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Paleoenvironmental conditions, source and maturation of Neogene organic matter from the siliciclastic deposits of the Orava-Nowy Targ Basin

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A R T I C L E   I N F O

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A B S T R A C T

The Orava-Nowy Targ Basin (ONTB) is an intramontane depression filled with Neogene and Quaternary deposits located at the junction of the Inner and Outer Carpathians. The Neogene infill of the basin consists mainly of siliciclastic rocks with very common lignite intercalations and is mostly of fluviial origin.

The organic matter molecular analysis of seventeen Neogene samples confirmed the terrigenous origin of organic matter with a predominance of higher plant input in most samples, based on the distribution of n-alkanes and steranes, as well as the presence of tri- and tetracyclic diterpenoids, and triterpenoids representingoleanane, ursane, lupane, chrysene and picene derivates. High concentrations of compounds originating from both angiosperms and gymnosperms suggest the presence of mixed forests. Additionally, important input of mosses into the primary organic matter is indicated by the high concentrations of n-C25 and presence of hop-17(21)-enes in most samples. A high Average Aromatic Ring and Conifer Wood Degradation Index > 0.7 indicate high activity of bacteria and wood-degrading fungi in the sedimentary environment. There was no evidence of weathering and scarce signs of biodegradation were identified. All samples were subjected to water washing.

Huminite reflectance and biomarker-based parameters, as well as the presence of unsaturated pentacyclic triterpenoids and steroids indicate an immature organic matter. A trend of decreasing maturation of sediments from east to the west was observed, as was a similarity of thermal maturity between the Podhale Synclinorium and the ONTB, although the latter seems to be coincidental. A thermal gradient value of 35 °C/km was assumed for calculating the maximum thickness of eroded strata, resulting in 1–1.6 km for the SE area and a maximum temperature of the deepest buried samples equal to 45–65 °C.

1. Introduction

The Orava-Nowy Targ Basin (ONTB) is in the Slovak-Polish cross-border area in the Western Carpathians. It constitutes an intramontane depression, which developed in a fully continental setting upon bedrock border area in the Western Carpathians. It constitutes an intramontane depression filled with Neogene lignites intercalated with thin lignite seams, making them suitable for organic geochemical investigation. Therefore, organic matter appears to be a potentially valuable source of information in this regard, especially as the basin has not been deeply buried. The Neogene siliciclastic deposits exhibit variable contents of organic matter and are intercalated with thin lignite seams, making them suitable for organic geochemical investigation. Thus, the principal goal of this work was to characterize the paleoenvironmental conditions and the source of organic matter through biomarker analysis.

Organic matter is frequently used for the reconstruction of the thermal and burial histories. One of the older units underlying the ONTB is the Podhale Synclinorium (PS) (Fig. 1), where systematic studies of thermal maturity were completed by Wagner (2011), Marynowski et al. (2006) and Środoń et al. (2006) using vitrinite reflectance, biomarkers and illite/smectite measurements, respectively. The above methods revealed a clear trend in the thermal maturity...
2. Geological setting

The Orava-Nowy Targ Basin (ONTB) is in the Polish-Slovak cross border area north and north-west from the strongly elevated Tatra Mountains (Fig. 1). The ONTB is an E-W stretching intramontane basin, which can be divided into two parts – eastern (Nowy Targ) and western (Orava). The basin infill consists of terrigenous Neogene and Quaternary strata, which overlays partially eroded older units (e.g., Watycha, 1976). The sedimentation in the ONTB started on the eastern (Nowy Targ) side of the basin. The sedimentation onset is still discussed and has been estimated to be Late Oligocene/Early Miocene (Watycha, 1976), Badenian (Oszast and Stuchlik, 1977) or Sarmatian (Nagy et al., 1996; Wysocka et al., 2018). Provenance studies of the basin infill revealed that detrital material was derived mainly from the Podhale and Magura Units. Lithoclasts from the PKB are also common in places, but material eroded from the Tatra Mountains is found only in the Quaternary deposits (Watycha, 1976; Tokarski et al., 2012).

Previous paleoenvironmental studies of the ONTB Neogene infill are especially important for this work. Oszast and Stuchlik (1977) have shown that the main type of plant communities present in the examined area during the Neogene was forest, which differed depending on water availability in different parts of the ONTB. Swamps were covered with swamp forests with Cupressaceae-Taxodiaceae trees or swamp thickets with Betulaceae-Myricaceae-Cyrtiellaceae and herbaceous plants. Forests with alder, willow, poplar, platanus and pterocarya trees have also been identified. The slopes of the mountains surrounding the basin were overgrown by mixed forests with a predominance of broad-leaved trees.

The presence of such plant communities allowed the formation of lignites. Lignites are up to 2 m thick, and their lateral extent is relatively small, but they are very common in the studied sediments, especially in the Miocene strata. They exhibit a relatively high abundance of cutinite and a high degree of gelification (Nagy et al., 1996). Their origin has been interpreted as both autochthonous, from local swamps and shallow lakes, and allochthonous, from the fragments of trees brought into the basin by rivers and streams (Nagy et al., 1996).

