Origin, migration and secondary processes of oil and natural gas in the western part of the Polish Outer Carpathians: geochemical and geological approach

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Received: 28 August 2020 / Accepted: 5 April 2021 / Published online: 28 April 2021
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Abstract

The origin, migration pathways, as well as the influence of secondary processes of oil and natural gas accumulated in lower Cretaceous to lower Miocene strata of the western part of the Polish Outer Carpathians (between Kraków and Pilzno towns) based on results of organic geochemical analyses are investigated in this paper. Oil and thermogenic hydrocarbon gases were generated mainly from type II kerogen, and type II and III kerogen mixed in various proportions. These kerogens mainly occur in the Oligocene Menilite beds of the Silesian and Dukla nappes. Oils were generated from early to late “oil window”. Secondary cracking was recorded in oils from Dukla nappe, other secondary processes including biodegradation, water washing and evaporative fractionation were also developed to a various extent in many oils. The most biodegraded oils occur in seep S-Li, and the most extensive water washing is observed in the oil from seep S-Sa/1. The evaporative fractionation processes most significantly occur in the selected deepest parts of the multi-horizontal Biecz field. Hydrocarbon gases originated during both microbial and thermogenic processes of organic matter transformation. Natural gas has not been subjected to biodegradation processes. Carbon dioxide is derived from both microbial and thermogenic decomposition processes of organic matter and was generated together with hydrocarbon gases.

Keywords Polish Outer Carpathians · Origin of oil and natural gas · Biomarkers · Stable carbon and hydrogen isotopes · Secondary processes · Petroleum migration and mixing

Introduction

The study area of the western part of the Polish Outer Carpathians between the towns of Kraków and Pilzno (Fig. 1a) covers about 950 km². Oil, condensate and gas fields were discovered in sandstone reservoirs within the lower Cretaceous to lower Miocene lithostratigraphic units in the Silesian, Dukla and Magura nappes of the Polish Outer Carpathians (Fig. 2). Some oil and gas fields occur at shallow depths, where circulation of edge water can be observed (Karnkowski and Konarski 1973; Karnkowski 1999), creating suitable conditions for secondary processes of biodegradation and water washing. At the same time effective source

rocks generate petroleum from strata within deeply buried Dukla nappe beneath the Magura nappe (Kotarba et al. 2017), where oils may undergo secondary cracking. Oil with associated natural gas and non-associated natural gas occur in sandstone reservoirs, having distinct geochemical signatures indicating a range of genetic and post-accumulation histories.

The aim of this paper is establishing the origin, migration and mixing of oil and natural gas and influence of secondary processes (biodegradation, water washing, cracking and evaporative fractionation), occurring in the study area (Fig. 1) based on the results of oil analyses of sulphur content, vanadium and nickel concentrations, GC and GC–MS analyses (fraction composition, *n*-alkanes and isoprenoids distribution, biomarker composition of saturated and aromatic hydrocarbon fractions) and stable carbon isotope composition of oil and its four fractions, as well as gas analyses of molecular composition of hydrocarbon and non-hydrocarbon components, and stable carbon and hydrogen isotope composition of hydrocarbon components and carbon

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dioxide. Interpretation of results of mentioned above analyses is performed in relation to geological setting and genetic type and maturity of source rocks.

Geological setting and petroleum occurrence

Geological setting

The Carpathian Mts. form an almost perfect arc extending from the Vienna Basin in the west through Slovakia, Poland and Ukraine to Romania in the southeast (Fig. 1a). The Carpathian Orogen comprises two main tectonic zones of different geological settings and history: the Outer and the Inner Carpathians (see e.g. Oszczytko et al. 2008). The Inner Carpathians are the older (late Cretaceous) fold belt whereas the Outer Carpathians are the younger (Oligocene–middle Miocene) fold-and-thrust belt, known also as the Flysch Carpathians. The nappes of the Outer Carpathians form a strongly arcuate (oroclinal) fold-and-thrust belt overthrusting along its full length onto the younger foreland molasses, which cover (with a stratigraphic gap) the Meso–Palaeozoic structural stages of the platform slope or rest directly upon the Precambrian basement.

The Outer Carpathians comprise a number of nappes and slice-folds containing various lithostratigraphic profiles and showing complicated tectonic styles (Figs. 1, 2) (e.g., Golonka et al. 2011; Siemińska et al. 2018; Waśkowska et al. 2018). The lithostratigraphic profiles are dominated by upper Jurassic to lower Miocene, deep-marine, siliciclastic strata (see e.g. Oszczytko et al. 2008) deposited in separate sedimentary basins, each of them showing different geological development. In the late Oligocene–middle Miocene, the flysch strata were detached from the basement and thrusting over both the West and the East European platforms (see e.g. Cieszkowski et al. 1985; Oszczytko 1992). From the south to the north of the Polish Outer Carpathians, the nappes occur: Dukla, Silesian, Sub-Silesian and Skole.

The study area includes the Silesian and Magura nappes, parts of the Dukla (Grybów) nappe exposed in the tectonic windows and the Silesian nappe (Fig. 1a). Each nappe comprises its own stratigraphic sub-units and zones, which reveal specific lithostratigraphic columns (Fig. 2) and/or specific patterns of tectonic deformations. The spatial relations of these three nappes and structure of Kryg-Libusza-Lipinki and Fellnerówka-Hanka fields in the Silesian nappe within the study area are shown in Figs. 3 and 4, respectively. Their lithostratigraphic profiles comprise depositional systems ranging from the late Jurassic through the whole Cretaceous up to the early Miocene, composed of various associations of clayey-sandy strata dominated by turbidites and other sand-mud gravity flow deposits accompanied by

minor carbonates and pyroclastics (Fig. 2). The division of these lithostratigraphic sequences into formal (Formation) or informal (beds, shales) units remains unresolved (e.g., Dziadzio et al. 2006).

Petroleum occurrence

In the study area, a total of 19 oil and gas fields have been discovered, in that 7 oil and 4 gas fields in the Silesian nappe (Table 1), 4 oil and 1 oil-condensate-gas fields in the Dukla (Grybów) nappe (Table 2) and 3 oil fields in the Magura nappe (Table 2). Exploitation of oil began in 1858 (Kłęczany field) and natural gas production in 1939 (Szalowa-Heddy-Bystra field) (Tables 1, 2). Eleven fields had been discovered already before World War II (Tables 1, 2). At present, only six oil fields and three gas fields are exploited (Tables 1, 2).

Location of samples and sampling procedure

Seventeen oil and ten natural gas samples were collected in the study area (Figs. 1, 3, 4, Table 3). Eleven crude oil and eight natural gas samples from Biecz (Fig. 1b), Kryg-Libusza-Lipinki (Fig. 1c), Dominikowice-Kobylanka, Gorlice-East and Gorlice-Glinik (Fig. 1d), and Fellnerówka-Hanka (Fig. 1e) fields in the Silesian nappe, two crude oil and one natural gas samples from Limanowa-Słupnice oil-condensate-gas field (Fig. 1a) and one oil sample from Kłęczany seep in the Dukla nappe, and four oil and two gas samples from Łosie, Sękowa, Siary and Trzebunia seeps in the Magura nappe were collected from the Lower Cretaceous–Oligocene sandstone reservoirs (Table 3). Moreover, two Le/6 and Le/21 subsurface gas samples (Magura nappe) near Leśniówka-2 well were also taken out (Fig. 1a).

Crude oil samples were collected in a glass container ($\sim 1000 \text{ cm}^3$) from the separators or wellheads of producing wells and from seeps. Free gas samples were collected directly at the wellhead into a metal container ($\sim 1000 \text{ cm}^3$) with head pressure at least 5 MPa. Associated gases (dissolved in oil) were taken from a separator into a glass container ($\sim 500 \text{ cm}^3$) at pressures of at least 0.2 MPa. Natural gases from seeps were collected to glass containers filled with NaCl-saturated solution. General information on the sampling sites is given in Table 3, whereas their locations are shown in Fig. 1.

In Leśniówka-2 (Le-2) well a gas-condensate accumulation was found within the upper Cretaceous–Palaeocene beds (Dukla nappe) at a depth of 4043–4210 m (Table 3). However, technical conditions were very bad, cementing of the lining pipe was wrong, and gas escaped to the surface. The migration of methane and higher hydrocarbons to the near-surface zone may be hazardous to buildings and

Fig. 1 a Geological sketch map of the study area showing the location of nappes, oil and gas sampling sites (wells and seeps), and structural scheme and oil and gas sampling wells of b Biecz, c Kryg-

Libusza-Lipinki, d Dominikowice-Kobylanka, Gorlice-Glinik and Gorlice-East, and e Fellnerówka-Hanka fields

Fig. 2 Generalized lithostratigraphic columns of the Silesian, Dukla and Magura nappes of the Outer Carpathians in the study area modified after Ślaczka and Kamiński (1998), Dziadzio et al. (2006, 2016) and Kotarba et al. (2020a, b) showing distribution of petroleum reservoirs and source rock horizons after Kotarba and Koltun (2006) and Kotarba et al. (2013, 2014, 2020a). **PETR. ACCUM.** petroleum (oil and gas) accumulations (fields), *Ciężk.* Ciężkowice, *Fm.* formation, *Ga. b.* Gaize beds, *Hier.* Hieroglyphic, *La* Łącko marls, *Pasier.* Pasierbiec, *Sp.* Spangiolites, *Ss ss* sandstones, *sh.* shales, *Tr.* transitional

NAPPE		SILESIA		DUKLA		MAGURA	
STRATIGRAPHY		LITHOSTRATIGRAPHY	PETR. ACCUM.	SOURCE ROCKS	LITHOSTRATIGRAPHY	PETR. ACCUM.	SOURCE ROCKS
Neogene	Miocene	Chaotic complex			Krosno beds		
		Krosno beds			Tr. beds		
		Magdalena ss	● ○	■	Magdalena ss		
		Globigerina marls			Globigerina marls		
Palaeogene	Oligocene	Green shales			Hieroglyphic beds & Green shales		
		Hieroglyphic beds			Variegated shales		
		Ciężkowice ss	● ○	■	Rdzawka ss		
		Upper Istebna ss	● ○	■	Proszyn ss		
Palaeocene	Eocene	Lower Istebna ss	● ○	■	Hieroglyphic beds		
		Variegated shales & marls			Variegated shales		
		Godula beds			Majdan beds		
		Green and Radiolarian shales			Cisna beds		
Cretaceous	Upper	Lgota beds	● ○	■	Łupków beds		
		Grodziszcz ss	● ○	■	Variegated shales		
		Vebvice beds			Lgota beds		
		Grodziszcz ss					
Lower	Upper	Upper Cieszyn beds					
		Cieszyn limestone					
		Lower Cieszyn beds					
Jura-ssic	Upper

Fig. 3 a Schematic geological cross-section A–A' through Łosie (S-Li), Sękowa (S-Sa) and Siary (S-Sy) seeps, and Kryg-Libusza-Lipinki (cf. Figure 4a), Dominikowice-Kobylanka, Fellnerówka-Hanka (cf. Figure 4b) and Biecz fields and modified after Kuśmerek and Baran (2013), and distributions of Fig. 4a geochemical indices

for b oil and c natural gas. See Fig. 1 for location of the geological cross-section line. Values of parameters and indices for oils listed in Tables 4, 5, 6, 7, and for natural gases in Table 9. Biodegradation level for oil listed in Table 5. a.s.l. above sea level, Aro aromatics; ΣMN sum of methyl-naphthalenes

human health. In 2009, oil–gas survey near Leśniówka-2 well (Dzieniewicz et al. 2009) in the Quaternary sediments (Magura nappe) revealed that a higher concentration of methane (> 10 ppm) in the near-surface zone reached 150 m

around this well, and maximum value 17 vol%. Since then the Polish Oil and Gas Company has conducted periodical controls hammering down 3-m-long holes from the surface by special percussive hammers. In 2017, Le/6 and Le/21

