# Oil-oil and oil-source rock correlations in the northern Vienna Basin and adjacent Carpathian Flysch Zone (Czech and Slovak area)

J. Franců<sup>1</sup>, M. Radke<sup>2</sup>, R. G. Schaefer<sup>2</sup>, H. S. Poelchau<sup>2</sup>, J. Čáslavský<sup>3</sup> and Z. Boháček<sup>1</sup>

<sup>1</sup>Czech Geological Survey (ČGÚ), Leitnerova 22, 658 69 Brno, Czech Republic.

<sup>2</sup>Forschungszentrum Jülich GmbH (KFA), ICG4, D-52425 Jülich, Germany.

<sup>3</sup>Dept. of Environmental Studies, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic.

ABSTRACT: The geochemistry of oils was studied to characterize their origin and possible relationships to the source rocks in the contact region of the Bohemian Massif, Western Carpathians, and the northern part of the Vienna Basin in the Czech Republic and Slovakia. The reservoir depths range from 700 to 6000 m and temperatures from 36 to 150 °C. Their stratigraphic and structural positions comprise the Neogene of the Vienna Basin, underlying Inner Carpathian units, adjacent Carpathian Flysch and foredeep, autochthonous Palaeogene, Palaeozoic, and the crystalline basement of the Bohemian Massif. The genetic potential of the source rocks increases from the Palaeozoic through the autochthonous Palaeogene, and from the Jurassic to the Oligocene Menilite Fm. in the Flysch nappes. The Jurassic and Palaeogene enter the oil window at a depth of at least 3.5 km. Oils were expelled from the source rocks buried deeper than 4-5 km where they have reached maturation levels equivalent to 0.8 to 1.17% vitrinite reflectance. Oil families differ mainly in oleanane content and other indicators of either marine or terrestrial organic facies. Biodegradation of oils occurs in reservoirs at depths down to 1.8 km. The compositions of some of the oils may be explained as a result of evaporative fractionation and gas percolation through the deeper oil accumulations. Mixing of biodegraded oils with allochthonous gas condensates suggests two principal migration events.

KEYWORDS: oil, source rock, correlation, Vienna Basin

### INTRODUCTION

In the Carpathian, Pannonian and Alpine region, several oil families and source rocks have been characterized:

- (1) (a) Upper Jurassic marls of the Bohemian Massif: main source rock of oils in the Vienna Basin and adjacent Molasse Zone in Lower Austria (Welte et al. 1982–pre-Tertiary source in general; Ladwein 1988; Ladwein et al. 1991; Wehner & Kuckelkorn 1995), and possibly some oils in the eastern Czech Republic (Müller & Krejčí 1992; Wehner & Kuckelkorn 1995).
  - (b) The *Upper Jurassic of the Helveticum*, northern alps: possible source of oils in the Tertiary base and the Cretaceous in the Upper Austrian and German Molasse (Wehner & Kuckelkorn 1995).
- (2) The Oligocene Menilite shales: main source rock of the oils in the overthrust and foredeep of the Carpathians in Poland (ten Haven et al. 1993; Lafargue et al. 1994). The good oilsource potential of this unit is also characterised by Šimánek et al. (1981), Vetö (1987), Kruge et al. (1991), Koltun (1992) and Köster et al. (1995). Stratigraphic equivalents comprise:
  - (a) autochthonous Eocene to Oligocene Nesvačilka and Tešany Fms. of the eastern Bohemian Massif (Müller and Krejčí 1992);

- (b) autochthonous Early Oligoene Fischschiefer. considered to be the main source rock below the overthrust of the Austrian Alps (Zimmer & Wessely 1996), and a possible source of oils in the Tertiary base and the Cretaceous in Upper Austria and the German Molasse (Hufnagel et al. 1979; Ladwein 1988; Wehner & Kuckelkorn 1995);
- (c) laminated euxinic Tard Clay Fm. of the Lower Oligocene, with good source potential for oil and gas in the North Hungarian Palaeogene basin (Brukner-Wein et al. 1990; Milota et al. 1995).
- (3) The Upper Triassic Kössen mark: main potential source rock of the oils in the western Pannonian Basin (Brukner-Wein & Vetö 1986; Hetényi 1989; Szalay & Koncz 1991; Clayton & Koncz 1994).
- (4) The Miocene: source rocks of some oils in the Pannonian Basin in Hungary (Szalay & Koncz 1991; Koncz & Etler 1994; Clayton & Koncz 1994) and possibly in the Styrian (Graz) Basin, Austria (Sachsenhofer 1994). The Miocene was considered to be the main source of oil and gas in the Vienna Basin in earlier studies (Šimánek 1977; see Kratochvil & Ladwein 1984), but introduction of advanced geochemical techniques such as pyrolysis and biomarker analysis has shown that in general the Miocene has poor source potential and is often not sufficiently mature.

Some authors admit to the occurrence of other possible oil and gas source rocks within the autochthonous platform sediments: e.g. Devonian limestones and dolomites, and Upper Jurassic carbonates (Kotarba & Jawor 1993), and an unspecified Palaeozoic unit (ten Haven et al. 1993; Lafargue et al. 1994).

The above-mentioned formations or their equivalents occur in different structural positions in the studied area. The scope of this paper is to give an overview of the organic facies and maturity of the oils and potential source rocks, and their possible mutual genetic relationships, in the northern part of the Vienna Basin and the adjacent area in the Czech Republic and Slovakia.

### GEOLOGICAL SETTING AND SAMPLES

The region studied comprises four principal units from which the source rocks and more than 60 oils were sampled. Selection of the best source rocks was based on screening analyses of the total organic carbon (TOC) content, and Rock-Eval pyrolysis of several hundred samples. The numbers of samples given here represent the more detailed analyses.