Sedimentation in the Magura Unit and Podhale Basin halted in the Early Miocene and was followed by the uplift and folding of the sediments. Thrusting of the Magura Unit started in the north, and the deformation front migrated towards the south. At the transition from the Early to Middle Miocene, the PS was already folded, and tectonic contacts between all three units underlying the ONTB were formed (e.g., Watycha, 1976). The sedimentation in the ONTB started on the erosional surface of the PS, PKB and Magura Unit (Oszast and Stuchlik, 1977). The origin of the ONTB has been widely discussed in the literature, but most authors suggest that it must have been related to a strike-slip mechanism (Baumgart-Kotarba, 1996; Tokarski et al., 2012). The regional fault systems started to form during the Late Oligocene-
of the basin in the ONTB, and the collected samples represent the same basal interval. The Nove Ústie, Oravica River, Czarny Dunajec River and Bystry Stream were chosen for geochemical studies (Fig. 1). Nine lignite samples (L-Ch, L-Or1 and L-Or2) were identiﬁed based on retention time and mass spectra in comparison with previously published data. Extraction and separation were carried out at the Faculty of Geology, University of Warsaw, Poland, while the instrumental analyses (TOC, TS, Rn, GC–MS) were completed at the Faculty of Earth Sciences, University of Silesia, Poland.

### 3. Material and methods

Seventeen samples of Neogene deposits from different locations were chosen for geochemical studies (Fig. 1). Nine lignite samples (marked with a “L” preﬁx) were collected from the well-exposed strata at the banks of the Oravica River near Čimhova (L-Or7, L-Or1, L-Or2, L-Or10), the Syhleec Stream near Lipnica Mała (L-Sy), the Chýzýn Stream near Chýžný (L-Ch), the Czarny Dunajec River near Chocholów (L-CD) and from the southern shore of Orava Lake near Nove Ústie (L-NU1 and L-NU2). Five claystone samples (marked with a “C” preﬁx) were obtained from outcrops at the banks of the Oravica River near Čimhova (C-Or4, C-Or8), a stream near Chýžný (C-Ch), the Czarna Orava River (C-CD) and from the Czarny Dunajec IG-1 borehole (C-CD; depth 240.6–241.6). Three siltstone samples (marked with a “S” preﬁx) were collected from the Bystry Stream bank near Mietutwos (S-By1, S-By2) and from a small stream bank near Lipnica Wielka (S-LW). The material was collected from deposits of marshy and swampy areas (lignites and claystones), as well as from extensive ﬂoodplains with small ﬂow channels and ephemeral ponds (sandstones, siltstones and claystones). The Nove Ústie, Oravica River, Czarny Dunajec River and Bystry Stream sections are located along the southern margin and close to the base of the ONTB, and the collected samples represent the same basal interval of the basin inﬁll.

Total organic carbon (TOC) and total sulfur (TS) contents were determined for all the samples, except for sample C-CD, using an ELTRA CS-S30 analyzer. Vitritine refection (Rv) was determined using an Axio Imager M2M in three lignite samples (L-CD, L-Or1 and L-Or2). One-hundred measurements were performed for each sample. All seventeen samples were crushed and powdered. Extraction of bitumens was performed in a Soxhlet apparatus for 72 h with a dichloromethane/methanol (93/7, v/v) mixture. To separate extracts into aliphatic, aromatic and polar fractions, modiﬁed column chromatography was used (Bastow et al., 2007). Samples were placed at the top of a Pasteur pipette ﬁlled with silica gel which had been activated for 8 h at 110 °C. Hydrocarbon aliphatic, aromatic and polar fractions were eluted under gravity with 2 ml of an n-pentane, n-pentane/dichloromethane (7/3) mixture and a dichloromethane/methanol (1/1) mixture, respectively. Aliquots of the polar fractions were converted to trimethylsilyl (TMS) derivatives by reaction with N,O-bis(trimethylsilyl)triﬂuoroacetamide (BSTFA), 1% trimethylchlorosilane, and pyridine for 3 h at 70 °C.

GC–MS analyses were performed on aliphatic and aromatic fractions with an Agilent Technologies 6890 series II gas chromatograph (GC) and an Agilent 5973 Network mass spectrometer (MS). Helium was used as a carrier gas (ﬂow rate of 1 ml/min). A J&W DB5-MS capillary column (60 m, 0.25 mm id., 0.25 µm ﬁlm thickness) coated with a chemically bonded phase (35% polydimethylsiloxane 65% diphenylsiloxane) was used. A GC oven was preheated to 50 °C, which was held constant for 1 min and then heated to 120 °C at a 20 °C/min rate and to 300 °C at a 3 °C/min rate. The column was then held isothermal for 50 min. The GC column outlet was connected directly to the ion source of the mass spectrometer. Mass spectra were recorded from m/z 45–550 (0–40 min) and m/z 50–700 (above 40 min). The MS was operated in electron impact mode (ionization energy 70 eV). Individual compounds were identiﬁed based on retention time and mass spectra in comparison with previously published data. Extraction and separation were carried out at the Faculty of Geology, University of Warsaw, Poland, while the instrumental analyses (TOC, TS, Rn, GC–MS) were completed at the Faculty of Earth Sciences, University of Silesia, Poland.