Fig. 4 Schematic geological cross-sections **a** B–B' through Kryg-Libusza-Lipinki field, and **b** C–C' and D–D' through Fellnerówka-Hanka field. Explanation of lithostratigraphy of the Silesian nappe see Fig. 3. See Fig. 1c, e for location of lines of geological cross-sections

Table 1 Oil and gas fields of the Silesian nappe in the study area, years of their discovery and abandoned, and new and previously published oil and gas samples from wells used for genetic interpretation

Field	Discovery (year)	Abandoned (year)	Fluid type	Reservoir horizon: Lithostratigraphy (Stratigraphy)			
				Krosno beds (U. Olig.–L. Mioc.)	Ss (Magdalena) horizons within Menilite shales (Olig.)	Ciężkowice ss (Pal.–Eocene)	Istebna beds (U. Cr.–Pal.)
Biecz	1888	2017	OIL			X	DI-25, DI-51
Dąbrówka Tuchowska	1966	In exploitation	GAS	Bn-6^a		DTu-4^c	X
Dominikowice- Kobylanka	1860	In exploitation	OIL			Wl-16 ^d	So-9, Wl-3, Wl-15, Go-8^c
Fellnerówka- Hanka	1936	In exploitation	OIL	Ha-6	X		F-8 ^e
Gorlice-East	1976	2017	OIL	Go-2 ^d /Go-2 ^c			
Gorlice-Glinik	1978	In exploitation	GAS	Go-11^c			
Kryg-Libusza- Lipinki	1860	In exploitation	OIL			El-58, Jo-44, Pl-8, SB-32	
Magdalena	1931	2014	OIL		M-5 ^e		
Rzepiennik	1930	In exploitation	OIL				X
Strzeszyn	1972	2017	GAS			Sn-5^c	
Szalowa- Heddy- Bystra	1939	In exploitation	GAS			Bs-4^b, He-3^c, He-4^c, He-6^c	

El-58 oil sample from well, **Bn-6** gas sample from well, **DI-25** oil and gas samples from well, *L. Mioc.* lower Miocene, *Olig.* Oligocene, *Pal.* Palaeocene, *U. Cr.* upper Cretaceous, *OIL* oil with dissolved gas, *GAS* free gas, *X* reservoir horizon (no analysed)

Geochemical data after: ^aKotarba and Nagao (2008), ^bKotarba et al. (2009), ^cKotarba et al. (2013), ^dMatyasik and Dziadzio (2006), ^eten Haven et al. (1993)

Table 2 Oil and gas fields of the Dukla and Magura nappes in the study area, years of their discovery and abandoned, and new and previously published oil and gas samples from wells used for genetic interpretation

Field	Discovery (year)	Abandoned (year)	Fluid type	Reservoir horizon: Lithostratigraphy (Stratigraphy)			
				Krosno beds (U. Oligocene)	Cergowa ss. within Menilite shales (Oligocene)	Hieroglyphic beds (Eocene)	Cisna beds/ Ropianka Fm. ^a (U. Cr.–Pal.)
Dukla nappe							
Kłęczany	1858	1963	OIL	KI-135 ^f		X	
Męcina Wielka	1870	In exploitation	OIL	X			
Limanowa-Słupnice	1974	In exploitation	OIL/CON-DESATE/ GAS	<i>Pr-2</i> ^b , SI-7 ^g , SI-23 ^g , <i>SI-20</i> ^c , <i>SI-24</i> ^d	SI-13, <i>SI-3</i> ^d		Le-2/ <i>Le-2</i> ^c
Stara Wieś-Librantowa	1900	1950?	OIL	X			
Skrzydlna	1950	1955	OIL	X			
Magura nappe							
Męcina Wielka	1870	2000	OIL				X
Sękowa-Ropica-Górna-Siary	1860	2000	OIL				X
Szymbark	1881	2000	OIL				By-4 ^g

SI-7 oil sample from well, *SI-20* gas sample from well, *U.* upper; *Pal.* Palaeocene, *Cr.* Cretaceous, *OIL* oil with dissolved gas, *GAS* free gas, *X* accumulation occurs (no analysed)

^aCisna beds in the Dukla nappe and Ropianka Formation in the Magura nappe (=equivalents of Inoceranian beds)

Geochemical data after ^bKotarba (1987), ^cKotarba (1992), ^dKotarba et al. (2009), ^eKotarba et al. (2017), ^fWięclaw (2002), ^gten Haven et al. (1993)

samples (Table 3) were collected in selected holes situated about 5 m to W and 10 m to SW from Le-2 well, respectively (Fig. 1a and Table 3). After the installation of a special probe, near-surface gas samples were collected from the deepest 1.0 m interval of the holes and transferred into 1000 cm³ volume glass vessels filled with saturated NaCl solution. Such sampling depth enabled us to eliminate the impact of atmospheric air (Klusman 1993; Saunders et al. 1999; Tedesco 1995).

The results of the previous geochemical studies of 15 crude oil (ten Haven et al. 1993; Więclaw 2002; Matyasik and Dziadzio 2006) and 17 natural gas (Kotarba 1987, 1992; Kotarba and Nagao 2008; Kotarba et al. 2009, 2013, 2017) samples from 11 fields, one uneconomic accumulation and 3 seeps in the study area were also used for genetic interpretation. Locations of these fields and samples are shown in Fig. 1.

Analytical procedure

Oil

Oils were analysed for the American Petroleum Institute (°API) gravity using an Anton Paar DMATM 5300 M

density meter and for sulphur content with a Leco[®] SR-12 analyzer. Before fractionation by column chromatography, the oils were topped under nitrogen (5 h) at a temperature of 60 °C and the asphaltene fraction was precipitated from oil with petroleum ether. The maltenes were separated into fractions of saturated hydrocarbons, aromatic hydrocarbons and resins by column chromatography using alumina/silica gel (2:1 v/v) columns (0.8×25 cm). The fractions were eluted with petroleum ether, toluene and toluene:methanol (1:1 v/v), respectively. The oils and their individual fractions were combusted in an on-line system for the measurement of stable carbon isotope composition. The stable carbon isotope analyses were performed using a Thermo ScientificTM Delta V Plus mass spectrometer (MS) and the results are expressed in the δ -notation ($\delta^{13}\text{C}$, ‰) relative to the VPDB (Coplen 2011) using international standard NBS 22 for isotopic normalization. Analytical precision established as standard deviation from 10 measurements is estimated to be $\pm 0.2\text{‰}$. Whole oils were analysed by high resolution gas chromatography using a Hewlett[®]Packard 5890 series II gas chromatograph (GC) equipped with a flame ionization detector (FID). The isolated saturated hydrocarbon fractions were diluted in isoctane and analysed by a GC coupled to a mass selective detector (MSD) for biomarker composition. The analysis was carried out with an Agilent 7890A GC

Table 3 Location of analysed oil and natural gas samples from wells and seeps

Well/seep	name	Sample code	Field name/ sampling place	Symbol	Sampled horizon depth (m)	Lithostratigraphy reservoir rock	of Surface (m a.s.l.)	Sample
Silesian nappe				★	Samples from previous studies			
Upper Cretaceous-Palaeocene				●				
Długosz-25	DI-25	Biecz			200-356	Istebna ss	255	DG&O
Długosz-51	DI-51	Biecz			419-447	Istebna ss	256	DG&O
Sobieski-9	So-9	Dominikowice-Kobylanka			599-632	Istebna ss	301	O
Władysław-3	WI-3	Dominikowice-Kobylanka			163-219	Istebna ss	305	O
Władysław-15	WI-15	Dominikowice-Kobylanka			200-223	Istebna ss	309	DG&O
Palaeocene-Eocene				○				
Elżbieta-58	EI-58	Kryg-Libusza-Lipinki			217-258	Ciężkowice ss	304	O
Joasia-44	Jo-44	Kryg-Libusza-Lipinki			477-495	Ciężkowice ss	313	O
Petrol-8	PI-8	Kryg-Libusza-Lipinki			170-207	Ciężkowice ss	311	DG&O
Szczęście Boże-32	SB-32	Kryg-Libusza-Lipinki			221—266	Ciężkowice ss	312	DG&O
Oligocene-Lower Miocene				○				
Gorlice-2	Go-2	Gorlice-East			2930-2962	Krosno beds	314	O
Hanka-6	Ha-6	Fellnerówka-Hanka			390-450	Krosno beds	346	DG&O
Dukla nappe				★	Samples from previous studies			
Upper Cretaceous-Palaeocene				▼				
Leśniówka-2	Le-2	Limanowa-Słopnice			4043-4210	Cisna beds	527	DG ^a &O
Oligocene				▽				
Słopnice-13	SI-13	Limanowa-Słopnice			1032-1059	Cergowa ss	437	O
Seep-Kłęczany	S-KI	seep			surface	Krosno beds	486	O
Magura nappe				☆	Samples from previous studies			
Upper Cretaceous-Palaeocene				◆				
Seep-Losie	S-Li	seep			surface	Ropianka Formation	408	DG&O
Seep-Sękowa	S-Sa/1	seep			surface	Ropianka Formation	399	O
Seep-Siary	S-Sy/1	seep			surface	Ropianka Formation	381	O
Eocene				◇				
Trzebunia	S-Ta	seep			surface	Łabowa Formation	359	FG
Quaternary				◇				
Le/6	Le/6	dug-well (subsurface)			3.0 m from surface	Quaternary sediments	527	NSG
Le/21	Le/21	dug-well (subsurface)			3.0 m from surface	Quaternary sediments	528	NSG

U. Cr. upper Cretaceous, Pal. Palaeocene, Eoc. Eocene, Olig. Oligocene, L. Mioc. lower Miocene, ss sandstones, S seep, O oil, Gas: DG dissolved in oil, FG free, NSG near surface

^aResults of molecular and isotopic compositions of dissolved gas in Leśniówka-2 well (Tables 8 and 9) after Kotarba et al. (2017)

equipped with the Agilent 7683B automatic sampler. The aromatic hydrocarbons fractions of the oils were analysed by the GC-MSD for naphthalene, phenanthrene, dibenzothiophene and their methyl derivatives and triaromatic steroids relative concentrations. The analysis was carried out using the same equipment as for the saturated hydrocarbon fraction. Details of analytical procedures of oils were described in Kotarba et al. (2019, 2020a).