- (1) The Bohemian Massif belongs to the North European Platform and includes the crystalline basement (5 oils) and the autochthonous sedimentary cover comprising Devonian to Namurian carbonates and siliciclastics (2 rocks, 2 oils), Jurassic carbonates, siliciclastic rocks and marls (7 rocks, 1 oil), and Palaeogene siltstones, shales and sandstones (7 rocks, 3 oils).
- (2) The Carpathian Foredeep Basin with Lower Miocene fill (4 oils).
- (3) The Carpathian Flysch Belt (allochthonous nappes) with the external, Krosno-Menilite Group (U. Jurassic to Lower Miocene) (2 rocks, 1 oil) and the internal, Magura Group (Lower Cretaceous to Oligocene) (6 oils).
- (4) The superimposed Vienna Basin (Miocene to Quaternary) (18 oils).
- (5) Central Carpathian nappes with dominant carbonate lithologies (2 oil samples).

More details of the geological evolution of these basins and thrust complexes are given e.g. by Krejčí *et al.* (1996).

### **METHODS**

Rocks were ground and extracted using a modified flow-blending technique (Radke et al. 1978; Radke & Welte 1983) using a mixture of dichloromethane and methanol (99:1 vol.) as a solvent. Internal standards were added to rock powders and oils. Total extracts and oils were separated into saturated and aromatic hydrocarbons, and heterocompounds by medium-pressure liquid chromatography (Radke et al. 1980). The aromatic fraction of some samples was further separated into ring classes using high-performance liquid chromatography (HPLC) in order to avoid coelution problems in susequent GC analyses. The aromatic compounds were evaluated by established methods (see Radke 1987 for review).

The whole oils as well as the saturated and aromatic fractions were analysed by capillary gas chromatography (GC). The gas chromatograph was equipped with a flame ionization detector (FID), which in the case of analysis of the aromatic fraction was coupled with a HALL<sup>TM</sup> electrolytic conductivity detector (sulphur-selective mode). Gas chromatography-mass spectrometry (GC-MS) was applied to identify a range of isoprenoids and a C<sub>30</sub> hopane in the GC-FID traces, and to assess biomarker distribution in the SIM and partly also MRM mode. The ratios of hopanes and steranes were evaluated from the selected mass

chromatograms (m/z 191, 217, 218) by established methods (see Mackenzie 1984 and Peters & Moldowan 1993 for reviews).

Whole oils were analysed after dissolution in n-pentane. Light hydrocarbons (C6–C7) were analysed in the oils using a static head-space method originally developed for analysis of source rocks, but which is also applicable to petroleum (Schaefer *et al.* 1984a).

Source-rock maturation and hydrocarbon generation were simulated using the 1-D PDI<sup>TM</sup>-PC (IES) modelling software based on the principles of Welte *et al.* (1981) applying chemical reaction kinetics (Tissot & Espitalié 1975). Measured organic maturity parameters—vitrinite reflectance (R<sub>o</sub>) and biomarker ratios—were used as a record of the total thermal history of the rocks, for calibration of a simulated burial and thermal history. Geothermal data are from Čermák (1979).

### SOURCE ROCKS

The screening TOC and Rock-Eval analyses suggested that four lithostratigraphic units include intervals with potential source-rocks. More geological details are given in Krejčí et al. (1996).

- (1) The Lower–Upper Carboniferous: the Myslejovice and Ostrava Fms.
- (2) The Upper Jurassic: the Mikulov marls.
- (3) The Palaeogene shales and siltstones: the Tešany and Nesvačilka Fms. (both belong to the autochthonous cover of the Bohemian Massif).
- (4) The Oligocene: Menilite Formation of the Krosno-Menilite Group of the Carpathian Flysch nappes.

The differences in organic facies among these formations are inferred from the variation in distribution of certain organic species e.g. n-alkanes and isoprenoids in immature samples (Fig. 1). The alkane fingerprints of the Carboniferous and Jurassic rocks show a maximum at about C1- with odd/even preference both in the lower and higher molecular ranges. Such distributions are typical of marine algal-derived organic matter, with minor input of terrestrial plant debris. Microscopic observation in the fluorescence and reflected light modes confirms the presence of planktonic and benthic algae along with abundant vitrinite in the Carboniferous shales. Flattened planktonic algae are abundant in the Jurassic marls, where the matrix shows a weak greenish fluorescence, due to amorphous organic matter supposed to consist mainly of ultralaminae of algae. Indigenous vitrinite is a minor component, while redeposited vitrinite and inertinite are abundant macerals in reflected light. The marine planktonic origin of the Jurassic kerogens is also shown by higher amount of C<sub>27</sub> steranes (Fig. 2).

The autochthonous Palaeogene rocks and the Menilite Fm. show bimodal n-alkane and isoprenoid distribution with contributions from both terrestrial plant lipids (around C<sub>29</sub> n-alkane) and algal and/or bacterial organic matter (with a maximum of around C<sub>15</sub> to C<sub>17</sub>). The high proportion of pristane typical of coaly material suggests deposition in a fluvial/deltaic, partly aerated environment. This is in agreement with the microscopic observations of the Palaeogene (Nesvačilka Fm.) where vitrinite is the dominant maceral. The hydrogen index (HI) of 100–200 mg HC/g TOC and the sterane distribution is typical of humic kerogen (type III). These source rocks are gas-prone rather than oil-prone, but they may be more oil-prone in a more distal part of the basin, presently buried deeply under the Carpathian Flysch nappes in the southeast.