### 4. Results

#### 4.1. Bulk organic geochemistry

Total organic carbon (TOC) content ranges from 0.2% to 15.4% in clastic samples and from 31.0% to 56.9% in lignites (Table 1). Total sulfur (TS) content is rather low in the clastic samples (< 0.5%) (Table 1). Total sulfur content ranges from 0.2% to 15.4% in clastic samples and from 31.0% to 56.9% in lignites (Table 1). Only two claystones (C-Or8 and C-CD) show elevated sulfur content (3.1% and 1.3%, respectively). TS in lignites ranges from 0.8% to 8.8%. Lignite samples can be divided into two populations: samples with relatively low (< 2%) TS values (L-CD, L-Sy and L-Or7) and samples with higher sulfur content (> 3.5%: L-Or1, L-Or2, L-Or10, L-Ch, L-NU1 and L-NU2) (Table 1). Extractable organic matter (EOM) content ranges from 0.21 to 27.67 mg/g of rock with lignites showing considerably higher values than clastic rocks (Table 1). The polar fraction is dominant in almost all samples, ranging from 82.3% (C-CD) to 97.3% (L-Or1) (Table 1). Aliphatic and aromatic fraction contents range from 1.3% (L-Ch) to 11.8% (C-CD) and from 1.1% (sample C-Or4) to 5.9% (sample C-CD), respectively (Table 1). Sample C-Or4 is an exception with equal amounts of all three hydrocarbon fractions. This pattern is likely related to an extremely small amount of EOM in this sample. Unresolved complex mixture (UCM) (Milner et al., 1977; Rubinstein et al., 1977; Killops and Al-Juboori, 1990; Peters et al., 2005a) is present in sample C-CD. It is also noticeable in sample C-Or4, although not as signiﬁcant as in the former sample.

#### 4.2. n-Alkanes and acyclic isoprenoids

The distribution of n-alkanes in the samples studied is usually in the range from n-C16 to n-C33 (Figs. 2 and 3). Most samples show a unimodal distribution with notable odd-over-even predominance and a maximum at n-C29 or n-C31. One sample (C-Or8) has a unimodal distribution with a maximum at n-C23 (Fig. 2). Other samples (S-By2, L-Or2 and L-NU1) are characterized by odd-over-even predominance and a bimodal distribution, with the first maximum at n-C23 and the second
at \( n-C_{31}, n-C_{29} \) and \( n-C_{27} \), respectively (Figs. 2 and 3).

Samples C-CO and L-Sy (Fig. 3) show slightly different characteristics. The distribution of \( n \)-alkanes is bimodal with maxima at \( n-C_{22} \) and \( n-C_{29} \). In the range between \( n-C_{17} \) and \( n-C_{23} \), a slight even-over-odd predominance can be observed, while among the long-chain \( n \)-alkanes, a significant odd-over-even tendency is present. Moreover, the distribution of \( n \)-alkanes in all the samples show a specific “cut” shape of chromatogram in the range of short-chain compounds.

The Carbon Preference Index (CPI) provides information about the origin and thermal maturity of organic matter (Killops and Killops, 2005; Peters et al., 2005a). CPI values were calculated according to the following formula: 0.5\( \left[ \Sigma (n-C_{25}-n-C_{33})_{\text{odd}} + \Sigma (n-C_{23}-n-C_{31})_{\text{odd}} \right] / \Sigma (n-C_{24}-n-C_{32})_{\text{even}} \) (Bray and Evans, 1961). CPI values vary from 1.53 to 8.41 (Table 2), which indicates terrigenous and immature organic matter (Bray and Evans, 1961; Scalas and Smith, 1970; Peters et al., 2005b). The ratio of short-chain to long-chain \( n \)-alkanes, \( \text{SCh/LCh} = (n-C_{17}-n-C_{19})/(n-C_{27}-n-C_{29}) \), also helps to determine the source of organic matter (Tissot and Welte, 1984; Bourbonnier and Meyers, 1996; Killops and Killops, 2005; Peters et al., 2005b). The SCh/LCh values range from 0.01 to 0.32 (Table 2).

The Alkane Index, \( \text{AI} = n-C_{31}/(n-C_{31} + n-C_{29}) \), is higher than 0.5 in only three samples (C-Or4, S-By1 and S-By2) (Table 2), which suggests that grasses were the main type of vegetation. Other samples show values lower than 0.5, which indicates trees as the main source of vegetation.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Total Ion Current (TIC) of the aliphatic fractions (samples L-Or2 and C-Or8). \( n \)-Alkanes are marked by dots.}
\end{figure}
organic matter (Schefuss et al., 2003; Zhang et al., 2006). Generally, most samples from Oravica exhibit lower values than other samples, while lignites have slightly lower values than the clastic rocks. Worth mentioning is also the relatively high abundance of \( n\)-C\(_{23}\) in many samples (Figs. 2 and 3). A \( n\)-C\(_{23}/n\)-C\(_{31}\) ratio higher than 0.35 indicates a significant input of Sphagnum organic matter (Pancost et al., 2002) in many samples, especially in L-Or2, L-NU1, S-By2 and C-Or8, with the maximum value of 16.37 in sample C-Or8 (Table 2).

Fig. 3. Gas chromatograms (\( m/z = 71 \)) of the \( n\)-alkanes distribution of the samples S-By2, L-NU2 and L-Sy. \( n\)-Alkanes are marked by dots, Pr – pristane, Ph – phytane.

Pristane and phytane are acyclic isoprenoids that may originate from chlorophyll or from cell membranes of archaeons, zooplankton, plants or algae (Goossens et al., 1984; Ten Haven et al., 1987; Peters et al., 2005b). These compounds are present in most samples, but their concentrations are low. The pristane to phytane (Pr/Ph) ratio may provide information about the redox conditions of the sedimentary environment, if their source is limited to chlorophyll. However, this index should be treated with caution in the case of lignites, as smaller
Pentacyclic hopanoid triterpenoids were present in most samples, although in relatively low amounts. Both hopanes and hopenes were identified in most samples, although in rather small amounts with the exceptions of samples L-Or10, L-Ch, L-CD, and C-CD. The most common tetracyclic diterpenoid is 16αβ-kaurane and 16βα-kaurane, which were identified as well; pimarane, isopimarane and abietane were the most abundant (Fig. 4), but norpimarane, rimenuene and fichtelene were also present. Although isopimarane was identified only in a few samples, a certain relation was observed, as it was more abundant in the lignites than in clastic rocks.