Natural gas

Molecular compositions of natural gases (CH₄, C₂H₆, C₃H₈, *i*-C₄H₁₀, *n*-C₄H₁₀, *i*-C₅H₁₂, *n*-C₅H₁₂, C₆H₁₄, C₇H₁₆, CO₂, O₂, H₂, N₂, He) were analysed in a set of columns on two Agilent 7890A GCs equipped with a gas sampling valve plumbed with a dual sample loop. Stable carbon isotope analyses were performed using a FinniganTM Delta Plus mass spectrometer (MS) coupled through a GC combustion III interface with a 6890 gas chromatograph. Methane, ethane, propane, butanes, pentanes and carbon dioxide were separated chromatographically, and carbon dioxide produced by the on-line system was transmitted to the MS. The stable carbon isotope

data are expressed in the δ -notation ($\delta^{13}\text{C}$, ‰) relative to VPDB (Coplen 2011). The stable hydrogen isotope analyses of methane, ethane and propane were performed in a Thermo ScientificTM Delta VTM Plus MS connected through Conflo IV and GC IsolinkTM interfaces with a Trace GC Ultra chromatograph. The stable hydrogen isotope data were reported in δ -notation ($\delta^2\text{H}$, ‰) relative to VSMOW (Coplen 2011). The stable nitrogen isotope analyses were performed using a FinniganTM Delta Plus MS coupled through a GC combustion III interface with a 6890 gas chromatograph. Molecular nitrogen was separated chromatographically for stable nitrogen isotope analysis and was transmitted to the MS via the on-line system. The results of stable nitrogen isotope analysis were presented in the δ -notation ($\delta^{15}\text{N}$, ‰) relative to atmospheric nitrogen. Details of analytical procedures of natural gas were described in Kotarba et al. (2019, 2020a) and Więclaw et al. (2020).

Results

Oil

The analysed crude oils accumulated in the Upper Cretaceous-Palaeocene to Oligocene sandstone reservoirs in the study area (Table 3) vary in their physical and geochemical properties. Gravity of oils varies from 24.5 (S-Sy/1) to 45.1 °API (S-Kl) (values from 30 to 40 °API dominate), density from 0.797 to 0.903 g/cm³ with sulphur content ranging from traces (S-Kl) to 0.27 wt% (Pl-8) (average 0.14 wt%) (Table 4). The concentration of saturated hydrocarbons usually exceeds 50 wt%. The lowest content of this fraction was recorded in the Jo-44 oil (41.8 wt%, Table 4). Correspondingly, in all analysed oils, low content of asphaltenes (below 5 wt%) was recorded. This fraction's highest content was recorded in oil samples taken from Jo-44 and Pl-8 (10.9 and 10.4 wt%, respectively) (Table 4). Stable carbon isotope composition of oils and their fractions varies in a narrow range: saturated hydrocarbons from − 28.8 to − 25.6‰, aromatics from − 27.7 to − 24.7‰, resins from − 27.6 to − 24.7‰ and asphaltenes from − 28.3 to − 25.7‰ (Table 4).

Selected indices calculated based on crude oil GC-FID analysis are presented in Table 5. GC analyses indicate that most oils have a full range of *n*-alkanes (up to C₃₅). The CPI (formula see Table 5) values are near or greater than 1.0, except for sample Ha-6. Pristane/phytane (Pr/Ph) ratio values are above 2.0, with a maximum value of 3.41 for DI-25 oil (Table 5). Only for sample DI-51 Pr/Ph ratio is 1.04. Selected indices calculated based on sterane and terpane distributions and relative concentrations of *n*-alkanes, *iso*-alkanes and steranes + terpanes of currently analysed oils are presented in Table 6. The sterane/terpane ratios are similar for oils from Silesian and Magura nappes, with average of 0.32; also the tricyclic/pentacyclic terpane ratios for these oils are close—on average of 0.07 (for the explanation of formulas, see Table 6). Only both oils collected from Dukla nappe have elevated values, over 0.41 and 0.14.

The relative concentration of regular 20R C₂₇, C₂₈ and C₂₉ steranes for all oils, except Go-2 and S-Kl samples, is similar and ranges from 30 to 40% for each component. For the oils from S-Kl seep and Go-2 well, the relative concentration of 20R C₂₉ regular sterane is higher and equals 42%; correspondingly, these oils contain the lowest 20R C₂₇ regular sterane. For all oil samples, values of C₂₉20S/(20S + 20R) ratio are above 0.30, and Ts/(Ts + Tm) values are greater than 0.4. The only exception is for Jo-44 oil, where these indices are 0.29 and 0.16, respectively (Table 6). The values of C₂₉ββ/(ββ + αα) index are at least 0.34. The above-mentioned elevated values of C₂₉ββ/(ββ + αα) index correlate with high values of C₂₇ dia/(dia + reg) ratio, up to above

0.5 for Le-2, SI-13, S-Kl and S-Li oils. The C₃₁ homohopane 22S/(22S + 22R) ratio values are all approximate 0.55 (Table 6). Values of C₂₄t/C₂₃t and C₂₂t/C₂₁t ratios of tricyclic terpanes vary from 0.52 to 1.08 and from 0.07 to 0.49, respectively. In all oils, the gammacerane/17α hopane ratio (GI) is not higher than 0.1 (Table 6). The C₂₉ norhopane/17α hopane ratio is consistently below 0.1 and C₃₅/C₃₄ ratio below 1.0, respectively. There is a visible distinction in oil indices among oil from Dukla nappe and remaining oils (from Silesian and Magura nappes).

Indices calculated based on GC-MS analysis of the aromatic hydrocarbon fraction of analysed oils are presented in Table 7. For all oils, the MPI index (Radke et al. 1982) ranges from 0.44 to 1.24. The elevated values above 1.0 were recorded for DI-25 (Silesian nappe, Biecz field) and all oils accumulated in Dukla nappe. The highest MDR ratio values (Radke et al. 1986) are noted for the same oils. In contrast, some oils collected from seeps in Magura nappe have low values (below 2.0). All oil samples are characterised by a dibenzothiophene/phenanthrene ratio below 0.15. Values of short-chain to long-chain triaromatic steroids ratio [TA(I)/TA(I + II)] range from 0.07 to 0.99. This index's highest values (greater than 0.2) come from samples DI-25 and DI-51 (both from the Biecz field in the Silesian nappe), all oils from Dukla nappe and S-Li from the Magura nappe. The highest contents of methyl- and dimethylnaphthalenes were recorded in oils Wl-15 and S-Li (above 100 ppm and 2000 ppm, respectively). In contrast, the lowest concentrations of MN and DMN were measured in the Le-2 oil. In some oils, renieratane, a significant amount was recorded: So-9, El-58, Jo-44 and Wl-15 (Table 7).

Natural gas

The analysed natural gas from the Upper Cretaceous to Lower Miocene strata accumulated within the Silesian, Dukla and Magura nappes and subsurface gas from the Quaternary sediments of the Magura nappe in the study area (Table 3, Fig. 1) are variable in both molecular and stable isotopic compositions (Tables 8, 9). In molecular composition of natural gas dominate the hydrocarbon components (C₁–C₇) (Table 8). Methane is the most abundant component of the analysed gas from field and seep accumulations. Its concentration varies from 71.1 vol% in Pl-8 well (Kryg-Libusza-Lipinki field) to 94.4 vol% in S-Ta seep (Trzebnia) and higher hydrocarbons (C₁–C₇) range from 3.9 vol% in S-Ta seep to 25.8 vol% in SB-32 well (Kryg-Libusza-Lipinki field) (Table 8). Concentrations of methane and higher hydrocarbons in subsurface gas in Quaternary sediments of two dug-wells of Leśniówka-2 well are 74.8 and 62.5 vol%, 0.92 and 0.75 vol%, respectively (Table 8). The dryness described by C_{HC} (hydrocarbon index) = CH₄/(C₂H₆ + C₃H₈) of natural and subsurface gases ranges from

Table 4 Density, API gravity, sulphur, vanadium, nickel and iron contents, fraction and stable carbon isotope compositions of oil and its fractions from wells and seeps

Sample code	Density (g/cm ³)	Gravity (°API)	S _{org} (wt%)	V (mg/kg)	Ni	Fe	V/(V+Ni)	Fractions (wt%)				Stable carbon isotopes (‰)				CV		
								Sat	Aro	Res	Asph	Sat	Oil	Aro	Res		Asp	
Silesian nappe																		
Upper Cretaceous–Palaeocene																		
DI-25	0.827	38.7	0.04	n.a.	n.a.	n.a.	n.c.	54.1	35.4	9.8	0.7	1.5	–27.3	–27.2	–26.9	–26.8	–27.0	–2.34
DI-51	0.832	37.7	0.14	n.a.	n.a.	n.a.	n.c.	69.2	19.9	9.9	1.0	3.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.c.
So-9	0.837	36.6	0.04	n.a.	n.a.	n.a.	n.c.	79.5	13.3	5.3	1.9	6.0	–27.6	–27.3	–26.5	–27.4	–27.9	–0.61
WI-3	0.847	34.7	0.10	1.00	8.95	0.7	0.10	65.5	20.5	10.5	3.5	3.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.c.
WI-15	0.845	35.0	0.12	0.56	5.55	0.5	0.09	66.5	22.1	7.8	3.6	3.0	–27.6	–27.3	–26.9	–27.0	–27.0	–1.54
Palaeocene–Eocene																		
El-58	0.869	30.4	0.19	n.a.	n.a.	n.a.	n.c.	59.3	23.5	12.0	5.2	2.5	–28.7	–28.1	–27.4	–27.6	–27.5	0.10
Jo-44	n.a.	n.a.	0.20	n.a.	n.a.	n.a.	n.c.	41.8	23.8	23.5	10.9	1.8	–28.7	–28.2	–27.7	–27.6	–27.9	–0.48
Pl-8	0.880	28.6	0.27	3.14	27.4	3.8	0.10	53.7	24.8	11.1	10.4	2.2	–28.8	–28.1	–27.7	–27.4	–27.3	–0.27
SB-32	0.860	32.3	0.09	n.a.	n.a.	n.a.	n.c.	66.2	18.9	8.7	6.2	3.5	–27.9	–27.5	–27.0	–26.9	–27.0	–0.93
Oligocene–lower Miocene																		
Go-2	0.826	38.8	0.09	n.a.	n.a.	n.a.	n.c.	76.6	14.2	6.9	2.3	5.4	–28.2	–27.9	–27.0	–27.5	–28.3	–0.21
Ha-6	0.859	32.3	0.16	n.a.	n.a.	n.a.	n.c.	58.4	24.5	16.4	0.7	2.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.c.
Dukla nappe																		
Le-2	0.798	44.7	tr	n.a.	n.a.	n.a.	n.c.	96.1	3.6	0.3	0.0	26.7	–26.6	–26.4	–25.5	–26.1	n.a.	–1.07
SI-13	0.838	36.4	0.05	n.a.	n.a.	n.a.	n.c.	84	12	2.2	1.2	6.9	–27.1	–26.8	–25.8	–26.3	–26.4	–0.41
S-KI	0.797	45.1	tr	n.a.	n.a.	n.a.	n.c.	84.2	9.6	2.4	3.8	8.8	–25.6	–25.5	–24.7	–24.7	–25.7	–1.74
Magura nappe																		
Upper Cretaceous–Palaeocene																		
S-Li	0.890	26.7	0.04	<0.30	<0.50	24	n.c.	72.8	18.3	7.1	1.8	4.0	–27.0	–26.7	–26.4	–26.6	–26.7	–1.83
S-Sa/I	0.894	26.1	0.26	1.72	22.6	7.1	0.07	63.4	23.1	8.0	5.4	2.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.c.
S-Sy/I	0.903	24.5	0.23	0.84	13.2	6.0	0.06	61.0	28.2	9.0	1.9	2.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.c.

