source rocks: relationship of yields to petroleum formation and expulsion. Geochim. Cosmochim. Acta, **58** (23): 5223–5244.

RADKE M., WELTE D. H. and WILLSCH H. (1986) — Maturity parameters based on aromatic hydrocarbons: influence of the organic matter type. Org. Geochem., **10**: 51–63.

SEIFERT W. K., and MOLDOWAN J. M. (1978) — Applications of steranes, terpanes, and monoaromatics to the maturation, migration, and source of crude oils. Geochim. Cosmochim. Acta, **42**: 77–95.

SENKOWICZOWA H. (1956) — Muschelkalk on the northern periphery of the Święty Krzyż Mountains (in Polish with English summary). Biul. Inst. Geol., **113**: 65–137.

SENKOWICZOWA H. (1957*a*) — Contribution to the cognizance of the Muschelkalk in the Święty Krzyż Mountains (in Polish with English summary). Kwart. Geol., **1** (3–4): 482–497.

SENKOWICZOWA H. (1957*b*) — The Muschelkalk on the southern slope of the Święty Krzyż Mts. between Czarna Nida and Chmielnik. Biul. Inst. Geol., **122**: 5–81.

SENKOWICZOWA H. (1958) — Notes on the Middle Triassic in the region of Radoszyce (in Polish with English summary). Kwart. Geol., **2** (2): 347–361.

SENKOWICZOWA H. (1959) — Röth and Muschelkalk in the vicinity of Chęciny (Święty Krzyż Mountains) (in Polish with English summary). Biul. Inst. Geol., **159**: 53–97.

SENKOWICZOWA H. (1961) — The Röth and Muschelkalk in the western marginal area of the Święty Krzyż Mountains (in Polish with English summary). Biul. Inst. Geol., **167**: 41–90.

SENKOWICZOWA H. (1970) — Triassic (without Rhaetian deposits). In: The Stratigraphy of the Mesosoic in the Margin of the Góry Świętokrzyskie (in Polish with English summary). Prace Inst. Geol., **56**: 7–44.

SENKOWICZOWA H. (1973) — Trias. Góry Świętokrzyskie. In: Budowa Geologiczna Polski. Stratygrafia. **2**, Mezozoik (ed. S. Sokołowski): 56–71. Wyd. Geol.

SENKOWICZOWA H. and SZYPERKO-ŚLIWCZYŃSKA A. (1961) — Geological atlas of Poland. Stratigraphic and facial problems. Trias, **8** (in Polish with English summary). Inst. Geol., Warszawa.

SINNINGHE DAMSTÉ J. S., KENIG F., KOOPMANS M. P., KÖSTER J., SCHOUTEN S., HAYES J. M. and DE LEEUW J. W. (1995) — Evidence for gammacerane as an indicator of water column stratification. Geochim. Cosmochim. Acta, **59**: 1895–1900.

SKOMPSKI S. (1995) — The Holy Cross Mountains — post-Variscan cover. Stop 7. Gałęzice. In: M. Lipiec *et al.* Development of the Variscan Basin and Epi-Variscan Cover at the Margin of the East European Platform (Pomerania, Holy Cross Mts., Kraków Upland). XIII Int. Congr. Carbonif.-Permian, August 28–September 2, 1995, Kraków, Guide to Excursion, **A2**: 29–31.

SZCZEPANIK Z. (1997) — Preliminary results in thermal alteration investigations of the Cambrian acritarchs in the Holy Cross Mts. Geol. Quart., **41** (3): 257–264.

SZULC J. (2000) — Middle Triassic evolution of the northern Peri–Tethys area as influenced by early opening of the Tethys Ocean. Ann. Soc. Geol. Polon., **70** (1): 1–48

ten HAVEN H. L., DE LEEUW J. W., RULLKÖTTER J. and SINNINGHE DAMSTÉ J. S. (1987) — Restricted utility of the pristane/phytane ratio as a palaeoenvironmental indicator. Nature, **330**: 641–643.

ten HAVEN H. L., DE LEEUW J. W. and SCHENCK P. A. (1985) — Organic geochemical studies of a Messinian evaporitic basin, northern Apennines (Italy). In: Hydrocarbon Biological Markers for a Hypersaline Environment. Geochim. Cosmochim. Acta, **49**: 2181–2191.

ten HAVEN H. L., DE LEEUW J. W., SINNINGHE DAMSTÉ J. S., SCHENCK P. A., PALMER S. E. and ZUMBERGE J. E. (1988) — Application of biological markers in the recognition of palaeohypersaline environments. Lacustrine Petroleum Source Rocks, (eds. A. J. Fleet *et al*.). Geol. Soc. Spec. Publ. **40**: 123–130. Blackwell Sc. Publ., Oxford.

TISSOT B. and WELTE D. H. (1984) — Petroleum formation and occurence. Springer-Verlag, New York.