The Menilite Fm. shows a similar alkane distribution to the Nesvačilka Fm. but has considerably greater source potential (S1 + S2 15–20 mg/g rock) and hydrogen index (above 400–

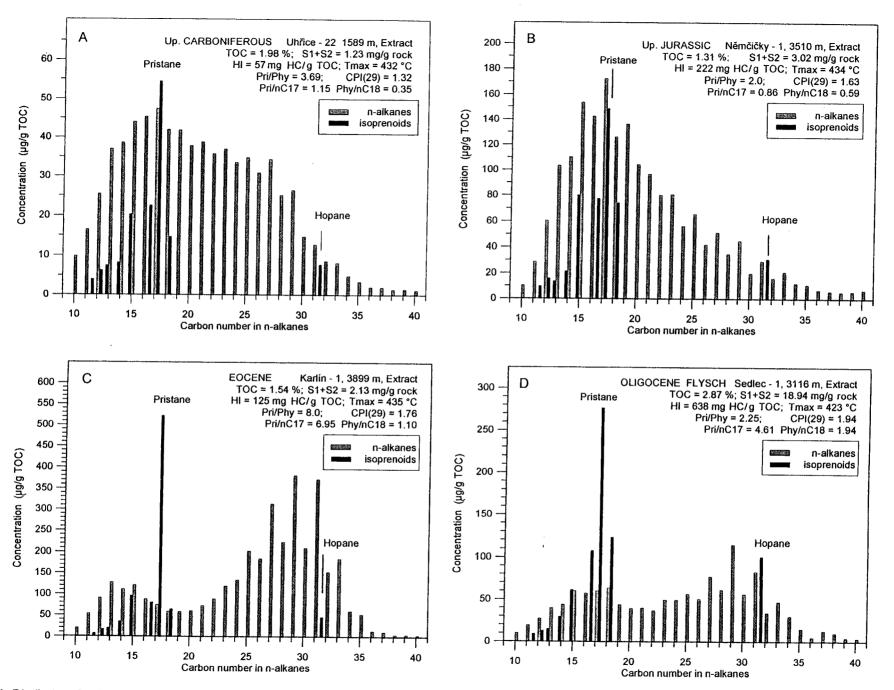


Fig. 1. Distribution of n-alkanes, isoprenoids, and a  $C_{30}$  hopane in extracts of immature to early mature source-rocks. (A) Carboniferous; (B) Upper Jurassic with the dominant range of alkanes around n-C17 typical of algae; (C) autochthonous Palaeogene with bimodal n-alkane distribution typical of mixed marine and terrestrial kerogen; (D) Menilite Formation of the Krosno-Menilite Flysch of the Carpathians.

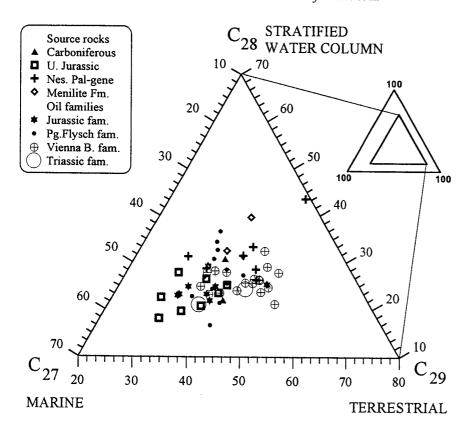


Fig. 2. Ternary diagram of  $C_{27-28-29}$   $\beta\beta$  (S+R) regular steranes in the source rocks and oils (m/z = 218).

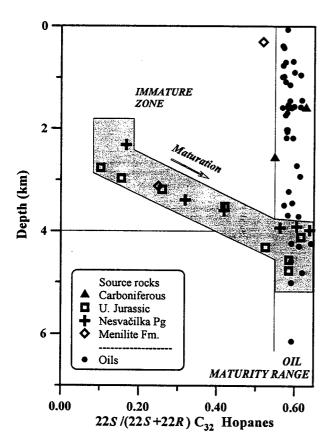


Fig. 3. Depth plot of source-rock and oil maturity based on the 22S and 22R isomer ratio of  $C_{32}$  hopanes (m/z = 191). The narrow oil maturity range suggests migration from depths greater than 4 km. All shallower Palaeogene and Jurassic source rocks are distinctly less mature.

650 mg/g TOC). These sediments are enriched in C<sub>28</sub> sterane, suggesting a possibly stratified water column. Under the microscope the flattened greenish-yellow planktonic algae are abundant, and the matrix has a yellow-green fluorescence, probably due to amorphous liptinite and alginite ultralaminae. Menilite shales are good to excellent oil source-rocks. They have the highest liptinite contents of all the studied source rocks, and vitrinite is only a minor maceral.

These findings support the palaeo-environmental characteristics of the Menilite Fm. given by Roth & Hanzlíková (1982) and Vetö (1987), who suggested a narrow isolated sea, about 2000 m deep, with possible upwelling bringing nutrients from the ocean depths and rivers freshening the upper water layer (up to 1000 m), with abundant bioproductivity (e.g. diatoms). Density stratification of the water caused anoxia above and below the sea floor and created excellent conditions for accumulation and preservation of organic matter. Concomitant volcanism supplied silica and contributed to the formation of silicite layers.

### **MATURITY**

Source rock and oil maturity is estimated from 22S/(22S+22R) ratios of  $C_{32}$  hopanes and 20S/(20S+20R) and  $\beta\beta/(\alpha\alpha+\beta\beta)$  ratios of  $C_{29}$  steranes, and the Methylphenanthrene Index (MPI 1) values. These parameters show good correlation with the Rock-Eval  $T_{max}$  and measured vitrinite reflectance ( $R_o$ ) of the rock samples. As shown in Figs 3, 4, and 5, the maturity of the source rocks is clearly lower than that of the oils, down to a depth of at least 4–5 km. The equivalent vitrinite reflectance  $R_c$  calculated from the MPI 1 using the correlation of Radke (1988), suggests that the oils were expelled from the source rocks at a fairly advanced maturity ranging from 0.8 to 1.15 %  $R_c$  (i.e. during and after the peak oil generation).