Sat. saturated, Aro. aromatic, Res. resins, Asph. asphaltenes, CV (canonical variable) $[-2.53*\delta^{13}\text{C}(\text{Sat.}) + [2.22*\delta^{13}\text{C}(\text{Aro.})] - 11.65$ (Sofer 1984), tr. traces, n.a. not analysed, n.c. not calculated

Table 5 Selected indices calculated based on GC-FID analyses of oil from wells and seeps

Sample code	$CPI_{(Total)}$	$CPI_{(17-23)}$	$CPI_{(25-31)}$	Pr/Ph	$Pr/n-C_{17}$	$Ph/n-C_{18}$	$n-C_6/2,2DMB$	Benzene/ $n-C_6$	Toluene/ $n-C_7$	$n-C_7/MCH$	HR	$(n-C_6 + n-C_7)/(CH + MCH)$	CH/MCH	IHR	$n-C_7/2-MH$	$\Sigma xylenes/n-C_8H_{18}$
Silesian nappe																
Upper Cretaceous–Palaeocene																
DI-25	1.03	1.02	1.04	3.41	7.15	3.73	6.78	1.63	3.40	0.37	17.8	0.37	0.38	1.34	3.18	0.98
DI-51	1.17	1.31	0.96	1.04	0.99	0.42	3.96	1.26	2.79	0.36	15.9	0.37	0.46	1.22	3.04	0.93
So-9	1.02	1.02	1.00	3.24	1.01	0.33	4.10	0.37	0.95	39.00	16.1	0.44	0.48	1.08	2.99	1.69
WI-3	1.06	1.05	1.10	2.12	1.15	0.57	3.75	0.61	1.02	0.44	16.7	0.52	0.48	0.98	2.95	0.71
WI-15	1.06	1.05	1.12	2.30	1.12	0.54	2.30	0.86	1.35	0.16	9.3	0.15	0.19	0.71	2.82	2.93
Palaeocene–Eocene																
EL-58	1.05	1.03	1.15	2.14	1.20	0.57	3.87	0.47	0.82	0.56	19.8	0.67	0.41	0.73	3.78	1.54
Jo-44	1.01	1.08	0.88	2.46	1.52	0.66	3.21	0.56	1.20	0.47	28.5	2.01	0.36	0.61	3.80	1.02
PI-8	1.10	1.06	1.20	2.18	1.44	0.71	1.89	0.81	1.64	0.20	9.7	0.20	0.20	0.47	3.11	2.65
SB-32	1.05	1.04	1.08	2.21	1.03	0.49	3.87	0.65	1.15	0.44	16.8	0.51	0.49	0.90	3.17	0.75
Oligocene–lower Miocene																
Go-2	1.03	1.03	1.04	2.86	1.08	0.40	4.19	0.39	0.84	0.44	16.5	0.51	0.55	0.99	3.01	1.58
Ha-6	0.90	0.84	0.99	2.25	1.03	0.52	3.67	0.33	0.72	0.48	17.2	0.55	0.48	0.71	3.55	0.70
Dukla nappe																
Upper Cretaceous–Palaeocene																
Le-2	1.04	1.02	1.04	2.20	0.69	0.37	n.c.	0.48	2.03	0.51	19.2	0.49	0.11	1.82	4.72	2.11
Upper Oligocene																
SI-13	1.04	1.02	1.12	2.44	0.89	0.39	15.34	0.26	0.79	0.40	17.5	0.43	0.33	1.23	3.48	1.21
S-K1	1.01	1.01	0.99	2.34	1.14	0.50	4.80	0.13	0.65	0.40	16.7	0.48	0.39	1.48	2.39	0.68
Magura nappe																
Upper Cretaceous–Palaeocene																
S-Li	1.94	1.83	1.59	2.07	22.1	15.3	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
S-Sa/1	1.65	2.26	1.02	2.16	24.4	29.8	3.53	0.05	0.02	0.26	11.5	0.27	0.32	0.58	2.79	9.79
S-Sy/1	1.09	1.13	0.99	2.09	5.09	2.65	1.98	0.87	0.04	0.18	7.1	0.22	0.34	0.53	1.77	5.15

$CPI_{(Total)} = [(C_{17} + C_{19} + \dots + C_{27} + C_{29}) + (C_{19} + C_{21} + \dots + C_{29} + C_{31})]/[2 * (C_{18} + C_{20} + \dots + C_{28} + C_{30})]$; $CPI_{(17-23)} = [(C_{17} + C_{19} + \dots + C_{23})]/[2 * (C_{18} + C_{20} + \dots + C_{24})]$; $CPI_{(25-31)} = [(C_{25} + C_{27} + C_{29}) + (C_{27} + C_{29} + C_{31})]/[2 * (C_{26} + C_{28} + C_{30})]$

Pr: pristane, *Ph*: phytane, *DMB*: dimethylbutane, *MCH*: methylcyclohexane, *HR* = $100 \times n-C_7/(CH + \Sigma C_7HCs)$, *CH*: cyclohexane, *IHR* = $(2- + 3-MH/1c3- + 1t3- + 1t2-DMCP's)$; DMCP—dimethylcyclopentane; MH—methylhexane; Σ xylenes = meta- + ortho- + paraxylene; n.c.: not calculated due to low concentration of hydrocarbons

[illegible]

Silesian nappe																									
Upper Cretaceous–Palaeocene																									
DI-25	0.33	0.08	31	34	35	15	79	6	0.39	0.50	0.40	0.34	0.55	0.56	0.27	0.01	0.36	0.93	l.i.	0.08	0.23	93.2	5.5	++	
DI-51	0.26	0.07	32	34	34	44	54	2	0.50	0.43	0.50	0.49	0.56	0.62	0.30	0.02	0.40	0.87	l.i.	0.08	0.2	50.1	6.2	+	
So-9	0.29	0.08	30	34	36	50	48	2	0.51	0.58	0.52	0.40	0.57	1.08	0.15	0.05	0.36	0.61	0.07	0.06	0.23	n.a.	n.a.	+	
WI-3	0.35	0.09	34	36	30	46	47	7	0.41	0.44	0.38	0.28	0.55	0.66	0.49	0.02	0.41	0.88	0.03	0.09	0.21	43.7	1.0	++	
WI-15	0.31	0.05	34	34	32	41	54	5	0.37	0.63	0.41	0.25	0.58	0.73	0.44	0.02	0.4	0.82	0.05	0.07	0.26	164.2	1.0	++	
Palaeocene–Eocene																									
EI-58	0.36	0.05	28	40	32	40	52	8	0.34	0.58	0.52	0.23	0.57	0.73	0.07	0.08	0.4	0.93	0.04	0.09	0.20	n.a.	n.a.	+++	
Jo-44	0.35	0.05	23	40	37	35	56	9	0.29	0.16	0.36	0.21	0.57	0.74	0.14	0.10	0.4	0.88	0.04	0.11	0.22	n.a.	n.a.	+++	
PI-8	0.31	0.04	31	35	34	10	50	40	0.32	0.69	0.34	0.21	0.56	0.59	0.38	0.02	0.36	0.86	0.06	0.09	0.32	309.7	0.3	+++	
SB-32	0.33	0.07	32	36	32	50	44	6	0.36	0.46	0.35	0.26	0.54	0.52	0.37	0.02	0.4	0.93	0.03	0.09	0.24	152.5	0.9	++	
Oligocene–lower Miocene																									
Go-2	0.28	0.08	19	39	42	51	46	4	0.39	0.54	0.49	0.31	0.60	1.01	0.15	0.07	0.4	0.96	0.05	0.06	0.19			+	
Ha-6	0.33	0.06	32	34	34	49	42	9	0.38	0.47	0.37	0.28	0.56	0.62	0.36	l.i.	0.37	0.83	0.02	0.08	0.23	182.0	0.4	++	
Dukla nappe																									
Upper Cretaceous–Palaeocene																									
Le-2	1.00	0.75	39	32	30	36	64	<1	0.59	0.84	0.57	0.53	0.47	0.92	0.35	l.i.	0.36	0.70	0.08	l.i.	1.48	9.0	0.3	l.i.	
Upper Oligocene																									
SI-13	0.45	0.14	35	36	29	40	58	2	0.68	0.55	0.53	0.51	0.55	0.89	0.32	0.06	0.43	0.86	0.02	0.04	0.3	27.8	0.2	l.i.	
S-KI	0.41	0.25	26	32	42	42	57	1	0.50	0.80	0.53	0.69	0.60	0.80	0.33	l.i.	0.26	0.78	l.i.	l.i.	1.04	13.0	1.7	l.i.	
Magura nappe																									
Upper Cretaceous–Palaeocene																									
S-Li	0.37	0.11	34	32	34	2	93	5	0.47	0.62	0.55	0.51	0.54	0.69	0.29	0.01	0.35	0.70	0.05	0.04	0.22	55.2	0.8	++	
S-Sa/I	0.34	0.07	31	36	33	0	87	13	0.35	0.45	0.38	0.28	0.56	0.61	0.30	0.01	0.4	0.86	0.03	0.08	0.18	205.6	0.5	++	
S-Sy/I	0.31	0.07	34	33	33	17	72	11	0.36	0.47	0.38	0.29	0.55	0.68	0.29	0.01	0.40	0.91	0.04	0.07	0.2	182.3	0.2	+++	

S/T steranes/terpanes, *steranes* all regular steranes identified at $m/z = 217$, *terpanes* all tri-, tetra- and pentacyclic terpanes identified at $m/z = 191$, *Tri/Pen* tricyclic/pentacyclic terpanes, *tricyclic terpanes* all C_{27} – C_{30} tricyclic terpanes, *pentacyclic terpanes* all C_{27} – C_{35} pentacyclic terpanes, *pentacyclic terpanes* all C_{27} – C_{35} pentacyclic terpanes, C_{27} $C_{27}/\alpha\alpha\alpha 20R$ sterane/($C_{27} + C_{28} + C_{29}/\alpha\alpha\alpha 20R$ steranes)*100, C_{28} $C_{28}/\alpha\alpha\alpha 20R$ sterane/($C_{27} + C_{28} + C_{29}/\alpha\alpha\alpha 20R$ steranes)*100, C_{29} $C_{29}/\alpha\alpha\alpha 20R$ sterane/($C_{27} + C_{28} + C_{29}/\alpha\alpha\alpha 20R$ steranes)*100, C_{29} $C_{29}/\alpha\alpha\alpha 20R$ sterane/($C_{27} + C_{28} + C_{29}/\alpha\alpha\alpha 20R$ steranes)*100, Σn -alkanes/(Σn -alkanes + Σ ($S + T$))*100, Σ iso-alkanes/(Σ iso-alkanes + Σ ($S + T$))*100, Σ ($S + T$) = $\Sigma S + T$ /(Σn -alkanes + Σ ($S + T$))*100, $C_{29} S/(S + R)$ 20S/(20S + 20R) of C_{29} regular steranes ratio, $1\gamma/(1\gamma + 1m)$ of C_{27} 18 α trisnorhopane/(C_{27} 18 α trisnorhopane + C_{27} 17 α trisnorhopane), $C_{29} \beta\beta/(\beta\beta + \alpha\alpha)$ $\beta\beta$ -epimers and sum $\beta\beta$ - and $\alpha\alpha$ -epimers of C_{29} regular steranes ratio, C_{27} $Dia/(Dia + Reg)$ C_{27} $\beta\alpha$ 20S(+R) diasteranes/(C_{27} $\beta\alpha$ 20S(+R) diasteranes + Σ C_{27} regular steranes), $H_{31} S/(S + R)$ C_{31} homohopanes 22S/(22S + $\alpha\alpha$ -epimers of C_{29} regular steranes), GI gammacerane/17 α hopane, $C_{29} H/Hop$ C_{29} norhopane/17 α hopane, $C_{31} \beta/C_{34}$ (22S) homohopane, *nor-25H/Hop* C_{29} nor-25-hopane/17 α hopane, C_{31} 2-MPH/Hop C_{31} 2-methyl hopane/17 α -hopane, *Ol/Hop* oleane/17 α -hopane, 4-MD + 3-MD sum of concentration of 4-methyldiamantane + 3-methyldiamantane [ppm], *i.e.* low intensity, *n.a.* not analysed