4.4. Pentacyclic hopanoid triterpenoids

Pentacyclic hopanoid triterpenoids were present in most samples, although in relatively low amounts. Both hopanes and hopenes were identified (Fig. 5). A predominance of C29 hopene was observed (Fig. 5). Among hopanes, C29 to C32 compounds with configurations of αβ, βα and ββ were identified (Fig. 5), although C32 hopanes were registered mainly in lignites. Samples S-By1 and S-By2 show much higher concentrations of C29 hopanes and C31 hopanes, whereas C28 hopane was observed (Fig. 5). Among hopanes, C29 compounds predominated (Fig. 6). Among steranes and stigmastanes, both isomers, R and S, of the ααα (R) isomer, only.

Fig. 4. Gas chromatogram (m/z = 123) showing the typical diterpenoid distribution for the investigated samples.

4.5. Steroids

Cholestanes and ergostanes are more abundant in siltstones. Various cholesterol and ergosterol isomers and values of C27 steranes, both isomers, R and S, of the ααα (R) isomer, only.

The distribution of steroids demonstrates a C29 compounds predominance (Fig. 6). Among cholestanes and stigmastanes, both isomers, R and S, of the ααα (R) isomer, only.

Cholestanes and ergostanes are more abundant in siltstones.
The sterane 20S C29 ααα to the sum of isomers 20S and 20R (20S/20S + 20R) (e.g., Mackenzie and McKenzie, 1983; Beaumont et al., 1985; Seifert and Moldowan, 1986; Farrimond et al., 1998) ratio values range from 0.13 to 0.34, with the highest values calculated for the samples from Orava Lake (L-NU1 and L-NU2) and the lowest for the siltstones (Table 2). For the most samples the ratio of sterane to sterene for C27,C28 and C29 compounds (Amo et al., 2007) ranges from 0.05 to 0.40 (Table 2). Samples S-By1 and S-By2 were the exceptions, having sterane/sterene ratios of 0.91 and 0.58, respectively. Both parameters are indicators of rather low organic matter thermal maturity.

The ratio of regular steranes vs. αβ hopanes allows the estimation of the origin of organic matter. Regular steranes are calculated as the sum of C27, C28 and C29 steranes with the ααα and αββ configurations (both, R and S isomers are included), while αβ hopanes are determined by the sum of C29-C33 hopanes (R + S isomers), having the αβ configuration (Tissot and Welte, 1984; Moldowan et al., 1985; Peters et al., 2005b). The ratio ranges from 0.28 to 0.96, except for sample L-Or10, which has a significantly lower value (0.004) (Table 2), leading to the conclusion that there was a high microbial activity in the sediment.

4.6. Aromatic non-hopanoid terpenoids

Numerous derivatives of chrysene and picene, mostly representing the des-A degraded and aromatized or aromatized products of triterpenoids with oleanane and ursane skeleton were present in all the samples, except of sample C-CO. Trimethyltetrahydro- and tetramethyloctahydrochrysenes were identified, together with dimethyl- and trimethyltetrahydrodipocenes and tetramethyloctahydrodipocenes (Fig. 7). The most common compounds were 2,2,9-trimethyl-1,2,3,4-tetrahydrodipocene, 3,3,7-trimethyl-1,2,3,4-tetrahydrochrysenes and isomers of 3,3,7,12a-tetramethyl-1,2,3,4,4a,11,12,12a-octahydrochrysende of an unknown exact structure. Chrysene and picene derivatives are more abundant in lignites than in clastic rocks. Other triterpenoid constituents of aromatic fraction are dinoroleana(ursa)-1,3,5(10),12-tetraene, dinoroleana(ursa)-1,3,5(10)-triene and aromatic triterpene with an open C-ring (Fig. 7). Amounts of total oleanane, ursane and lupane derivatives are quite uniform in lignites (usually around 40–50% of aromatic fraction) but highly variable in the clastics (constituting from few to over 70% of aromatic fraction).

The Average Aromatic Ring (AAR) value reflects the mean number of aromatic rings in the oleane derivatives. It can provide information about the oxygen availability during sedimentation (Huang et al., 2013). The AAR calculated according to the formula defined by Huang et al. (2013) ranges from 3.89 to 4.00 in the samples examined (Table 3), leading to the conclusion that there was a high microbial activity in the sediment.

Aromatic derivatives of diterpenoids, such as retene, simonellite, dehydroabietane and abietatetraene were present in the samples studied, mainly in lignites. For some samples cadalene in relatively high concentrations has been determined.

The ratio of diterpenoids to the sum of diterpenoids and triterpenoids originating from angiosperms, can determine the relative gymnosperm and angiosperm contribution to the primary organic matter (Bechtel et al., 2007). The diterpenoids taken into consideration in this ratio are ent-beyerane, 16α(H)-phyllocladane, 16β(H)-phyllocladane, nor-abietane, pimarane, abietane, 19-norabieta-3,8,11,13-tetraene, 19-norabieta-8,11,13-triene, abiet-6,8,11,13-tetraene, simonellite and retene. Triterpenoids originating from angiosperms are understood as the sum of des-A-oleanenes, des-A-lupanes, olean-12-ene, olean-13(18)-
dinorrsa-1,3,5(10),12-tetraene, 24,25,26-trisnorlupa-1,3,5(10)-triene, tetramethylchadropinecenes, dimethyltetrahydropinecenes and tri-
methyltetrahydropinecenes (Bechtel et al., 2007). This ratio ranges from
0.004 to 0.30 in the samples examined (Table 3).