During maturation source rock generates light hydrocarbons

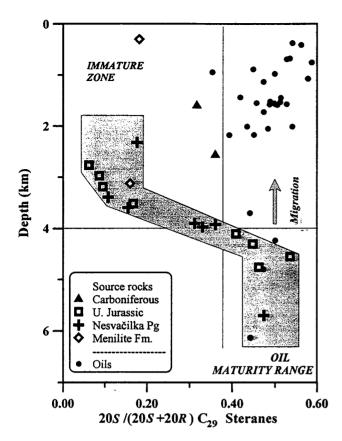


Fig. 4. Depth plot of source-rock and oil maturity based on the 20*S* and 20R isomer ratio of  $C_{29}$  steranes (m/z = 217). The equilibrium is reached deeper than in the case of hopanes (Fig. 3).

 $(C_2-C_7)$  with a characteristic distribution controlled by kerogen type and catagenic temperature (Leythaeuser *et al.* 1979; Thompson 1983; Schaefer 1992). Oil maturity was evaluated from the slightly modified J ratio (see appendix) and expressed as an equivalent vitrinite reflectance  $R_c$  using the correlation plot of Schaefer (1992) based on data from Posidonia shale (Lower Toarcian) source rocks. It is evident from this iso-/cyclo-alkane ratio in the  $C_7$  range (Fig. 6) that the maturity of most of the oils varies within a range that does not change with depth. Only at shallow depths do some of the oils show a false lower maturity because of the faster removal of the branched alkanes than the cyclo-alkanes due to biodegradation.

This suggests that oil migration occurred over a vertical distance of at least 3–4 km, as was also concluded by Welte *et al.* (1982) and Ladwein (1988) for the Austrian part of the Vienna Basin.

### MODEL OF MATURATION HISTORY AND HYDROCARBON GENERATION

The burial and thermal history of the Němčičky-2 borehole section is shown in Fig. 7. This example represents the area of the Nikolčice–Kurdějov Ridge, with thick Upper Jurassic limestones and marlstones and almost no autochthonous Palaeogene. The greater maturity of Carboniferous formations indicates deéper burial and early oil and gas generation, followed by uplift during and after the late Palaeozoic Variscan orogeny. Deposition of the Upper Jurassic was followed by minor erosion and deposition of the Upper Cretaceous and Palaeogene. The Palaeogene sediments are restricted to two deep canyons shown in Fig. 15 (see also Krejčí et al. 1996.

Jurassic and Palaeogene source rocks were buried to the main zone of oil generation during early Miocene thrusting and sedimentation in the Carpathian region.

The Menilite Formation occurs in the lower part of the Krosno-Menilite Flysch unit. This was imbricated and tectonically thickened in the frontal part of the nappes during overthrusting in the Early Miocene (see the upper part of the section in Fig. 7). Its pre-tectonic sedimentary thickness was not very great, but due to tectonic thickening and good source potential it may be considered as a source of oil and gas in the deeper part of the Flysch nappes and also below the Vienna Basin (Fig. 15; Krejčí et al. 1996). In many boreholes the Flysch nappes have greater maturity than expected considering the present burial depth and temperature. Hence, these units must have been buried deeper prior to emplacement upon the platform. Similar conclusions were drawn by Ladwein et al. (1989) in the case of the Calcareous Alpine and Helvetikum nappes thrust over the Molasse and Bohemian Massif in Upper Austria. Koltun (1992) also concludes that the maturity level of the Menilite Fm. in the Ukrainian Carpathians is preserved from the pre-emplacement phase of evolution, since it is marginally mature, does not change in the upper 4 km in the present profile, and continues to increase only below 4-5 km.

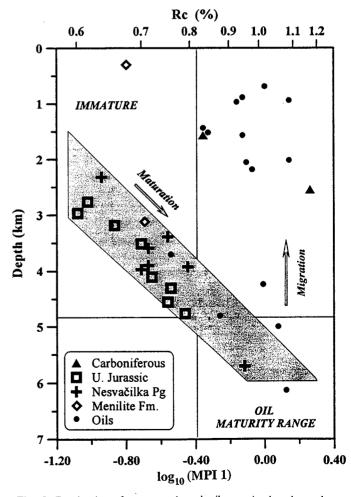


Fig. 5. Depth plot of source-rock and oil maturity based on the logarithm of the MPI 1 (Radke 1988) and the equivalent (calculated) vitrinite reflectance  $R_{\rm c}$  (for details see appendix). The maturity of oils ranges from 0.8 to 1.15%  $R_{\rm c}$ , suggesting expulsion of oils from the source rocks slightly beyond the maximum of oil generation.

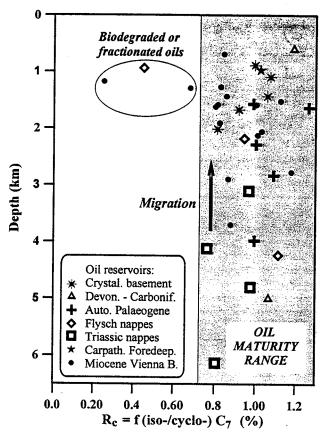
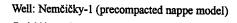


Fig. 6. Estimation of oil maturity in relationship to depth in the northern Vienna Basin, based on the J ratio  $(2-, +3-MC_0)/\sin(DMCYC5)$  (see appendix). Data are plotted as equivalent vitrinite reflectance  $(R_c)$  using the correlation of Schaefer (1992), and are in good agreement with the conclusions based on biomarkers and methylphenanthrenes.