Table 7 Indices calculated based on GC–MS (aromatic hydrocarbons) analyses of oil from wells and seeps, and evaluation of secondary processes

Sample code	MPII	R _{cal} (MPII) (%)	MDR	R _{cal} (MDR) (%)	DBT/Phen	TA(I)/TA(I+II)	Naph/ Phen (*10 ⁴)	ΣMN (ppm)	ΣDMN (ppm)	ΣMN/ΣDMN	Renie-ratane	Secondary processes	
												BIOD*	WW** EF***
Silesian nappe													
Upper Cretaceous–Palaeocene													
DI-25	1.15	1.06	6.99	1.02	0.06	0.25	4	7	583	0.01	+	m	sm sig
DI-51	0.82	0.86	4.93	0.87	0.06	0.21	5	17	596	0.03	+	u	sm sig
So-9	0.74	0.81	5.29	0.98	0.08	0.18	17	n.c.	n.c.	0.01	+++	vs	sm u
WI-3	0.65	0.76	3.40	0.76	0.08	0.17	8	9	349	0.03	l.i.	u	sm u
WI-15	0.64	0.75	3.49	0.76	0.10	0.10	7	151	2008	0.08	+++	vs	s u
Palaeocene–Eocene													
EL-58	0.56	0.71	2.97	0.75	0.11	0.08	37	n.c.	n.c.	0.10	+++	vs	sm u
Jo-44	0.56	0.70	2.36	0.73	0.13	0.07	371	n.c.	n.c.	0.28	+++	s	sm u
PI-8	0.57	0.71	2.51	0.69	0.12	0.07	7	4	204	0.02	l.i.	s	sm u
SB-32	0.64	0.75	4.17	0.81	0.09	0.19	5	70	1435	0.05	l.i.	u	s u
Oligocene–lower Miocene													
Go-2	0.70	0.79	4.49	0.85	0.07	0.16	24	n.c.	n.c.	0.04	l.i.	s	sm u
Ha-6	0.62	0.74	2.89	0.72	0.11	0.12	22	18	484	0.04	l.i.	vs	sm u
Dukla nappe													
Upper Cretaceous–Palaeocene													
Le-2	1.05	1.00	13.40	14.01	0.08	0.65	204	<1	9	0.02	l.i.	u	m min
Upper Oligocene													
SI-13	1.03	0.99	8.55	2.97	0.08	0.46	850	2	132	0.02	+	u	m u
S-KI	1.24	1.11	10.8	1.30	0.11	0.99	9	7	711	0.01	l.i.	vs	sm u
Magura nappe													
Upper Cretaceous–Palaeocene													
S-Li	0.71	0.80	2.77	0.71	0.11	0.39	6	110	2724	0.04	l.i.	m	s u
S-Sa/1	0.65	0.76	1.87	0.65	0.10	0.11	10	0.6	101	0.01	l.i.	sm	m u
S-Sa/2	0.55	0.70	–	–	–	–	–	–	–	–	–	–	–
Sa	0.48	0.66	–	–	–	–	–	–	–	–	–	–	–
S/Sy/1	0.63	0.75	1.68	0.63	0.12	0.13	17	11	844	0.01	+	m	sm u
S-Sy/2	0.51	0.68	1.63	0.63	–	–	–	–	–	–	–	–	–
Sy	0.44	0.63	2.90	0.72	–	–	–	–	–	–	–	–	–

MPII = 1.5(2MP + 3MP)/(Phen + IMP + 9MP), MP methylphenanthrene, Phen phenanthrene, $R_{cal(MPII)}$ 0.6(MPII) + 0.37, MDR 4-MDBT/1-MDBT, MDRBT methylbenzothiophene, $R_{cal(MDR)}$ 0.073MDR + 0.51, DBT dibenzothiophene, TA(I) ($C_{20} + C_{21}$) triaromatic steroids, TA(II) ($C_{26} + C_{27} + C_{28}$) triaromatic steroids, Naph naphthalene, MN methyl naphthalene, DMN dimethyl naphthalene, + present, +++ significant abundant, l.i. low intensity, BIOD* biodegradation after criteria of Wenger et al. (2002), WW** water washing after criteria of the current study, EF*** evaporative fractionation after criteria of Thompson (1987), u unchanged, vs very slight, s slight, sm slight-moderate, m moderate, sig significant, min minimal, n.c. not calculated

4 (Pl-8 and SB-32 wells, Kryg-Libusza-Lipinki field) to 27 (S-Ta seep), as well as 91 and 96, respectively (Table 9).

In all studied gas accumulations, N₂ and CO₂ occur in insignificant contents and their concentrations vary from 0.83 to 2.79 vol% and 0.04–2.26 vol%, respectively (Table 8). High concentration of molecular nitrogen found in two dug-wells (23.2 and 35.7 vol%) of subsurface gases in Quaternary sediments Leśniówka-2 well (Table 8). The concentration of helium is very low from 0.00 up to 0.02 vol%. Molecular hydrogen occurs only in one gas sample (0.02 vol%) from Leśniówka-2 well (Limanowa-Słupnice field), and in two dug-wells (0.04 and 0.05 vol%) of subsurface gases in Quaternary sediments Leśniówka-2 well (Table 8).

Stable carbon isotope composition of CH₄, C₂H₆, C₃H₈, *i*-C₄H₁₀, *n*-C₄H₁₀, *i*-C₅H₁₂, *n*-C₅H₁₂ and CO₂ as well as stable hydrogen isotope composition of CH₄, C₂H₆ and C₃H₈ are presented in Table 9. The stable hydrogen analyses of ethane and propane obtained in our current study were among the first applied in natural gas in Poland. Stable hydrogen isotope composition of ethane and propane range as follows (Table 9): $\delta^2\text{H}(\text{C}_2\text{H}_6)$ from – 188 (Ha-6 well, Fellnerówka-Hanka) to – 124‰ (DI-25 and DI-51 wells, Biecz), and

$\delta^2\text{H}(\text{C}_3\text{H}_8)$ from – 185 (Ha-6 well, Fellnerówka-Hanka) to – 114‰ (DI-51 wells, Biecz).

Discussion

Oil

Origin

For the evaluation of oil origin results of bulk oil analyses, distribution of biomarkers and stable carbon isotope composition were applied. The sulphur concentration below 0.5 wt%, mostly at gravities below 40 °API suggests a connection of the analysed oils with the low-sulphur type II kerogen (Orr 2001). However, generation from type III or type I kerogen is also possible (Duan et al. 2009). The CPI values above 1.0 indicate that shales are the dominating source of rock lithology (Moldowan et al. 1985). The above suggestion is supported by the V/(V + Ni) values ranging from 0.06 to 0.10 (Lewan 1984). Also values of saturate/aromatics ratio ranging from 1.5 to 26.7 (average 5.1, Table 4) suggest the

Table 8 Molecular composition of natural gas from analysed wells and seeps

Sample code	Molecular composition (vol%)														O ₂
	He	H ₂	N ₂	CO ₂	Alkanes										
					CH ₄	C ₂ H ₆	C ₃ H ₈	<i>i</i> -C ₄	<i>n</i> -C ₄	<i>neo</i> -C ₅	<i>iso</i> -C ₅	<i>n</i> -C ₅	C ₆	C7	
Silesian nappe															
Upper Cretaceous–Palaeocene															
DI-25	0.01	0.00	0.83	0.75	90.6	3.83	1.50	0.39	0.60	0.04	0.35	0.31	0.52	0.33	0.00
DI-51	0.00	0.00	0.83	1.08	87.0	5.94	3.21	0.71	0.66	0.02	0.27	0.18	0.04	0.01	1.51
WI-15	0.01	0.00	0.24	2.26	78.0	5.48	6.65	2.26	3.04	0.05	1.06	0.71	0.13	0.07	0.00
Palaeocene–Eocene															
PI-8	0.00	0.00	2.79	1.91	71.1	10.07	7.35	1.52	3.11	0.06	0.94	0.76	0.30	0.05	0.00
SB-32	0.01	0.00	0.95	0.73	72.6	10.44	8.35	1.68	3.38	0.08	1.00	0.84	0.00	0.00	0.10
Oligocene–lower Miocene															
Ha-6	0.01	0.00	1.11	0.47	79.9	5.07	6.66	1.41	3.53	0.07	0.87	0.72	0.12	0.02	1.39
Dukla nappe															
Upper Cretaceous–Palaeocene															
Le-2 ^a	0.01	0.02	1.40	0.09	86.3	7.34	3.35	0.41	0.73	n.a.	0.37		0.07	0.00	0.00
Magura nappe															
Quaternary															
Le/6	0.00	0.05	23.2	0.97	74.8	0.66	0.16	0.04	0.031	0.00	0.02	0.02	0.00	0.00	19.2
Le/21	0.00	0.04	35.7	1.01	62.5	0.51	0.14	0.03	0.033	0.00	0.02	0.02	0.00	0.00	19.1
Upper Cretaceous–Palaeocene															
S-Li	0.00	0.00	1.85	1.43	89.9	4.14	1.83	0.40	0.35	0.00	0.08	0.02	0.01	0.00	3.14
Lower Eocene															
S-Ta	0.02	0.00	1.61	0.04	94.4	2.58	0.86	0.18	0.16	0.00	0.05	0.03	0.01	0.01	0.49

O₂ concentration (vol%) in sampled gas; sum of He + H₂ + N₂ + CO₂ + alkanes = 100 (vol%) without O₂ and N₂ excessive, N₂ excessive = (N₂ atmospheric/O₂ atmospheric) O₂ meas. (vol.%) = 3.73 O₂ measured (vol%)

^aData from Kotarba et al. (2017)

Table 9 Molecular indices and stable isotope composition of natural gas from analysed wells and seeps

Well code	Indices	Stable isotopes (‰)										Processes of gas generation and biodegradation							
		C _{HC}	C ₁ /C ₂	C ₂ /C ₃	C ₃ /C ₄ + i-C ₄ /n-C ₄	CDMI	CDHI	δ ¹³ C (CH ₄)	δ ² H (CH ₄)	δ ¹³ C (C ₂ H ₆)	δ ² H (C ₂ H ₆)		δ ¹³ C (C ₃ H ₈)	δ ² H (C ₃ H ₈)	δ ¹³ C (i-C ₄ H ₁₀)	δ ¹³ C (n-C ₄ H ₁₀)	δ ¹³ C (i-C ₃ H ₁₂)	δ ¹³ C (n-C ₃ H ₁₂)	δ ¹³ C (CO ₂)
Silesian nappe																			
Upper Cretaceous–Palaeocene																			
DI-25	17	24	2.56	0.59	0.65	0.82	0.76	−43.8	−179	−27.3	−124	−26.0	−114	−25.5	−24.9	−25.1	−24.5	−4.7	TG
DI-51	10	15	1.85	1.69	1.08	1.23	1.09	−37.7	−160	−27.5	−124	−26.1	−119	−25.7	−25.3	−25.4	−24.8	−13.7	TG
WI-15	6	14	0.82	0.91	0.75	2.81	2.27	−47.6	−212	−30.2	−151	−28.1	−143	−28.5	−27.9	−28.1	−27.2	1.3	TG and possible SMM
Palaeocene–Eocene																			
PI-8	4	7	1.37	1.09	0.49	2.62	1.97	−45.3	−184	−30.4	−159	−29.9	−157	−28.9	−29.3	−27.4	−28.5	−6.2	TG
SB-32	4	7	1.25	1.20	0.50	1.00	0.74	−43.0	−184	−30.6	−155	−29.6	−150	−29.3	−28.6	−28.0	−28.1	−9.6	TG
Oligocene–lower Miocene																			
Ha-6	7	16	0.76	0.99	0.40	0.58	0.47	−58.8	−189	−34.5	−188	−31.2	−185	−31.3	−29.5	−28.6	−28.3	−0.6	PMM and TG
Dukla nappe																			
Upper Cretaceous–Palaeocene																			
Le-2 ^a	8	12	2.19	2.12	0.56	0.1	0.09	−37.5	−156	−26.8	n.a.	−25.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	TG
Magura nappe																			
Quaternary																			
Le/6	91	113	4.13	1.14	1.28	1.26	1.58	−33.8	−144	−24.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−15.5	TG
Le/21	96	123	3.62	0.98	1.59	1.57	1.27	−33.9	−143	−23.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−14.5	TG
Upper Cretaceous–Palaeocene																			
S-Li	15	22	2.26	2.15	1.14	1.56	1.45	−48.6	−243	−31.2	−153	−27.1	−116	−28.7	−25.5	−26.6	−24.9	−4.9	TG
Lower Eocene																			
S-Ta	27	37	2.99	1.94	1.13	0.04	0.04	−58.1	−177	−31.9	−151	−26.9	−116	−27.7	−25.7	−26.1	−25.3	n.a.	PMM and TG