4.7. Perylene and other PAHs

Perylene is present in relative high concentrations, especially in
the clastic samples (Fig. 7). Other polycyclic aromatic hydrocarbons
(PAHs) were also found, although in relatively small amounts: antha-
cene (mostly in lignites), pyrene and fluoranthene (mostly in clastic
rocks), phenanthrene and its methyl derivatives (Fig. 7). Another phe-
nanthrene derivative, 1-methylisopropyl-7,8-cyclopentenophenan-
threne, is also present in the studied samples, with a significantly higher
abundance in lignite samples.

For lignite samples, the Conifer Wood Degradation Index (CWDI)
was calculated according to the following formula:

\[
\text{CWDI} = \frac{\text{perylene}}{\text{perylene} + \text{cadalene} + \text{retene} + \text{simonellite} + \text{de-
hydroabietane}}
\]

(Marynowski et al., 2013).

The CWDI is an indicator of the degree of wood decay in sediments
driven by wood-degrading fungi (Marynowski et al., 2013). The CWDI
ranges from 0.73 to 0.98, except for the samples L-Nu2 and L-Or10
where CWDI is 0.09 and 0.27, respectively (Table 3).

4.8. Polar compounds

In all samples including lignites, claystones and siltstones, long-
chain n-fatty acids (> n-C23) and long-chain n-alkanols predominates.
In case of some lignites (L-Or1 and L-Or2), succinic acid as well as n-C16
and n-C18 n-fatty acids are important constituents of polar fraction as
well. Significant group of polar compounds in majority of the samples
are phenols, phenolic acids, ketones and aldehydes characteristic for
both angiosperm and gymnosperm lignin degradation products. In that
group vanillin, hydroxyacetophenone, syringaldehyde as well as ben-
zoeic, 3- and 4-hydroxybenzoic, vanillic, protocatechuic and syringic
acid are major compounds (Fig. 8). Degradation products of cellulose
and possibly also hemicellulose (e.g. Marynowski et al., 2018) are much
less common, but α- and β-glucose, α- and β-arabinose and α- and β-
arabinofuranose has been identified in two lignite samples (L-Or1 and
L-Or2), and one siltstone (S-By1; Fig. 8). Polar diterpenoid biomole-
cules, including ferruginol and sugiol (e.g. Otto and Simoneit, 2001) are
rare and were found in one lignite sample only (L-Ch). Dehydroabietic
acid is more common, but its relative abundances except two samples
(L-Or7 and L-Or10) are small. Polar triterpenoid natural products
identified in lignite samples are quite common α- and β-amyrins. Sterols
represented by β-sitosterol and stigmastanol are common polar com-
ponents present in investigated rocks.

4.9. Huminite reflectance

Huminite reflectance (R_h) was measured in three lignite samples. L-
Or1 and L-Or2 samples exhibit similar values of 0.20% (s.d. 0.06) and
0.26% (s.d. 0.04), respectively, while L-CD shows a slightly higher re-
reflectance of 0.43% (s.d. 0.10) (Table 3). The distribution of measured
R_h values was monomodal for each sample examined.

5. Discussion

5.1. Secondary processes

Weathering causes various modifications of organic matter on a
molecular level. During weathering, TOC content decreases, and the
vitrinite reflectance values and distributions of n-alkanes, steranes and
hopanes are also altered (e.g., Faure et al., 1999; Elie et al., 2000;
Marynowski et al., 2011a). One of the most important changes is an
increase in short-chain n-alkanes and a decrease in long-chain n-alkane

Table 3
Huminite reflectance and calculated aromatic biomarker parameters for the samples studied.

| Sample | R_h [%] | AAR | CWDI | di- / (di- + triterpenoids) |
|--------|--------|-----|------|-----------------------------|
| L-Or7  | –      | 3.98| 0.98 | 0.04                        |
| L-Or1  | 0.20   | 3.95| 0.93 | 0.01                        |
| L-Or2  | 0.26   | 3.94| 0.85 | 0.01                        |
| L-Or10 | –      | 3.96| 0.27 | 0.21                        |
| L-Sy   | –      | 3.91| 0.73 | 0.12                        |
| L-Ch   | –      | 4.00| 0.88 | 0.10                        |
| L-CD   | 0.43   | 3.91| 0.97 | 0.004                       |
| L-NU1  | –      | 3.97| 0.90 | 0.03                        |
| L-NU2  | –      | 3.98| 0.09 | 0.24                        |
| C-Or4  | –      | –   | –    | –                           |
| C-Or8  | –      | 4.00| –    | 0.02                        |
| C-Ch   | –      | –   | –    | –                           |
| C-CO   | –      | –   | –    | –                           |
| C-CD   | –      | 3.96| –    | 0.30                        |
| S-By1  | –      | 4.00| –    | 0.05                        |
| S-By2  | –      | 3.91| –    | 0.04                        |
| S-LW   | –      | 3.89| –    | 0.10                        |

