

Mariusz ROSPONDEK¹, Leszek MARYNOWSKI²

PHENYL-POLYAROMATIC COMPOUNDS AND TERPHENYLS IN THE
POLISH CARPATHIAN SEDIMENTARY ROCKS

Abstract: In the Carpathian Podhale Paleogene Flysch sedimentary rocks the PhPAC are important constituents indicating most of all diagenetic oxidation of organic matter. The phenylated PAC derivatives comprise phenylnaphthalenes, phenylphenanthrenes, and in some samples phenylfluorenes, phenyldibenzo[*b,d*]furans and phenyldibenzo[*b,d*]thiophene. All these compounds are accompanied by polyphenyls, and binaphthalenes. Their isomers distribution pattern varies regularly with increasing maturity showing their applicability for the assesment of organic matter maturity. However, each homologues series is represented by the most thermodynamically stable isomers indicating advanced maturation of the organic matter. The maturation increases eastward. This observation is complementary with the results based on the diagenesis of clay minerals.

Keywords: Podhale Through, polyphenyls, maturity, organic matter oxidation

INTRODUCTION

Polycyclic aromatic compounds (PAC) containing phenyl (Ph) groups and polyphenyls are formed during combustion and oxidative pyrolysis of coal and coal-derived materials (Meyer zu Reckendorf 2000 and references therein). Recently they have been described from deposited dust around industrial areas (Marynowski et al. 2004). This clearly reveals that their origin is related to oxidation processes. Phenylpolyaromatic compounds (Ph-PAC) and polyphenyls are sometimes the major constituents of the aromatic fraction of extracts from some marine sedimentary rocks (Marynowski et al. 2002 and references therein) and coals (Willsch and Radke 1995). These compounds are quantitatively the major group of PAC derivatives after the alkyl homologues series within oil window. Their isomers distribution pattern varies regularly with increasing maturity showing their potential applicability for the assesment of organic matter maturity for oil industry. Subsequently, they can be useful for reconstruction of sedimentary basin burial history, where they can serve as source of such information in the case of lack of other unambiguous maturity parameters. This is partly the case in the Inner Carpathian Podhale Paleogene Flysch sedimentary rocks, where vitrinite reflectance is misleading. This is due to the presence of wide maturity spectrum of reworked vitrinite in these rocks. This work presents the preliminary results on

¹ *Institute of Geological Sciences, Jagiellonian University, ul. Oleandry 2a, 30-063 Kraków, Poland, ros@ing.uj.edu.pl* ² *University of Silesia, Faculty of Earth Sciences, Będzińska 60, 41-200 Sosnowiec, Poland; e-mail: marynows@wnoz.us.edu.pl*

identification, occurrence and distribution of phenyl derivatives of the polyaromatic compounds and polyphenyls in selected sections of the Paleogene Podhale Flysch, and the Mesozoic basement of the Podhale Trough. The results are compared with the PAC compounds encountered in thermally metamorphosed rocks of the Cieszyn flysch limestones from the Outer Carpathian Flysch of the Silesia nappe.

MATERIALS AND METHODS

For the research reported here, the following drill-cores were sampled: Zakopane IG-1 (Paleogene and Mesozoic), Poronin PAN-1 (Paleogene and Mesozoic), Biały Dunajec PAN-1 (Paleogene and Mesozoic), Chochołów PIG-1 (Paleogene and Mesozoic), Furmanowa IG-1 (Paleogene), Bukowina Tatrzańska IG-1 (Paleogene) and Bańska IG1 (Paleogene). In addition five samples from Międzyrzecze, representing Cieszyn limestones from the Outer Carpathian Flysch of the Silesia nappe were analysed.

The major method for identification of molecular composition of the extracts of the analysed rocks was gas chromatography coupled with mass spectrometry (GC-MS). The operation conditions were described elsewhere (e.g. Marynowski et al. 2002).

RESULTS

In the Inner Carpathian Podhale Paleogene Flysch phenyl derivatives of polycyclic aromatic compounds are encountered frequently though in comparatively low concentration comparing to the most common PAC such as methyl-naphthalenes, methyl-phenanthrenes ect. In the Podhale Flysch the phenyl-naphthalenes, terphenyls and phenyl-phenanthrenes are present, while the Mesozoic basement of this sedimentary basin contains in addition phenylfluorenes, phenyldibenzofuranes, phenyldibenzothiophenes. Additionally, relative concentrations of Ph-PAC and terphenyls in comparison with most common PAC (e.g. dimethylpyrenes and dimethylfluorenes, see Fig. 1) are higher in the Mesozoic, than in the Paleogene samples. In all samples analysed, except the shallowest, the phenyl derivatives are dominated by the most thermally stable isomers such as e.g. 2-phenyl-naphthalene, 3-, 2-phenyl-phenanthrenes, *m*- and *p*-terphenyls. At the depth range from 0 to 2000 m, in the Chochołów PIG-1 borehole, 1-phenyl-naphthalene is present, which compound disappears below 2000 to 2400 m of the depth. This corresponds to R_c ca. 0.7-0.8 %. In all other wells, only thermally stable isomers of Ph-PAC and terphenyls are present. The presence of phenyldibenzothiophenes (PhDBT) in the rocks of the Mesozoic basement only is noteworthy. Perhaps this is a reflection of advanced diagenesis of more labile organic sulphur compounds originally produced in environments with operating bacterial sulphate reduction. These compounds are represented by all isomers with domination of most stable 2- and 3-PhDBT. Similarly, the samples from the Outer Carpathians (Międzyrzecze) contain most thermally stable isomers of Ph-PAC and terphenyls. Moreover, the Ph-PAC are accompanied by pyrolytic polycyclic

aromatic hydrocarbons represented by compounds with angular condensation of rings like chrysene and triphenylene, benzoanthracene, benzo[*j*]fluoranthene +