$C_{HC} = CH_4/(C_2H_6 + C_3H_8)$; $C_1/C_2 = CH_4/C_2H_6$; $C_2/C_3 = C_2H_6/C_3H_8$; $C_3/C_{4+} = C_3H_8/(i-C_4H_{10} + n-C_4H_{10} + C_5 + C_6 + C_7)$; $C_1 = CH_4$; $C_2 = C_2H_6$; $i-C_4 = i-C_4H_{10}$; $n-C_4 = n-C_4H_{10}$; CDMI = $(CO_2/[CO_2 + CH_4])100$ (%); CDHI = $(CO_2/[CO_2 + \Sigma(C_1-C_7)])100$ (%)

TG thermogenic gas, PMM primary microbial methane, SMM secondary microbial methane, n.a. not analysed

^aData from Kotarba et al. (2017)

generation of hydrocarbons from organic matter present in shales (Palacas 1984). Some oils are characterised by a reduced range of *n*-alkanes and higher *iso*-alkanes concentrations (Fig. 5a, b). In two samples (S-Li and S-Sa/1 from the Magura nappe), the concentrations of *n*-alkanes relative to the sum of *n*-alkanes, *iso*-alkanes and steranes + terpanes are very low and do not exceed 2% (Table 6). Correspondingly, the last-mentioned oil (S-Sa/1) is characterised by the highest relative concentrations of steranes and terpanes (13%) (Table 6). It is an effect of biodegradation, which is widely described in chapter about secondary processes. The $C_{24}t/C_{23}t$ and $C_{22}t/C_{21}t$ tricyclic terpane ratios above 0.5 and below 0.5, respectively, indicate that all oils were generated from organic matter deposited in marine shales (Peters et al. 2005, p. 558). Both indices' narrow ranges suggest a common source or sources containing the same organic material deposited in similar conditions. The prevalence of siliciclastics in the mineral matrix of the source rocks is also supported by low values of the C_{29} norhopane/ 17α hopane ratio (less than 0.5) and C_{35}/C_{34} ratio (below 1.0), and high values of C_{27} dia/(dia + reg) ratio, up to about 0.7 (Table 6) (ten Haven et al. 1988).

The $Pr/n-C_{17}$ and $Ph/n-C_{18}$ ratios range from 0.99 to 24.4 and from 0.42 to 29.8, respectively. Oils from S-Li and

S-Sa/1 seeps have the highest values of these ratios. A set of indices calculated based on C_6 – C_8 hydrocarbons distribution is presented in Table 5. These indices have similar values for most oils collected from producing wells and are distinctly different for oils from seeps. Distributions of *n*-alkanes are variable, usually mono-modal, with a distinct maximum in the short-chain range (C_8 – C_{11} , Fig. 5c), characteristic of hydrocarbons generated from marine organic matter (e.g., Bourbonniere and Meyers 1996). Visible irregularities are the result of secondary processes to be discussed later (Fig. 5a, b). The mono-modal distribution of *n*-alkanes may also result from increased maturity and/or fractionation during migration. The correlation of the $Pr/n-C_{17}$ and $Ph/n-C_{18}$ indices (Fig. 6) simultaneously suggests that mixed terrestrial and marine kerogen is responsible for the generation of analysed oils. The conclusions about II/III type kerogen are supported by the interpretation of the isoheptane (IHR) and heptane (HR) ratios (Fig. 7a). The highest share of the terrigenous organic matter in the source kerogen is indicated for oil from the Biecz (DI-25 and DI-51), Limanowa-Słupnice (Le-2) and Kłęczany fields (S-K1). The interpretation of some oils' origin (PI-8, S-Sy/1, S-Sa/1 and WI-15) in Fig. 8a may be erroneous due to biodegradation processes affecting the composition of hydrocarbons. The canonical

Fig. 5 a–c Examples of GC-FID whole oil chromatograms and a'–c' GC-MS chromatograms ($m/z = 142, 156, 170$ and 184) of aromatic hydrocarbon fraction of selected oils samples **a** and **a'** S-Li, **b** and **b'** S-Sy/1 and **c** and **c'** PI-8 representing different levels of biodegradation and water washing, respectively. Numbers refer to the quantity of carbon atoms in alkane or isoprenoid chain, *Pr* pristane, *Ph* phytane, *MN* methylnaphthalenes, *DMN* dimethylnaphthalenes, *TriMN* trimethylnaphthalenes, *TetMN* tetramethylnaphthalenes

variable (CV) values below 0.47 (Sofer 1984) indicate that analysed oils were generated from marine kerogen (Table 4). Dibenzo thiophene/phenanthrene and pristane/phytane (Pr/Ph) ratios identify the depositional environment of source rocks primarily as marine or lacustrine shales deposited under the anoxic/non-sulfidic conditions based on the criteria of Hughes et al. (1995). Gammacerane widely occurs in the analysed oils in low concentrations (Table 6), as noted in previous studies (ten Haven et al. 1993; Matyasik and Dziadzio 2006). It indicates that a stratified water column in source-rock depositional environments was not present (Sinninghe Damsté et al. 1995).

The distribution of C_{27} , C_{28} and C_{29} regular $5\alpha, 14\alpha, 17\alpha(H)$ -20R steranes in the crude oils is routinely used for identifying their source organic matter (Huang and Meinschein 1979). Generally, the relative proportion of sterane carbon numbers in the analysed oils indicates a mixture of marine plankton and land plants as the source of organic matter. Values of the analysed oils' sterane/terpane ratio (S/T) are usually in a narrow range of 0.26–0.45 (Table 6). It suggests that they come from a source rock enriched in terrigenous and/or reworked material (e.g., Moldowan et al. 1985). This conclusion is supported by mainly low values of the tricyclic/pentacyclic terpane ratio (Table 6). However, low values of this ratio are also found in freshwater depositional environments (Tao et al. 2015). The elevated values of this index, up to 0.75, are observed in oils accumulated in Dukla nappe and are connected with their increased maturity (Peters et al. 1990). The Carpathian fine-grained rocks (especially Oligocene Menilite and Krosno beds) often contain allochthonous, reworked organic material (Zielińska 2017; Waliczek et al. 2019) from eroded Pennsylvanian-age rocks. These particles' contribution to the organic matter mass is variable and decreases with total organic carbon content (Zielińska et al. 2020). In all oils collected from Silesian and Magurs nappes, β -carotane was identified (Table 6). The presence of this biomarker suggests a saline lacustrine or highly restricted marine depositional setting (Peters et al. 2005). In many oils, also isorenieratane, the β -carotene diagenesis product (Koopmans et al. 1996) was recorded (Table 7). The stable carbon isotope composition of the crude oils and their fractions (Table 4) generally support the biomarker data. They indicate that the analysed oils were generated from the same genetic type of kerogen. In most oils, asphaltenes are depleted in ^{13}C isotope relative to resins, which is characteristic of oil generated from algal kerogen (Galimov 2006). Because the aromatic hydrocarbon and asphaltene fractions are more resistant to biodegradation (Sun et al. 2005), the oil-oil correlation is more reliable using the stable carbon isotope composition of these fractions. Asphaltenes of all oils accumulated in the Silesian nappe show a narrow range of $\delta^{13}C$ values ($-27.5 \pm 1\text{‰}$), suggesting one common source. Visible enrichment in ^{13}C of

Fig. 6 Pristane/ $n\text{-}C_{17}H_{36}$ versus phytane/ $n\text{-}C_{18}H_{38}$ for genetic characterization of oils (after Shanmugam 1985). For oil codes and symbols, see Table 3. Previously analysed samples after ten Haven et al. (1993), Więclaw (2002) and Matyasik and Dziadzio (2006)

oils (and their fractions) accumulated in Dukla and Magura nappes suggests their genetic relation. It indicates a higher share of terrigenous material in source organic matter. The presence of oleanane in all oils (Table 6), a biomarker derived from angiosperms widely occurring in Cretaceous or younger organic matter (Ekweozor and Udo 1988), points to organic-rich Oligocene Menilite beds and Upper Cretaceous-Palaeocene Istebna shales (Matyasik and Dziadzio 2006) as the most probable source rocks.

Maturity

The maturity of crude oils was determined based on the composition of light hydrocarbons (Table 5), selected biomarkers (Table 6), and indices calculated from relative concentrations of phenanthrene (Phen) and dibenzothiophene (DBT) and their methyl derivatives, as well as triaromatic steroids (Table 7).

The distribution of methylphenanthrenes (MP) reveals a wide range of oil maturity. The methyl phenanthrene index (MPI1) (Radke et al. 1982) indicates generation from early mature to the late phase of the oil window (calculated vitrinite reflectance, $R_{cal(MPI1)}$ from 0.63 to 1.13%) (Table 5 and Więclaw 2002). The methyldibenzothiophene ratio (MDR) maturity index (Radke et al. 1986) generally confirms the same range of oil maturities (Table 7 and Więclaw 2002). Some discrepancies between the measured values, e.g., Le-2 and SI-13, may be related to the impact of biodegradation and water washing on MDBT isomers' distribution (Ugochukwu et al. 2014).

Fig. 7 **a** Heptane ratio and **b** toluene/*n*-heptane ratio versus isohexane ratio. Kerogen type curves and maturity ranges after Thompson (1983). For oil codes and symbols, see Table 3. Oils collected from seeps are marked by symbols with thick outline

The distribution of steranes is dominated in sample Jo-44 by $\alpha\alpha\alpha 20R$ -isomers (Fig. 8e) and change to domination of $\alpha\beta\beta$ -isomers in Le-2 (Fig. 8a). Moreover, the increasing role of tricyclic terpanes in the distribution of terpanes from sample Jo-44 (Fig. 8e') to Le-2 (Fig. 8a') is also visible. It indicates that analysed oils were generated from the organic matter at different maturities consistent with initial phase to peak of the “oil window”. The $C_{29}20S/(20S + 20R)$ and $C_{29}\beta\beta(\beta\beta + \alpha\alpha)$ sterane ratios show that the lowest maturity oil is the F-8 sample (Fig. 9) and the highest—oils collected from Słupnice and Klęczany fields. The plot of the $C_{29}\beta\beta(\beta\beta + \alpha\alpha)$ ratio versus the $20S/(20S + 20R)$ ratio for the C_{29} steranes (Fig. 9b) shows that the variability of analysed samples' maturity from early mature to peak of the “oil window” generally confirms conclusions from the MPI and MDR interpretation.