R_h = Huminite reflectance.
AAR = Average Aromatic Ring (Huang et al., 2013).
CWDI = Conifer Wood Degradation Index (Marynowski et al., 2013).
di- / di- + triterpenoids = ratio of diterpenoids to the sum diterpenoids and
angiosperm-derived triterpenoids (Bechtel et al., 2007).
concentrations. Moreover, aromatic terpenoids such as simonellite, cadalene or retene are eliminated. Weathering causes a decrease of perylene concentration and an increase of other PAHs such as phenanthrene and its methyl derivatives or fluoranthene (Marynowski et al., 2011b). Considering the predominance of long-chain and the scarcity of short-chain n-alkanes, the presence of aromatic terpenoids, perylene and small amounts of phenanthrenes and fluoranthene, no evidence of weathering was found in the samples examined. Nevertheless, the absence of weathering cannot be assumed with certainty, as it has been proven, that weathering can remove even over 25% of primarily present soluble organic matter, although highest values are obtained in dry, hot climates (Leythaeuser, 1973; Littke et al., 1991). Littke et al. (1991) have estimated that the organic carbon loss in Posidonia Shale in northern Germany amounted up to 16 wt%. Considering the general similarity of climate between northern Germany and southern Poland we could assume similar values. This could explain the relatively low TOC in lignites. Moreover, the prevalence of the polar fraction in the samples examined also indicates that they could have undergone some changes, as weathering depletes the organic matter in bitumen, especially aromatic hydrocarbons (Leythaeuser, 1973; Littke et al., 1991).

Biodegradation removes many compounds from organic matter, preferably n-alkanes, isoprenoids, C_{27}-C_{29} steranes and C_{30}-C_{35} hopanes. The reworking of organic matter by microorganisms results in the production of an unresolved complex mixture (UCM) visible on chromatograms (e.g., Gough and Rowland, 1990; Killops and Al-Juboori, 1990). An UCM was identified in samples C-Or4 and C-CO, which were interpreted as floodplain deposits. Additionally, neither diterpenoids, steranes nor hopanes were identified in these samples. Short-chain n-alkanes and aromatics were also partially removed. All these peculiarities evokes a high level of biodegradation for these samples.

Water washing effects are similar to those caused by biodegradation. Therefore, it might be difficult to distinguish between the effects of these processes. Water washing removes many aromatic and aliphatic compounds from the organic matter. The characteristic result of this process is the removal of short-chain n-alkanes according to their solubility in water. This removal leads to the characteristic “cut” shape of n-alkanes distribution (Palmer, 1993), observed in all the samples (Figs. 2 and 3) and distorts the Pr/Ph ratio, as both compounds are also easily removed. Water washing effects were observed in all the samples.

5.2. Origin of organic matter and sedimentary environment

A high percentage of polar fraction observed in the samples examined (Table 1) is typical for immature type III kerogen (Killops and Killops, 2005). This is confirmed by the presence of lignin and cellulose degradation products in polar fraction and products of wax lipids decomposition (long chain n-alkanols and fatty acids) (e.g., Otto and Simonite, 2001; Stefanova et al., 2002; Otto et al., 2005) but also the distribution of n-alkanes with high odd-over-even predominance maximizing at n-C_{29}, n-C_{27} or n-C_{25} (Figs. 2 and 3) characteristic for terrestrial organic matter with a predominance of higher plants (e.g., Bray and Evans, 1961; Connnan and Cassou, 1980; Rieley et al., 1991; Killops and Killops, 2005). Additionally, CPI values higher than 1 and a SCh/ LCh significantly lower than 1 support this view (Table 2) (e.g., Bray and Evans, 1961; Scanlan and Smith, 1970; Tissot and Welte, 1984; Bourbonnieri and Meyers, 1996; Peters et al., 2005b). In samples C-Or4, S-By1 and S-By2, Al values were higher than 0.5 (Table 2), suggesting grasses as the main source of organic matter. In other samples, organic matter is derived mainly from trees, as the dominant compound is n-C_{29} or n-C_{27} (Scheffus et al., 2003; Zhang et al., 2006). Odd n-alkanes of the range n-C_{21} – n-C_{25} are considered to originate from mosses, mainly from Sphagnum (Bechtel et al., 2007). A high n-C_{23}/n- C_{31} ratio is determined for a lot of samples (Table 2) and might argue for peatlands or flooded forest (Pancost et al., 2002). A relatively high amount of n-C_{22} in samples C-CO and L-Sy can be related to a presence of specific algae species (Ekpo et al., 2005; petrs et al., 2010).

The distribution of steranes with a C_{29} predominance (Fig. 6) confirms the higher plant origin of organic matter (Moldowan et al., 1985; Peters et al., 2005b) supported by a sitosterol, a typical higher plant natural product, predominance (Otto and Simonite, 2001). The ratio of regular steranes to αβ hopanes lower than 1 (Table 2) suggests a land plant origin or an organic matter highly reworked by bacteria (Peters et al., 2005b); however, considering the n-alkane distribution, the former interpretation can be considered as the dominant factor. The presence of tri- and tetracyclic diterpenoids, such as abietane, pimarane, isopimarane, fichtelitene, rimuene, phyllocladane, kauranen,
retene, simonellite and polar biomolecules like ferruginol, sugiol and squalene (Wakeham et al., 1979; Bechtel et al., 2005b). Water washing surely has led to the partial removal of compounds derived from mosses and ferns seems reasonable, especially for sample L-CD, which exhibits the highest Ro value. However, in the studied area during the Neogene. The presence of hop-17(21)-enes (Fig. 5) can also provide insight into the depositional conditions. They are most likely derived from alterations of hop-17(21)-enes in an acidic environment (Mackenzie et al., 1983). Inasmuch as both β- and α-amyrin derivatives originate from the investigated samples, thus disturbing their original proportions. Redox conditions can also be determined using AAR, which rises with increasing oxidation potential in sediments (Huang et al., 2013). For the studied material, the AAR mean value is 3.95 (Table 3) which, compared to the published data, is relatively high and indicates high activity of aerobic bacteria and well oxidized sediment (Huang et al., 2013). Considering that water washing is present in all the samples and the influencing Pr/Ph, the AAR seems to be a more reliable indicator of redox conditions. High microbial activity is also indicated by the presence of the derivatives of chrysene and picene (Wakeham et al., 1979). In addition to bacteria, wood-degrading fungi were active during the early stage of diagenesis, as suggested by the presence of perylene and by the CWDI values > 0.7 (Table 3), which are characteristic for highly decomposed wood (Marynowski et al., 2013). It is rather surprising because in the case of the Miocene lignites, CWDI values are very small (Marynowski et al., 2013).