## BIODEGRADATION AND OTHER ALTERATIONS OF OILS

Biodegradation is indicated by selective removal of the light n-alkanes, iso-alkanes and partly also isoprenoids from the oils (e.g. Týnec-109, Fig. 9), and is common in reservoirs of all ages down to a depth of 1.7 km where the temperature is 60-75 °C. usually referred to as the limit for biodegradation (Tissot & Welte 1984). In Fig. 11 the level of biodegradation is shown in relation to depth by the calculated ratio of a branched to normal C6 alkane. Some of the shallow reservoirs, however, contain little- or non-biodegraded oils, and seem to be better sealed and filled more recently. At greater depths, oils are unaffected by biodegradation and show a continuous hydrocarbon distribution through the entire molecular range (Fig. 8). Several reservoirs in the crystalline basement and/or the Palaeozoic of the platform (see Krejčí et al. 1996) comprise older biodegraded oil mixed with gas-condensate originating from a more recent phase of oil and gas migration. In Figs 12 and 13 the maturity of the condensates (based on the C<sub>7</sub> range) is compared with that of the heavier oil fraction measured on the methylphenanthrenes. The position of these two molecular ranges in relation to n-alkanes is shown in the gas chromatogram in Fig. 8. The light hydrocarbon maturity is based on the slightly modified J parameter of Schaefer (1992) denoted as J<sub>n</sub>, the heptane value of Thompson (1983), and the MPI 1 after Radke (1988). The definitions of these parameters are given in the appendix. The application of  $J_n$  instead of J as a maturity parameter implies that the difference between the J-R<sub>o</sub> and J<sub>n</sub>-R<sub>o</sub> relationships is only lower than the error bars of the original data. All three maturity parameters are expressed as equivalent (calculated) vitrinite reflectance (Rc) using the correlations of the respective authors.

The crossplot of the  $J_n$  and MPI 1 maturity parameters suggests that the biodegraded oils and gas-condensates are of similar maturity ranging from 0.8 to 1.2%  $R_c$ . In Fig. 13, three groups of oils differ in the parameter based on the heptane value, which is more sensitive to biodegradation and gas stripping. The middle group (A) represents unaltered oils with similar maturity of both fractions. The characteristics of the other two may be best explained by evaporative fractionation (Thompson 1987). Allochthonous gas injected into an oil reservoir preferentially



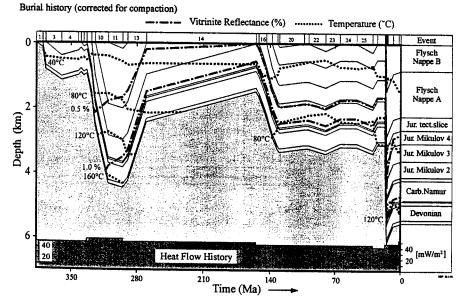


Fig. 7. Burial and thermal history of the autochthonous Palaeozoic and Mesozoic of the Bohemian Massif, and emplacement of the allochthonous nappes of the Flysch Carpathians, in the profile of the well Němčičky-1.

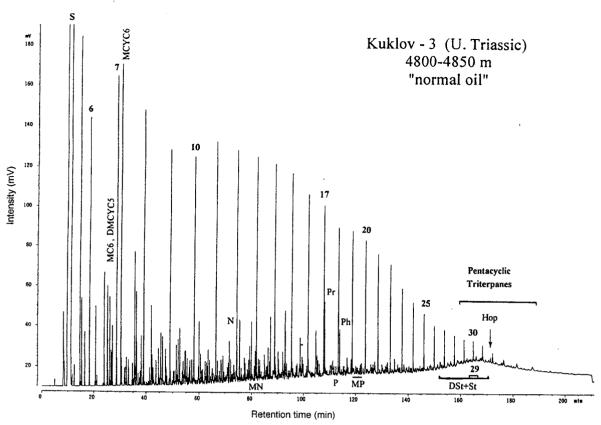


Fig. 8. Whole-oil GC analysis of a non-altered oil from a Triassic reservoir below the Neogene in the Vienna Basin. The distribution of hydrocarbons is continuous and suggests a single origin for the oils. Numbers indicate carbon atoms in n-alkanes. Positions of the following compounds are indicated: S, n-pentane solvent; MC6, methylhexanes; DMCYC $_5$ , dimethylcyclopentanes; MCYC $_6$ , methylcyclohexane; N, naphthaline; MN, methylnaphthalines; Pr, pristane; Ph, phytane; P, phenanthrene; MP, methylphenanthrenes; Hop, C30 hopane; DSt + St, dia- and regular  $C_{27-28-29}$  steranes.

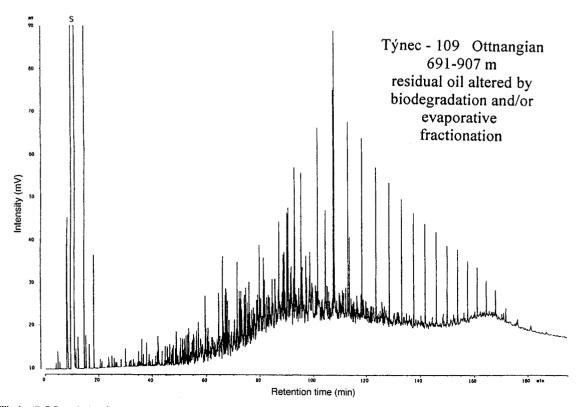


Fig. 9. Whole-oil GC analysis of an altered oil from the Ottnangian of the Vienna Basin. Light hydrocarbons are eliminated by biodegradation and/or evaporative fractionation due to gas percolation.