The relation between the stigmasterane and sum of 3- and 4-methyldiamantane concentration (Fig. 10a) after categories of Dahl et al. (1999) indicates that oils from the Limanowa-Słupnice field and Klęczany seep are at the initial stage of the cracking process. Oils from the Biecz field (DI-25 and DI-51) contain elevated amounts of methyldiamantanes and simultaneously high stigmasterane concentrations. It suggests that they are mixtures of high-mature cracked and low-mature uncracked oils. Maturity indices calculated based on triaromatic steroids distribution are effective even for oils with extensive water washing (Chang et al. 2018) and highly sensitive, especially for high maturity samples (Mackenzie et al. 1981). Heating experiments of Beach et al. (1989) indicate that the $TA(I)/TA(I + II)$ ratio (Table 7, Fig. 10b, c) increases due to preferential degradation of the long-chain triaromatic homologs rather than due to the conversion of long to short-chain homologs. The highest maturities, above 1.0% in Ro scale (based on MPI1, sterane and $TA(I)/TA(I + II)$ indices), were recorded for oils accumulated in the Dukla nappe (Limanowa-Słupnice and Klęczany fields and oil outflows in Karczyńska, Pod Rosochatką and Stara Wieś) (Tables 6, 7, Więclaw 2002; ten Haven et al. 1993).

Secondary processes

The physical and geochemical properties of migrating oil or oil accumulated in a field may be changed by secondary processes, such as biodegradation, fractional evaporation, cracking or water-washing (e.g., Connan 1984; Thompson 1983, 2010; Palmer 1984, 1993).

In the Magura nappe, a total of three insignificant oil and gas fields have been discovered (presently abandoned, Table 2). Most of the analysed oil from seeps occur in the Magura nappe (Table 3). In this tectonic unit's lithostratigraphic profile, Oligocene Menilite beds are characterised by poor source indices, and other source rocks do not occur (e.g., Sachsenhofer et al. 2017). Oil and natural gas migrated to traps in the Magura nappe from the Dukla and Silesian nappes and flew out to the surface, creating seeps, got partly oxidised or escaped to the atmosphere (Fig. 3).

Crude oil deposits in the Outer Carpathians have very favourable conditions for microbial activity due to reservoir temperatures, generally up to 55 °C (Karnkowski, 1999), and the introduction of water in the traps. Marcinkowski and Szewczyk (2008) reported that the extraction of water from oil fields in the eastern part of the Silesian nappe of the Polish Carpathians was sometimes four times higher than oil production. The highest water/oil ratio values were recorded for the shallowest traps within the Oligocene–lower Miocene Krosno beds (Marcinkowski and Szewczyk 2008).

The simplest and most sensitive method for identifying and estimating the extent of secondary processes is the

Fig. 8 Distribution of **a–e** steranes ($m/z=217$) and **a'–e'** terpanes ($m/z=191$) in selected oil samples **a** and **a'** Le-2, **b** and **b'** S-Kl, **c** and **c'** Sl-13, **d** and **d'** Dl-51 and **e** and **e'** Jo-44 representing different levels of maturity. *IS* internal standard

Fig. 9 Sterane $C_{29}20S/$ ($20S + 20R$) ratio versus **a** $Ts/(Ts + Tm)$ and **b** $C_{29}\beta\beta/(\beta\beta + \alpha\alpha)$ ratios for oils. Maturity fields after Peters and Moldowan (1993). For oil codes and symbols, see Table 3. Previously analysed samples after ten Haven et al. (1993) and Matyasik and Dziadzio (2006)

Fig. 10 Concentration of stigmastane versus **a** sum of 3- and 4-methyldiamantane after Dahl et al. (1999), **b** $TA(I)/TA(I + II)$ ratio and **c** oleanane/ 17α hopane ratio versus $TA(I)/TA(I + II)$ ratio. Maturity ranges after Peters et al. (2005)

complete oil GC analysis and the examination of the distribution of *n*-alkanes, *iso*-alkanes, acyclic isoprenoids, and short-chain hydrocarbons (C_6 – C_8) (Halpern 1995; Thompson 1987; Wenger et al. 2002; Więclaw et al. 2020). The PI-8 chromatogram presents a full range of *n*-alkanes and low content of isoprenoids (Fig. 5c). According to Wenger et al. (2002), this type of distribution is characteristic of

non-biodegraded oils. More extensive biodegradation causes a reduction in the range and relative concentration of *n*-alkanes, first revealed in Carpathian oils by Gondok and Pomykała (1982). At very slight biodegradation levels (Wenger et al. 2002), the relative concentrations of pristane and phytane (acyclic isoprenoids) are comparable with the neighbouring *n*-alkanes. Slight biodegradation results in

the domination of isoprenoids over neighbouring *n*-alkanes (Fig. 5b) and a “hump” representing an unresolved complex mixture (Wenger et al. 2002). The increased biodegradation level (moderate level) significantly reduces the concentration of *n*-alkanes, causing raised values of the $Pr/n-C_{17}$ and $Ph/n-C_{18}$ ratios (Table 5, Figs. 5a, 6). The increase in the extent of biodegradation to the heavy level results in the elimination (decomposition) of acyclic isoprenoids (Wenger et al. 2002). None of the oils in this study have reached this level of biodegradation. The above-mentioned hydrocarbon groups are not affected and the ratio of C_{29} 25-norhopane (biomarker created as a product of biodegradation of C_{30} hopane, Peters et al. 1996) to C_{30} hopane of the oils is low (Table 6).

In this study, the level of biodegradation is illustrated quantitatively by the relative proportions of *n*-alkanes, *iso*-alkanes, and steranes plus hopanes (Table 6, Fig. 11). It is useful if the extent of biodegradation is not severe (steranes and hopanes remain unaltered, Więclaw et al. 2020).

In the case of crude oil from the Biecz field (samples DI-25 and DI-51), significant differences in biodegradation level are observed (Table 6, Figs. 7, 11), although the accumulation depths are similar. The DI-51 oil comes from the deepest SW tectonic element of the deposit (Fig. 1b). The other crude oil (DI-25) comes from a shallower element located on another tectonic block. This may mean that the migration of fluids takes place in the SE–NW direction, and the pathways through which microorganisms enter the beds are S–N faults (Fig. 1d).

According to Thompson's (1987) criteria (Fig. 7), the highest biodegradation level was recorded in oils from PI-8 well and S-Sa/1 and S-Sy/1 seeps. This conclusion is consistent with the biodegradation evaluation by other criteria for oils collected from seeps (Table 5 and Figs. 5, 11), whereas the oil PI-8 is not biodegraded and probably water washing (Fig. 5c) influenced the distribution of C_7 hydrocarbons.

Because the higher density is generally associated with biodegraded oils (Baskin and Peters, 1992), the highest density oil, S-Sy/1 (0.903 g/cm³, 24.5 °API, Table 4), should be heavily degraded. This oil is evaluated in Wenger's et al. (2002) criteria as only slightly biodegraded. This sample was taken from a seep and the evaporation of low boiling-point compounds (Fig. 5b) has caused the lowering of the API gravity. Two other oils from seeps: S-Li and S-Sa/1, also have low gravities and are biodegraded (Fig. 5). The sulphur content of the analysed oils varies from traces in S-Kl to 0.27 wt% for oil from the PI-8 well (Table 4). Because all biodegraded and non-biodegraded oils in this study have low sulphur concentrations, this parameter does not correlate with biodegradation level. However, Więclaw (2002) found a significant increase in the sulphur content during biodegradation of crude oil from seeps in Stara Wieś (S-SW/1 and S-SW/2), Pod Rosochatką (S-PR/1 and

S-PR/2) and Karczyska (S-Ka/1 and S-Ka/2). The content of the saturated hydrocarbon fraction in the analysed oils is consistent with the level of biodegradation. Non-biodegraded oils have $\pm 70\%$ aliphatic hydrocarbons on average and biodegraded oils have $\pm 55\%$ (Table 4). Lowered values of saturates/aromatics ratio are observed in oils with elevated biodegradation levels (Table 4).

To sum up, the extent of biodegradation ranges from non-degraded to moderately degraded. The most degraded oils occur in seeps S-Li and S-Sa (upper Cretaceous–Palaeocene Ropianka Formation).

A significant reduction in the concentration of methyl-naphthalenes (MN) and dimethylnaphthalenes (DMN) in the aromatic fraction of oil and simultaneously a decrease in naphthalene/phenanthrene (Naph/Phen) and methyl-naphthalenes/dimethylnaphthalenes ($\Sigma MN/\Sigma DMN$) ratios indicate an increased extent of water washing due to differences of water solubility of the mentioned hydrocarbons (Forsythe et al. 2017). The highest content of MN and DMN and highest values of Naph/Phen and $\Sigma MN/\Sigma DMN$ ratios are recorded for oils from the WI-15 and SB-32 wells and S-Li seep. It suggests that these oils undergo the water washing process on a reduced scale (Fig. 12). The other oils have probably experienced water washing, with the most significant extent of this process recorded in the SI-13 and Le-2 oils (Fig. 12). However, Mikołajewski et al. (2019) evidenced that the migration process also controls the relative abundance of MN and DMN. In the Outer Carpathian region, shallow deposits have had significant water exposure due to the long exploitation history and rising of the oil–water contact (Dziadzio et al. 2006; Marcinkowski and

Fig. 11 Ternary diagram of relative concentrations of sum of *iso*-alkanes, sum of *n*-alkanes and sum of steranes and terpanes. For oil codes and symbols, see Table 3

Szewczyk 2008). Thus widespread water washing is not surprising.

Analysing relationships between concentrations of the above-mentioned aromatic hydrocarbons and calculated ratios (Fig. 12), two populations are different in the concentrations of MN and DMN. Oil characterised by MN concentration below 5 ppm is evaluated as significantly water washed (S-Sa/1, SI-13 and Le-2). The remaining oils were evaluated as being subjected to minimal water-washing.

In all analysed oils, methylcyclohexane (MCH) dominates over *n*-heptane resulting in the *n*-heptane/MCH ratio values from 0.14 to 0.48 (Table 5). Compared with elevated values of toluene/*n*-heptane ratio (usually above 1.0), these values indicate that all the oils have experienced evaporative fractionation (Thompson 1987; Holba et al. 1996). A significant evaporative fractionation developed in oils from DI-25 and DI-51 wells in Biecz field and Le-2 in Limanowa-Słopnice field (Fig. 7b). For the rest of the analysed oils, the evaporative fractionation process has been minimal (early phase of fractionation and possible biodegradation, according to Thompson (1987) and Holba et al. (1996). The extent of evaporative fractionation in oils collected from seeps in Magura nappe is hard to evaluate due to the biodegradation or evaporation of the low-boiling compounds (Table 5). Concluding, the evaporative fractionation processes occur in all reservoirs of the study area, most significantly in the deepest parts of the selected multi-horizontal Biecz field.