The presence of hop-13(18)-enes (Fig. 5) can also provide insight into the depositional conditions. They are most likely derived from alterations of hop-17(21)-enes in an acidic environment (Meredith et al., 2008; Pan et al., 2010). This interpretation appears to be appropriate, considering the high n-C_{29} amounts present in samples, indicating Sphagnum as one of the main constituents of plant communities in the studied area during the Neogene.

Pyrene, anthracene and fluoranthene occurring in many samples could have been formed by the incomplete burning of biomass and cutaostibiolates, e.g., during wildfires. These compounds can be transported by air- or waterborne processes and deposited in different locations (Killops and Massoud, 1992; Jiang et al., 1998; Marynowski and Simonite, 2009). As these compounds are present in almost all the samples, although in small concentrations, it can be assumed that they were transported by riverine or eolian transport from different source areas rather than formed in situ.

5.3. Thermal maturity of organic matter

The huminite reflectance values (Table 3; Fig. 9) indicate an immature character of the organic matter, although the sample from the SE part of the basin (L-Cr) shows a slightly higher maturity of the late diagenesis phase (R_{o} = 0.43%) (Peters and Moldowan, 2017). Thermal maturity can also be determined by biomarker-based indicators, such as CPI, which decreases to 1 with increasing maturity (e.g., Bray and Evans, 1961; Scalan and Smith, 1970). The CPI varies from 1.53 to 8.41 (Table 2), indicating that the organic matter examined is immature, with the minimum values representing the phase of early catagenesis. Direct correlation between CPI and R_{o} values in samples L-Or1, L-Or2 and L-CD is poor, which is probably related to the susceptibility of CPI to alterations caused by water washing and its dependence on the organic matter source (e.g., Palm, 1993). Thus, maturity determined based on the CPI is probably overestimated.

The presence of unstable ββ hopane isomers (Fig. 5) indicates very low maturation of organic matter, generally below or around R_{o} = 0.4% (Nytoft and Bojesen-Kofoed, 2001; Peters and Moldowan, 2017). The C_{30} metatane/hopane ratio decreases from 0.8 to 0.15 with an increase in thermal maturation (e.g., Peters et al., 2005b). The ratio was possible to calculate for three samples (Table 2; Fig. 9) and their values (0.18, 0.27 and 0.45) indicate that two of them (C-Or8 and S-LW) are immature and one (S-By2) is mature (Nytoft and Bojesen-Kofoed, 2001). The ββ/(ββ + αα) homohopane ratio decreases to 0 during increasing thermal maturation before the organic matter reaches the mature phase (Farrimond et al., 1998; Peters and Moldowan, 2017). This ratio ranges from 0.34 to 0.55 in most samples (Table 2; Fig. 9), indicating immature organic matter. The lowest values obtained in samples L-Cr and L-By1 were 0.28 and 0.15, respectively. Other maturity indicators show concordantly that these samples were relatively deeply buried, so their elevated maturity seems reliable, especially for sample L-Cr, which exhibits the highest R_{o} value. However, even samples L-Cr and S-By1 should be treated as immature, with R_{o} not exceeding ca. 0.45% (see Peters and Moldowan, 2017).
The 20S/(20S + 20R) parameter based on the C_{29} aza steranes is one of the most commonly used biomarker indicators of thermal maturity. Its values increase from 0 to 0.45–0.55 in clastic rocks and to 0.30–0.45 in lignites at the transition from diagenesis to catagenesis during increasing thermal maturation (Farrimond et al., 1998; Peters and Moldowan, 2017). In the clastic samples, the 20S/(20S + 20R) ranges from 0.13 to 0.26 (Table 2; Fig. 9), which means that they are immature. Lignites have slightly higher values, from 0.26 to 0.34 (Table 2; Fig. 9), which indicates a maturation stage of diagenesis and early catagenesis (Farrimond et al., 1998; Peters and Moldowan, 2017). The values of 20S/(20S + 20R) can be distorted by the presence of C_{29} steranes (Amo et al., 2007). The presence of those unsaturated steroids confirms the immature character of the organic matter. The steranes to sterene ratio increases rapidly with increasing thermal maturity, from 0.2 to 0.9 at the temperature range between 45 and 55 °C (Amo et al., 2007). The ratio ranges from 0.05 to 0.92 (Table 2) in the samples examined, which implies that the samples have not reached the catagenesis (oil window) phase.

