



STUDIES ON NITROGEN COMPOUNDS, V AND Ni CONCENTRATIONS AND NITROGEN ISOTOPIC COMPOSITION OF THE CRUDE OILS OF CENTRAL AND EASTERN PARTS OF THE POLISH OUTER CARPATHIANS

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Introduction

Nitrogen atoms in oil are bound mainly in alkylated heterocyclic compounds and undergo systematic fractionation as a result of a geochromatographic effect. Many factors, including the genetic type of source organic matter, maturity, and post-generative alterations may control abundance of various nitrogen-bearing compounds, and stable N isotope composition (Maracano et al. 2013). Among the nitrogen compounds in oils, carbazoles are main objective of interest, as migration distance and biodegradation indicators (Song et al., 2016). The proportionality of nickel and vanadium in oil is not affected by secondary processes and could be used in oil-oil correlation or source organic matter type assessment of even degraded oils (Lewan, 1984). The main objective of the study is the determination of the relationships between oils and range of secondary processes in the central and eastern parts of the Polish Outer Carpathians based on V and Ni concentration, concentrations of selected N-containing compounds and stable isotope composition of nitrogen of crude oils and their fractions.

Samples and methods

35 crude oils were collected from producing wells and surface seeps. 26 oil samples were collected from Silesian Nappe, 3 oils – from Sub-Silesian Nappe, 2 oils were collected from Dukla Nappe, 1 oil originates from Magura Nappe and 3 oils were collected from Skole Nappe.

Vanadium and nickel contents were determined by the ICP-OES method using the Perkin Elmer WMA400. The stable nitrogen isotope analyses were performed using the Finnigan Delta V Plus mass spectrometer (MS) and results are expressed in the δ -notation ($\delta^{15}\text{N}$, ‰) relative to atmospheric nitrogen standard. The applied MS configuration allows simultaneous determination of the nitrogen concentration during isotope ratio analysis. Due to extremely low concentration of nitrogen, results of $\delta^{15}\text{N}$ of saturated hydrocarbon fraction were unreliable. The alkyl-carbazoles distribution analysis was carried out with the Agilent 7890A GC coupled with an Agilent 5975C MSD.

Results

Content of vanadium in studied oils range from below 0.30 to 1.79 ppm (median 0.6 ppm) and nickel from below 0.50 to 16.8 ppm (median 4.28 ppm). Moreover, values of ratio $V/(V + \text{Ni})$ range from less than 0.06 to 0.33 and correspond with regime II in Lewan (1984) indicating marine and deltaic facies (the Type II and III kerogen) as responsible for generation of oils.

Concentration of nitrogen in studied oils ranges from 0.04 to 0.39 wt.%. Analysis of individual oil fractions revealed, that the highest concentration of nitrogen is present in either resin (0.49 – 1.56 wt.%, av. 1.03 wt.%) or asphaltene fraction (0.18 – 2.40 wt.%, av. 1.09 wt.%). The lowest concentrations are observed in saturated hydrocarbon fraction, where concentrations of nitrogen mostly do not exceed 0.15 wt.%. The highest relative N contents are recorded in resins (av. 40.2 wt.% of total nitrogen in oil), while the lowest - in asphaltenes (av. 8.0 wt.%).

The whole oil $\delta^{15}\text{N}$ values range from 0.2 to 3.2‰. Generally, oils accumulated in the Sub-Silesian and Silesian Nappes are isotopically enriched (av. 1.9 and 1.4‰, respectively) in comparison to oils from the Skole Nappe (av. 0.6‰). There doesn't seem to be any age or location trend differentiating the studied samples within Silesian Nappe, with only a vague hint of oils in Eocene fields being slightly isotopically depleted. Analyses of oil fractions indicate median values of: $\delta^{15}\text{N}(\text{aro})=1.0\text{‰}$, $\delta^{15}\text{N}(\text{res})=1.7\text{‰}$ and



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$\delta^{15}\text{N}(\text{asph})=2.4\text{‰}$; 24 samples of the 35 sample set show the isotopic trend: $\delta^{15}\text{N}(\text{aro}) < \delta^{15}\text{N}(\text{res}) < \delta^{15}\text{N}(\text{asph})$. From the remaining 11 samples only one (Dwernik-9) shows a complete reverse relationship: $\delta^{15}\text{N}(\text{aro}) > \delta^{15}\text{N}(\text{res}) > \delta^{15}\text{N}(\text{asph})$ while the rest show mixed trends.

The stable nitrogen composition of bulk oil appears to be independent from occurring biodegradation processes. Results from hydrocarbon fractions in which nitrogen presence was detected (aromatics, resins and asphaltenes) is consistent with data from whole oil analysis, and $\delta^{15}\text{N}$ values do not appear to be visibly influenced by the range of biodegradation processes.

Despite numerous proofs on biodegradation of nitrogen heterocompounds (Huang et al, 2003, Song et al., 2016) the total concentration of nitrogen in bulk oil and in hydrocarbon fractions (aromatics, resins and asphaltenes) doesn't seem to have any relation with neither commonly used biodegradation parameters applied in parallel research, nor overall assessment of range of biodegradation (Wenger et al., 2002). No imprint of microbial processes occurring in oils on $\delta^{15}\text{N}$ values may be connected to the intensity of biodegradation. Observed processes are only of levels ranging from untouched to heavy, which does not cover the full range of possible severities, and the nitrogen bearing compounds were left with little or none alterations.

Relative concentration of alkyl-carbazoles are: carbazole from 0 to 8% (av. 3%), methyl-carbazoles from 0 to 22% (av. 9%), dimethyl-carbazoles: 14-63%, (av. 35%), trimethyl-carbazoles 20-85% (av. 52%) indicating that in the majority of the analyzed oils the main fraction of carbazoles are di- and trimethyl-carbazoles. The carbazole and methyl-carbazoles are more susceptible to biodegradation than di- and tri- methyl-carbazoles (Song et al. 2016), which could be the reason of the very low concentration of alkylated carbazoles in biodegraded samples. There is no significant difference in alkyl-carbazoles distribution in relation to the age and location of sampled oils. Interpreting together nitrogen isotopic composition and the carbazole distribution, we may discern a negative correlation of $\delta^{15}\text{N}$ in resins and whole oil versus 1-/4-methyl-carbazole ratio. Moreover, the 1-/(2-+ 3-) methyl-carbazole ratio (increasing with biodegradation, but could be affected by facies, Song et al., 2016) has notably correlation with $\delta^{15}\text{N}$ in resins, asphaltenes and whole oil.

Conclusions

- Ni and V concentrations indicate analyzed oils as generated from Type II and III kerogen.
- The following trend: $\delta^{15}\text{N}(\text{aro}) < \delta^{15}\text{N}(\text{res}) < \delta^{15}\text{N}(\text{asph})$ is predominant within investigated population, showing systematic fractionation of nitrogen isotopes between hydrocarbon fractions.
- There is no imprint of biodegradation processes on nitrogen isotopic composition of studied crude oils.
- The distribution of alkyl-carbazoles may be used for estimation of biodegradation process extend.

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