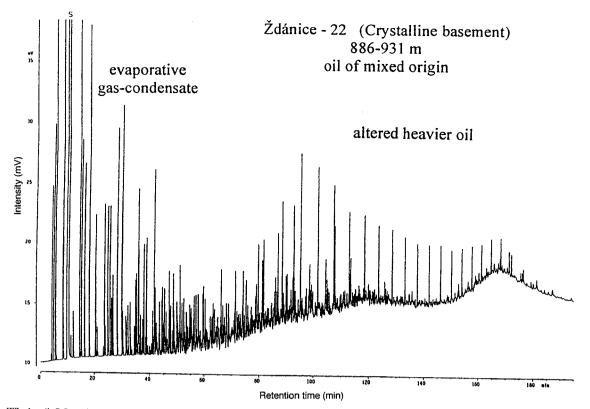


Fig. 10. Whole-oil GC analysis of an oil from a crystalline basement reservoir in the Bohemian Massif, sealed by the Flysch nappes. This is a mixture of a degraded oil which entered the reservoir at an earlier phase and a gas condensate of a later migration phase. The latter is likely to originate due to evaporative fractionation (stripping) of a 'normal' oil by allochthonous gas, which preferentially extracted light alkanes.

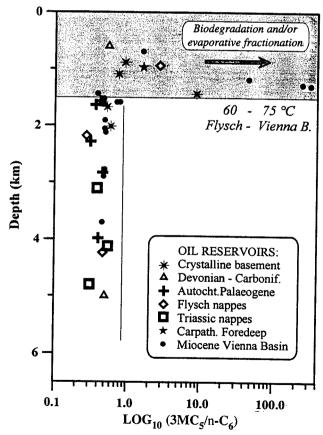


Fig. 11. Branched-to-normal alkane concentation ratio in the  $\rm C_6$  range (for explanation see appendix) with depth, as a biodegradation and/or evaporative fractionation parameter, in the northern Vienna Basin and adjacent Carpathian Flysch and Foredeep area.

strips the n-alkanes, which accumulate in the newly formed gascondensate (group B) and leaves behind the residual oil depleted in n-alkanes (group C). Welte et al. (1982) noticed this phenomenon in some of the condensates reservoired in the Calcareous Alpine nappes below the Vienna Basin. Thompson (1987) re-examined the data of Welte et al. (1982) and compared them with experimental evaporative fractionation of oils, which yielded residual oils depleted in n-alkanes and relatively enriched in aromatic compounds. These observations suggest that hydrocarbon generation and migration took place in at least two phases in the Vienna Basin and the adjacent Alpine-Carpathian region. The gases of the second phase altered many of the previously formed oil accumulations. The allochthonous (i.e. not oil-associated) origin of many gases in this region is proven by the methane carbon isotopic data (Schoell 1984; Milička et al. 1994), which support the proposed concept of generation and migration.

### OIL FAMILIES

Evaluation of possible oil—oil and oil—source rock correlations in this paper is based mainly on the proportion of marine to terrestrial sources, and on the occurrence of the angiosperm-biomarker 18α(H)-oleanane (Ekweozor et al. 1979). The occurrence of the latter may be used as proof of a Late Cretaceous or younger source rock or oil. However, its absence may not be only due to a greater age but also to the absence of land-derived organic material in the sediments (Moldowan et al. 1991; Peters & Moldowan 1993). This is indicated by the absence of oleanane in some of the Neogene shales in the Danube and Makó basins, both partial depressions of the Pannonian Basin system (Milička et al. 1996; Sajgó 1984).

Considering several geochemical parameters, the investigated oils may be classified into several families (Figs 2, 14, 15):

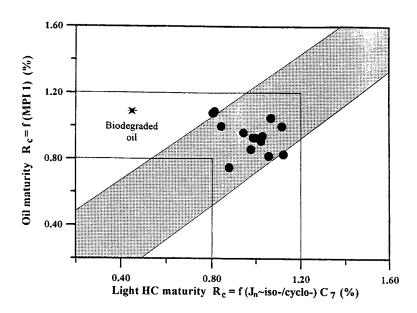


Fig. 12. Correlation of oil maturity parameters based on MPI 1 (Radke 1988) and the  $J_n$  value [(2,  $\pm$  3-MC $_0$ )/ sum(DMCYC $_5$ )] modified from J value of Schaefer (1992), both expressed as calculated equivalent vitrinite reflectance  $R_c$  (for details see appendix). Except for a biodegraded oil, both light and medium–heavy molecular ranges of oils are at a similar thermal maturity. Molecular ranges of  $J_n$  and MPI are shown in Fig. 8.