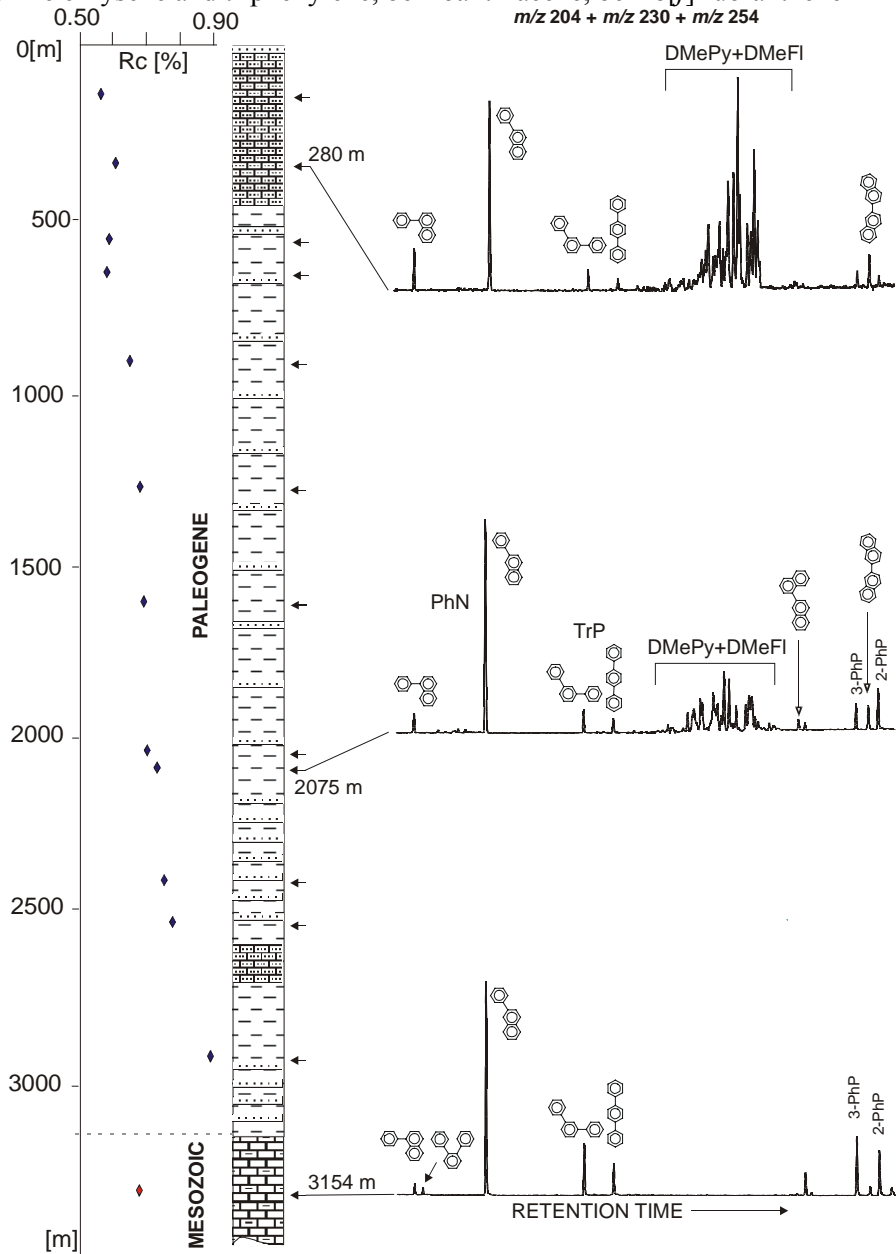


Fig. 1. Variation in the distribution of phenyl derivatives of PAC (PhN – phenylnaphthalenes, TrP – terphenyls, PhP – phenylphenanthrenes) along the section of the Chochołów PIG-1 well as the function of maturity (plotted as Rc) and lithology changes (the other compound abbreviations: DMePy- dimethylpyrenes; DMeFl- dimethylfluorenes).

benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene and coronene. The occurrence of these compounds is in agreement with the advanced alteration of organic matter due to thermal metamorphism caused by intrusive rocks.

CONCLUSIONS

The Paleogene sedimentary rocks of the Podhale Flysch contain phenyl derivatives of polycyclic aromatic compounds such as phenylnaphthalenes, phenylphenanthrenes. These are encountered frequently though in comparatively low concentration comparing to the most common PAC like methylnaphthalenes, methylphenanthrenes ect. In the Podhale Flysch shales the phenylnaphthalenes, terphenyls and phenylphenanthrenes are present, while the Mesozoic basement of this sedimentary basin contains in addition phenylfluorenes, phenyldibenzofurans and phenyldibenzothiophenes. Their presence reveals most of all diagenetic oxidation of organic matter. Their isomer distribution pattern depends on the maturation and in lower degree on the origin of sedimentary organic matter. The most regular variations are reflected by distribution of phenylnaphthalenes with both isomers present at shallow depths, and only 2-phenylnaphthalene present deeper in the section investigated, as best exemplified by samples of the Chochołów PIG-1 borehole (Fig. 1). Generally, the maturation increases eastward, which agrees well with the results based on the diagenesis of clay minerals (Kotarba 2004). Preliminary results on the Ph-PAC are available from the Outer Carpathian Flysch only from the Silesia nappe near Międzyrzecze, where these compounds were found in thermally metamorphosed rocks of the Cieszyn flysch limestines. There these are accompanied by polycondensed pyrolytic PAC represented by compounds of angular condensation of rings.

ACKNOWLEDGEMENTS: This study was partially supported by grant PB0354/P04/2003/25.

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