TRAMMER J. (1975) — Stratigraphy and facies development of the Muschelkalk in south western Holy Cross Mts. Acta Geol. Polon., **25** (2): 179–216.

van AARSSEN B. G. K., ALEXANDER R. and KAGI R. I. (1996) — The origin of Barrow sub-basin crude oils: a geochemical correlation using land-plant biomarkers. APEA J., **36**: 465–476.

van AARSSEN B. G. K., BASTOW T. P., ALEXANDER R. and KAGI R. I. (1999) — Distributions of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. Org. Geochem., **30**: 1213–1227.

van AARSSEN B. G. K., ALEXANDER R. and KAGI R. I. (2000) — Higher plant biomarkers reflect palaeovegetation changes during Jurassic times. Geochim. Cosmochim. Acta, **64**: 1417–1424

WAGNER R. (1994) — Stratigraphy and evolution of the Zechstein Basin in the Polish Lowlands. Prace Państw. Inst. Geol., **146**: 1–71.

WAN HASIAH A. (1999) — Organic facies variation in the Triassic shallow marine and deep marine shales of central Spitsbergen, Svalbard. Marine Petrol. Geol., **16**: 467–481.

YAWANARAJAH S. R. and 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.

ZACHARSKI J. (1995) — Stratygrafia i sedymentologia utworów wapienia muszlowego NE obrzeżenia Gór Świętokrzyskich. MSc. Thesis, Cracow University.

APPENDIX 1

LIST OF TRICYCLIC AND PENTACYCLIC TRITERPANES AND EXPLANATION OF ABBREVIATIONS IN FIG. 4

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)
28T-C_{28} — Tricyclic terpane (Cheilanthane)
29T-C_{29} — Tricyclic terpane (Cheilanthane)
24Te-C_{24} — Tetracyclic terpane
25Te-C_{25} — Tetracyclic terpane
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
30H-C_{30} — 17α, 21β (H)-hopane
30M-C_{30} — 17β, 21α (H)-hopane (moretane)
31H-C_{31} — 17α, 21β (H)-29-homohopane 22S and 22 R
32H-C_{32} — 17α, 21β (H)-29-bishomohopane 22S
33H-C_{33} — 17α, 21β (H)-29-trishomohopane 22S
34H-C_{34} —17α, 21β (H)-29-tetrakishomohopane 22S
35H-C_{35} — 17α, 21β (H)-29-pentakishomohopane 22S

APPENDIX 2

SAMPLED LOCALITIES

SOUTHERN AND WESTERN MARGIN

Zechstein (Gałęzice) — several small exposures of the 80 metres thick succession of diverse deposits: conglomerates, limestones and siltstones ascribed mostly to the Zechstein Limestone Unit (Ca1) of the Werra Cyclothem (Bełka 1978, 1991; see also Skompski, 1995). The investigated samples were taken from thin-bedded laminated cherty carbonates (Gałęzice 1 and Gałęzice 3) and cryptalgal limestones (Gałęzice 2).

Upper Röt (Starochęciny and Piekoszów) — sandstone with coalified plant remains, passing into marls interbedded with limestones (Senkowiczowa, 1959, 1961, 1973; Trammer, 1975).

Wellenkalk (Wolica) — grey limestone interbedded with banded limestone and clayey shale (Senkowiczowa, 1957*b*, 1959, 1973; Trammer, 1975).

Łuków Beds (Morawica and Wincentów) — light grey or creamy-coloured crystalline limestone with intercalations of pelitic marly and locally oolitic limestone (Senkowiczowa, 1957*b*, 1961, 1973; Trammer, 1975).

Beds with *Plagiostroma striatum* (Zajączków) — grey, crumbly limestone with intercalations of grey silty limestone and also grey and olive-green clayey shale (Senkowiczowa, 1961, 1973; Trammer, 1975).

Middle Muschelkalk (Lisów, Strawczynek area) — grey, thin-laminated limestone passing into dolomitic sediments, limestones intercalated with marls and shales and also yellow thick-bedded limestone and grey laminated limestone (Senkowiczowa, 1961, 1973; Trammer, 1975).

NORTHERN MARGIN

Zechstein (Kajetanów) — small abandoned quarry on the northern outskirts of Kielce. Dark marly limestones with brachiopods (Kajetanów 1 and Kajetanów 2) and plant remains (Kajetanów 3) have been known since the XIX century (see the literature review in: Kowalczewski and Rup, 1989).

Wolice Beds (Bliżyn) — light grey and yellow finely-crystalline limestone with numerous crinoids (Kleczkowski, 1959; Senkowiczowa, 1956).

Łuków Beds and/or Beds with *Plagistoma striatum* (Gębice) — compact calcareous dolomite, thick-bedded crinoidal coquina and grained limestone (Senkowiczowa, 1973; Zacharski, 1995).

Middle Muschelkalk (Kolonia Jakimowice) — limestone intercalated with marls and shales, passing into yellow coarsely-crystalline limestone and grey laminated limestone (Senkowiczowa, 1956, 1958, 1973).

Beds with *Entolium discites* (Bzin) — yellow or light grey crystalline limestone with glauconite or clay and sandy claystone intercalated with marls and limestone (Senkowiczowa, 1956, 1973).

Lower Keuper (Chyby) — sandstone and claystone intercalated with siltstone, limestone and remains of coalified flora (Senkowiczowa, 1973).