- (1) The first group of oils originates from a more marine source rock, and in the C<sub>27-28-29</sub> steranes ternary diagram these oils can be grouped together with organic extracts of the Upper Jurassic marls. Absence of oleanane also suggests Jurassic (or pre-Upper Cretaceous) age (Čáslavský 1991; Peters 1991, pers. comm.), These oils occur underneath or within the Flysch nappes northwest of the Vienna Basin, and correspond to the main family of Ladwein (1988) and Wehner & Kuckelkorn (1995). It is surprising that one oil from this family (Němčičky-1) has no oleanane, even though it occurs in an Oligocene reservoir very close to the Menilite Shale and during migration it must have passed by the autochthonous Palaeogene formations. This shows that the probability of the oil to pick up biomarkers from adjacent rocks during migration is not very high.
- (2) Oils of the second family occur in the crystalline reservoirs covered by the Flysch, or within the Flysch, north of the Vienna Basin (Fig. 15). Their sterane distribution is closer to the Palaeogene and Menilite source rocks (Fig. 2), with a mixed contribution from marine and humic organic matter.
- These oils show a distinctive Tertiary (and/or upper Cretaceous?) oleanane signature (Čáslavský 1991; Peters 1991, pers. comm.) which is also characteristic of both the autochthonous Palaeogene and Menilite (Flysch) source rocks (Figs 14, 15). The latter is considered to be the main source rock in the adjacent region of the Outer Carpathians in Poland (ten Haven et al. 1993; Lafargue et al. 1994) and in the Ukraine (Koltun 1992). This oil family may also have some genetic relationship to the oils possibly sourced from the Early Oligocene Fischschiefer in Upper Austria and the German Molasse (Hufnagel et al. 1980; Ladwein 1988; Wehner & Kuckelkorn 1995).
- (3) The third family includes most of the oils in the Neogene reservoirs of the Vienna Basin. They show variable proportions of marine and terrestrial kerogen, and a variable amount of oleanane suggests at least partly Tertiary origin. These findings extend earlier studies (Welte et al. 1982) that concluded that most of the oils in the Vienna Basin belong to a single family originating from a pre-Neogene source (the autochthonous Jurassic of the Bohemian Massif; Ladwein

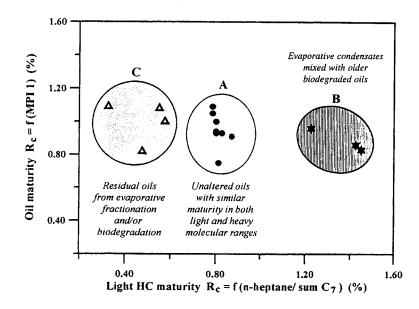


Fig. 13. Comparison of maturity parameters based on MPI 1 (Radke 1988) and heptane value of C<sub>7</sub> range in oils (Thompson 1983; for explanation see in appendix). The heptane value includes n-heptane, and hence is sensitive to biodegradation and evaporative fractionation. The group  $\Lambda$  represents 'normal' unaltered oils with similar maturity values in both molecular ranges. Group B is considered to include the gas-condensate products of the evaporative fractionation of 'normal' oils. Group C comprises biodegraded oils and/or residual oils from evaporatively fractionated 'normal' oils.

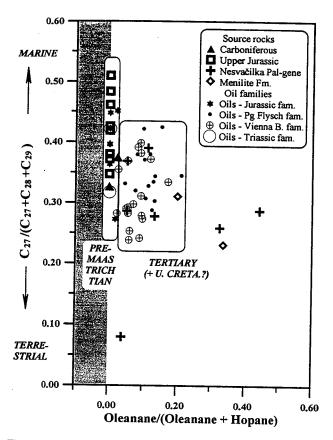


Fig. 14. Oil–source rock correlation based on  $\beta\beta$  (S+R) C<sub>27-28-29</sub> regular steranes and the ratio of  $18\alpha(H)$  oleanane to C<sub>30</sub> hopane.

1988). As the maturity-sensitive hopanes in these oils almost do not vary with depth and are strikingly different from those in the Miocene sediments, it is unlikely that the oils picked up a significant amount of oleanane during migration from dispersed organic matter of Tertiary age. We suggest that additional source rocks of Palaeogene age, most probably the Menilite Formation in the Flysch nappes and/or palaeogeographically related to the autochthonous Palaeogene, generated or at least co-sourced some of the Vienna Basin oils during the Early Miocene burial.

(4) Oils from the Mesozoic reservoirs (Fig. 8) of the Inner Carpathians (analogue of the Calcareous Alps in Austria) underneath the Neogene (NE part of the Vienna Basin, Fig. 15) form a fourth family. Absence of oleanane and the geological structure suggest the Mesozoic origin. An analogue of the Upper Triassic Kössen Marl described in western Hungary (Brukner-Wein & Vetö 1986; Hetényi 1989; Szalay & Koncz 1991; Clayton & Koncz 1994) is the most probable source rock.

The authors wish to thank the following: the Moravian Oil Company, Hodonín, for valuable geological information, data and samples; D. H. Welte, B. Horsfield and R. Littke (KFA Jülich); P. Müller (ČGÚ) for stimulating discussions; H. Willsch, W. Laumer, U. Disko, F.-J. Keller, J. Hoeltkemeier and E. Biermanns, ICG-4, KFA Jülich, for analytical assistance; IES Jülich GmbH. for providing the 1-D PDITM-PC modelling software; and the Czech–German Bilateral Co-operation Treaty in Science and Technology for travel funds in 1992–95. JF greatly appreciates the valuable suggestions of H. W. Ladwein, G. Wessely (OMV) and K. E. Peters at an earlier phase of the study.

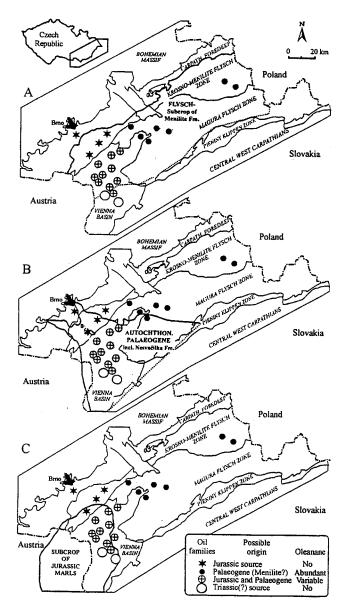


Fig. 15. Oil-source rock correlation in map showing the regional occurrence (subcrops) of; (A) Menilite Formation of the Krosno-Menilite Flysch group of nappes; (B) autochthonous Palaeogene; and (C) the autochthonous Jurassic (Mikulov Marl) source rock. The four oil families are based on biomarker similarities.