The stratigraphy in the ONTB is problematic and still poorly constrained, so it is difficult to assess the exact age relations between Nove Ústie, the Oravica River, the Czarny Dunajec River and the Bystrý Stream sections. However, since they are located along the southern margin of the basin of the inferred highest magnitude of uplift (Loziński et al., 2017), they presumably represent the basal part of the infil. Therefore, samples from these sections can be treated as roughly representing the same interval of the basin infil, and their thermal maturity parameters can be compared to reconstruct the history of subsidence, burial and exhumation along the E-W transect through the basin. Huminite reflectance values obtained from samples L-CD, L-Or1 and L-Or2 suggest a decrease in the maturation of sediments towards the west (Table 3; Fig. 9). This trend is confirmed by certain biomarker-based parameters. The \( \beta \alpha/\alpha \beta \) ratio increases from 0.18 to 0.45 towards the west (Table 2; Fig. 9), similar to the case of the \( \beta \beta/(\beta \alpha + \alpha \beta) \) ratio, which also tends to be lower in the eastern than in the western part of the basin. The only exception is sample S-By2, with a value of 0.77, similar to the western samples (Table 2; Fig. 9), most likely due to a higher influence of secondary processes such as water washing or biodegradation. The sterane/sterene ratio also generally decreases to the west (Table 2; Fig. 9), although this trend is not that clear due to large spread of values, even in a single section, e.g., between S-By1 (0.92) and S-By2 (0.58). All these biomarker-based indices clearly indicate a lower thermal maturity in the western part of the basin. The only biomarker-based parameter not following the described trend is 20S/(20S + 20R), which shows an increase in values in the direction opposite from what was suspected, i.e., from east to west (Table 2; Fig. 9). As mentioned above, it is difficult to expect reliable results based on the 20S/(20S + 20R) ratio with such a high contribution of sterenes, in the overall steroid composition of the samples examined.

Waliczek and Sołęcki (2014) measured the vitrinite reflectance in a claststone from Chocholów, which is the same area as the section of the Czarny Dunajec Stream examined in this work. They obtained a \( R_o \) value of 0.37%, which is very similar to our result (0.43%) from that locality and confirms the increased maturity of sediments in the SE part of the ONTB. However, Nagy et al. (1996) obtained relatively high \( R_o \) values for lignites from the SW part of the basin in Nove Ústie (from 0.35% to 0.43%), which contrasts with our biomarker-based results obtained for lignites from the same locality and does not fit the westward trend of maturity decrease. Such a discrepancy can relate to a partial oxidation of lignites from the Nove Ústie site, which influenced the vitrinite reflectance measurement. As it was shown, organic matter weathering can increase \( R_o \) values up to 0.2% (Marynowski et al., 2011b). If so, the \( R_o \) values obtained by Nagy et al. (1996) are not representative of burial conditions, and the extremely high calculated geothermal gradient of 50 °C/km is overestimated.

5.4. Magnitude and timing of exhumation

The Magura Nappe sediments near the northern margin of the ONTB were estimated to be heated up to 105 °C, but it is estimated that most of the sediments (4.4 km) had been eroded before the onset of Neogene sedimentation (Świerzewska, 2005), so the Magura Nappe in the region represents a different stage of thermal history. Thermal maturity of the PS, on the other hand, decreases from SE to NW, which is manifested by the decreasing illite/smectite ratio (Srodoń et al., 2006) and vitrinite reflectance (Wagner, 2011) measured for Paleogene sedimentary rocks (Fig. 9). The lowest \( R_o \) values of ~0.5% occur close to the junction between the PS, PKB and ONTB near Chocholów (Fig. 9). They are significantly lower than those reported for the Aalenian and Bajo

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6. Conclusions

Based on the molecular composition of organic matter and the geochemical indicators of the Neogene sediments in the Orava-Nowy Targ Basin, only type III kerogen was identified, which confirms that the sedimentation occurred in a continental setting. Higher plants, mainly grasses and trees, are indicated as the main source of organic matter. Considering the high input of peat-derived organic matter in most samples, such as Sphagnum-derived complexes, mixed swamp forests are proposed as the dominant plant community in the examined area, although other communities such as mixed forests and meadows, swamps and mires with a few trees were also present. The sedimentary environment of wetlands and floodplains was oxic and acidic, in which intensive activity of bacteria and fungi led to the partial decay of organic matter. Wildfires occurred in the examined area during the Neogene, as compounds such as pyrene, fluoranthene and anthracene were identified in most of the studied samples. The influence of water washing that disrupted the distribution of short-chain n-alkanes and acyclic isoprenoids is detectable in all the samples. Only two of the samples underwent biodegradation, which led to the removal of almost all the compounds from the aliphatic fraction and most compounds from the aromatic fraction. Signs of post-echamation weathering were not identified.

The huminite reflectance of the examined samples ranges from 0.20 to 0.43%, proving the organic matter immaturity. The presence of unsaturated compounds and the values of calculated geochemical indicators also confirm it and denote that examined organic matter has not reached further than late diagenesis stage. A comparison of R₀ and CPI indicates that the latter is a less reliable proxy of maturity due to water washing and its dependence on an organic matter source. The thermal maturity of samples collected from the basal part of sediments inffill along the southern margin of the ONTB exhibits a clear decreasing trend towards the west. Moreover, the comparison of different biomarker-based thermal maturity indicators from samples located at the southern margin of the basin allowed estimation of the applicability of different thermal maturity indices to relatively immature terrigenous sediments.

The C₂₀/C₄₀ ratio, δ¹⁴C, δ³³S and δ³⁴S show good correlations with the maturity trend based on the huminite reflectance.

The deepest buried samples were heated to a maximum temperature of ~45–65 °C, temperatures of late diagenesis-early catagenesis. Therefore, erosion must have removed 1–1.6 km of sediments in the SE part of the basin, where the outcrops of these strata and their contact with the basement is observed. Thermal maturity of samples representing the basal interval of the ONTB infill that are currently on the surface decreases to the west, which indicates that the amount of humification decreased in this direction. These results clearly imply that the ONTB extended beyond its current limits, at least in the southern part, and must have covered the rocks of the PS that are currently exposed. The Neogene sediments belonging to the ONTB must have formed the 1–1.6 km thick cover on the western part of PS.

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