Natural gas

Hydrocarbon gases

Stable carbon and hydrogen isotope and molecular compositions evidence the existence of two genetic groups of hydrocarbon gases—microbial and thermogenic ones, as shown on diagrams on Fig. 13. Microbial and thermogenic gases occur regardless their accumulation type in a particular nappe or reservoir (Fig. 13). Thermogenic gases were mainly produced from a source rock with the prevailing type III or mixed type II/III and III/II kerogen at maturity stages representing the whole stage of the “oil window” (Fig. 13). Natural gas in samples Le/6 and Le/21 collected from near-surface zone near Le-2 well does not contain microbial admixture as might be expected. Its molecular and isotopic signatures indicate that it comes from the same accumulation as natural gas exploited by Le-2 well (Figs. 13, 14a). The geochemical data indicate that the near surface zone adjacent to the well is supplied only by natural gas escaping from the accumulation Limanowa-Słopnice located within the reservoir in the Dukla nappe in the depth below 4000 m due to a leaky cementing of the lining pipe. Natural gas from this accumulation was produced from organic matter of mixed type and shows the highest maturity (Fig. 14). Maturity

Fig. 12 Concentration of dimethylnaphthalenes versus concentration of methylnaphthalenes in oils for estimation of water washing extent. For oil codes and symbols, see Table 3

curves constructed after Berner and Faber (1996, 1997) for two different types of kerogen: type II ($\delta^{13}\text{C} = -28.6\text{‰}$) and III ($\delta^{13}\text{C} = -24.6\text{‰}$) (Kotarba et al. 2017) confirm that thermogenic gases in the study area were produced during the whole stage of “oil window” assuming type II kerogen (Fig. 14). If type II kerogen contribution was highest, they might have been produced even during the “gas window” stage, but the common presence of C^{2+} hydrocarbons (Table 8) rather preclude the late mature thermogenic gas (Fig. 14). A normal isotopic trend of $\delta^{13}\text{C}$ values is observed in all analysed gases as evidenced in the diagram plotting stable carbon isotope composition of hydrocarbon gases versus the reciprocal of their carbon number constructed after Chung et al. (1988) (Fig. 15). This isotopic order indicates the simple generation (Zou et al. 2007), migration and accumulation processes of studied gases. $\delta^{13}\text{C}$ values of butanes and pentanes reflect their source related to types III, II and mixed kerogens. The shifts of $\delta^{13}\text{C}$ values of methane and ethane, especially demonstrated by gases from Go-11, Go-8 and He-4 wells are the evidence of microbial admixture (Fig. 15). Stable hydrogen isotope pattern of methane, ethane and propane data are uniform for analysed gases indicating similar thermogenic generation history. Methane from S-Li seep and WI-15 well is enriched in ^1H isotope due to microbial input (Fig. 16). Exceptional $\delta^2\text{H}$ arrangement shows natural gas from Ha-6 well in which methane, ethane and propane have very similar values. Relative ^2H enrichment in methane may be caused by gas diffusive migration changing original isotopic ratio (e.g., Qilin 2012). Natural gas in this field most likely contained more microbial components, but due to gas diffusion isotopically light methane

Fig. 13 Genetic characterization and influence of secondary processes of analysed natural gases using $\delta^{13}\text{C}(\text{CH}_4)$ versus **a** a hydrocarbon index (C_{HC}) and **b** $\delta^2\text{H}(\text{CH}_4)$. Compositional fields and arrow directions of maturity and secondary processes after Whiticar (1994) and Milkov and Etiope (2018). Key for sample codes, see Table 3 and previously analysed samples, see Kotarba et al. (2017). CR CO₂ reduction, F methyl-type fermentation, SM secondary microbial, EMT early mature thermogenic gas, OA oil-associated thermogenic gas, LMT late mature thermogenic gas, BIOD. biodegradation, Up. upper, Cret. Cretaceous, Quat. Quaternary

escaped more easily. This conclusion is also supported by relatively low ethane (5.07 vol%) concentration compared to propane (6.66 vol%) and ²H-enriched ethane compared to methane (Fig. 16), which can result from ethane diffusion from reservoir gas. Microbial gases without thermogenic addition occur in previously investigated accumulations (Kotarba 1992; Kotarba et al. 2009, 2013, 2017): Gorlice-Glinik (Go-11 well), Kobylanka (Go-8 well) and Szalowa-Heddy-Bystra (He-4 well) fields and Dołuszyce (De-4 and De-6) uneconomic accumulations of the Silesian nappe. Their isotopic similarity suggests a common origin from a comparable source rock, however natural gas in Dołuszyce uneconomic accumulation most likely is derived from the autochthonous Miocene strata of the Carpathian Foredeep and migrated to the Silesian nappe of the Outer Carpathians due to a privileged tectonic setting (Kotarba 1992; Kotarba et al. 2017). Relatively high microbial admixture is observed in Ha-6 well and S-Ta seep of Silesian and Magura nappes,

respectively (Fig. 13b). Similarly, both molecular and isotopic signatures of microbial gases suggest the uniform generation processes related to microbial CO₂ reduction (Fig. 13).

Natural gas in the study area does not show manifestations of biodegradation (Table 9, Figs. 13, 16, 17) as evidenced by low *i*-C₄/*n*-C₄ values below 1.2, and neither ¹³C nor ²H enrichments in individual hydrocarbon components and also no distinct ¹³C enrichment of carbon dioxide (e.g., Pallasser 2000; Milkov 2011; Kotarba et al. 2019, 2020a). Natural gas from WI-15 well of the Dominikowice-Kobylanka field is the only gas showing positive ¹³C values CO₂ which may result from the secondary microbial methane production (Table 9, Fig. 17).

Natural gas was generated from source rock of Oligocene Menilite beds in Dukla and Silesian nappes, then migrated through fissure zones of overthrusts and porous-sandstones and filled traps in the Magura nappe (Fig. 3).

Fig. 14 Genetic characterization of analysed natural gases using $\delta^3\text{C}(\text{C}_2\text{H}_6)$ versus **a** $\delta^{13}\text{C}(\text{CH}_4)$ and **b** $\delta^{13}\text{C}(\text{C}_3\text{H}_8)$. Vitrinite reflectance curves (R_o) for Type II and III kerogen after Berner and Faber (1996) based on average $\delta^{13}\text{C}$ data for Type II (−28.6‰) and III (−24.6‰) kerogen in Oligocene Menilite beds after Kotarba et al. (2017). Key for gas samples codes and symbols, see Table 3. Previously analysed samples after Kotarba et al. (2017)

Fig. 15 Stable carbon isotope composition of methane, ethane, propane, *i*-butane, *n*-butane, *i*-pentane and *n*-pentane versus the reciprocal of their carbon number for analysed natural gases. In diagrams, the order of $\delta^{13}\text{C}$ values for CH_4 , C_2H_6 and C_3H_8 is after Chung et al. (1988). $\delta^{13}\text{C}$ data for Type II (-28.6‰) and III (-24.6‰) kerogen from the Oligocene Menilite beds after Kotarba et al. (2017). Key for gas samples codes and symbols, see Table 3. Previously analysed samples after Kotarba et al. (2017)

Fig. 16 Stable hydrogen isotope composition of methane, ethane and propane versus the reciprocal of their hydrogen number for analysed natural gases. Key for gas samples codes and symbols, see Table 3

Carbon dioxide

Carbon dioxide is a common component of natural gas accumulated in the Outer Carpathians natural gas fields (e.g.,

Fig. 17 Genetic characterization and influence of biodegradation of the analysed natural gases using **a** $\delta^{13}\text{C}(\text{CH}_4)$ and **b** C_{HC} gas hydrocarbon index versus $\delta^{13}\text{C}(\text{CO}_2)$. Compositional fields and directions of maturity and secondary processes for diagram **a** from Milkov and Etiope (2018) and for diagram **b** modified from Milkov (2011, 2018). Key for gas samples codes and symbols, see Table 3. Previously analysed samples after Kotarba et al. (2017)

Kotarba et al. 2013, 2014, 2017, 2019, 2020a, b; Więclaw et al. 2020). It occurs in all natural gas accumulations and seeps in the study area in concentrations varying from 0.04 to 2.26 vol%, and its $\delta^{13}\text{C}$ values change from -15.5 up to 1.3‰ (Table 9, Fig. 17 and Kotarba et al. 2013, 2017). According to the diagnostic criteria after Milkov and Etiope (2018), Milkov (2011, 2018) and Dai et al. (1996, 2005), such low concentrations of CO_2 accompanied by its negative

$\delta^{13}\text{C}$ values indicate its biogenic origin. CO_2 from W1-15 well showing $\delta^{13}\text{C}$ of 1.3‰ may be related to secondary CO_2 reduction (e.g., Milkov and Etiope 2018) or dissolution and precipitation processes involving reservoir CO_2 that change its primary isotopic signature, which may also be responsible for ^{13}C enrichment in CO_2 in samples D1-25, Ha-6 and S-Li. The effect of CO_2 isotopic fractionation can be also much easier observed in gases containing low concentrations of this component. The origin of CO_2 in the study area is connected with hydrocarbon gas generation associated both with the microbial and thermogenic processes. However, in this case, the thermogenic component prevails (Fig. 17a).

Conclusions

The results of organic geochemical analyses of oils, as well as molecular and isotopic compositions of natural gases associated or non-associated with oil that accumulated in the lower Cretaceous–lower Miocene strata of the Silesian, Dukla and Magura nappes in the study area between Kraków and Pilzno of the western part of the Polish sector of the Outer Carpathians, indicate that:

1. Oils and thermogenic hydrocarbon gases were generated from marine shales containing primarily type II kerogen with admixture III kerogen, and sometimes type I kerogen. The oils from the Dukla and Magura nappes (e.g., Biecz, Limanowa-Słupnica and Kłęczany deposits) were generated from organic matter with significant terrestrial admixture.
2. Oils were generated from early through the peak to late “oil window”. Secondary cracking was recorded in oils from Dukla nappe. Other secondary processes, including biodegradation, water washing and evaporative fractionation, were also developed in many oils to a different extent.
3. Analysed oils are non-degraded to moderately degraded. The most degraded oils occur in seep S-Li of the upper Cretaceous–Palaeocene Ropianka Formation (Magura nappe).
4. The most extensive water washing is observed in the oil from seep S-Sa/1 in Sękowa. The remaining oils were evaluated as being subjected to minimal water-washing.
5. The evaporative fractionation processes occur in all reservoirs of the study area, most significantly in the selected deepest parts of the multi-horizontal Biecz field.
6. Hydrocarbon gases are of biogenic origin related to both microbial and thermogenic processes. Hydrocarbon gases show similar stable carbon and hydrogen isotope compositions suggesting their common origin from a source rock with prevailing type mixed III/II and II/III kerogen at maturity levels corresponding to the whole range of “oil window”.
7. Molecular and isotopic compositions reveal that natural gas has not been distinctly subjected to biodegradation processes.
8. Carbon dioxide is derived from both microbial and thermogenic transformation processes of organic matter and was generated together with hydrocarbon gases.

Acknowledgements The research has been financially supported by the statutory fund of Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Kraków, Poland (no. 16.16.140.315). Sample collecting, and analytical and editorial works by Joanna Gawęda-Skrok, Tomasz Kowalski, Adam Kowalski, Henryk Sechman and Hieronim Zych from the Faculty of Geology, Geophysics and Environmental Protection of the AGH University of Science and Technology is kindly acknowledged. Dr. Juraj Francu from the Czech Geological Survey in Brno and anonymous reviewer provided constructive remarks and comments that greatly improved the discussion of our results. The authors would like to thank Erwin Szwasz and Marek Pietrusiak from the Polish Oil and Gas Company for help in sample collecting and providing archival information about oil and gas fields.

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