### **APPENDIX**

Maturity parameters:

H = 100 × n-heptane/sum(cyclohexane through heptane + methylcyclohexane) in %; 'heptane value' or 'H paraffinicity' as defined by Thompson (1983) who gave a crossplot of H with vitrinite reflectance.

 $J_n$  = (2-, + 3-methylhexane)/(1,cis-3-, + 1,trans-3-, + 1,trans-2-, + 1,1-dimethylcyclopentane), similar to the Isoheptane Value of Thompson (1983) and modified from J of Schaefer (1992) which includes 1,cis-2-instead of 1,1-dimethylcyclopentane. The correlation of random vitrinite reflectance  $R_c$  ( $R_r$  in original) and J in the Posidonia Shale is given by the empirical relationship  $R_c$  = 0.84 + 1.1 log J.

MPI 1 = 1.5(2-MP + 3-MP)/(P + 1-MP + 9-MP) where P is phenanthrene and MPs are the four methylphenanthrene (Radke 1988). The correlation of random vitrinite reflectance ( $R_{\rm m}$ , here  $R_{\rm c}$ ) and MPI 1, based on rock samples with type III kerogen and coals

from northwest and west Germany and western Canada, is given by the empirical relationships:  $R_c=0.38+0.61$  MPI 1 ( $R_c$  from 0.55 to 1.40%) and  $R_c=2.59-0.59$  MPI 1 ( $R_c$  from 1.45 to 2.20%).

Biodegradation parameter:  $\log (3MC_5/n-C_6) = \log (3 \text{ methylpentane/} n-\text{hexane})$  (Welte *et al.* 1982).

#### REFERENCES

- BRUKNER-WEIN, A. & VETÖ, I. 1986. Preliminary organic geochemical study of an anoxic Upper Triassic sequence from W. Hungary. In: Leythaeuser, D. & Rullkötter, J. (eds) Advances in Organic Geochemistry. Pergamon Press, Oxford, 113–118.
- ——, HETÉNYI, M. & VETÖ, I. 1990. Organic geochemistry of an anoxic cycle: a case history from the Oligocene section, Hungary. Organic Geochemistry, 15, 123–130.
- ČÁSLAVSKÝ, J. 1991. Biomarkers in the Moravian Oils. PhD thesis, Czech Geological Survey Prague, Division Brno.
- ČERMÁK, V. 1979. Review of heat flow measurements in Czechoslovakia. In:Čermák, V. & Rybach, L. (eds) Terrestrial Heat-Flow in Europe. Springer Verlag, Berlin, 152–160.
- CLAYTON, J. L., KONCZ, I. 1994. Petroleum geochemistry of the Zala Basin, Hungary. AAPG Bulletin, 78, 1–22.
- EKWEOZOR, C. M., OKOGUN, S. I., EKONG, D. E. U. & MAXWEIL, J. 1979.
  Preliminary organic geochemical studies of samples from the Niger Delta (Nigeria) II.
  Analyses of shale for triterpenoid derivatives. Chemical Geology, 27, 29–37.
- HETÉNYI, M. 1989. Hydrocarbon generative features of the Upper Triassic Kössen marl from W. Hungary. Acta Mineralogica-Petrographica, 30, 137–147.
- HUFNAGEL, H., TESCHNER, M. & WEHNER, H. 1980. Correlation studies on crude oils and source rocks in the German Molasse basin. In: Douglas, A. G. & Maxwell, J. R. (eds) Advances in Organic Geochemistry 1979: Physics and Chemistry of the Earth 12. 51–66.
- KOLTUN, YU. V. 1992. Organic matter in Oligocene Menilite formation rocks of the Ukrainian Carpathians: palaeoenvironment and geochemical evolution. Organic Geochemistry, 18, 423–430.
- KONCZ, I. & ETLER, O. 1994. Origin of oil and gas occurrences in the Pliocene sediments of the Pannonian basin, Hungarv. Organic Geochemistry, 21, 1069–1080.
- KÖSTER, J., ROSPONDEK, M., ZUBRZYCKI, A., KOTARBA, M., DE LEEUW, J. W. & SINNINGHE DAMSTÉ, J. S. 1995. A molecular organic geochemical study of black shales associated with diatomites from the Oligocene Menilite Shale (Flysch Carpathians, SE Poland). In: Grimalt, J. O. & Dorronsoro, C. (eds) Organic Geochemistry: Developments and Applications to Energy, Climate, Environment and Human History. AIGOA, Donostia-San Sebastián, 87–89.
- KOTARBA, M. & JAWOR, E. 1993. Petroleum generation, migration and accumulation in the Miocene sediments and Palaeozoic-Mesozoic basement complex of the Carpathian Foredeep between Cracow and Pilzno (Poland). In: Spencer, A. M. (ed.) Generation. Accumulation, and Production of Europe's Hydrocarbons III. Springer-Verlag, Berlin, 295-301.
- KRATOCHVIL, H. & LADWEIN, H. W, 1984. Die Entwicklung der geochemischen Vorstellungen über das Wiener Becken und ihre Bedeutung als Explorationswerkzeug. Erdoel-Erdgas-Zeitschrift, 100, 334–338.
- KREJČÍ, O., FRANCÍ, J., POELCHAU, H. S., MÜLLER, P. & STRÁNÍK, Z. 1996. Tectonic evolution and oil and gas generation model at the border of the North European Platform with the West Carpathians (Czech Republic). This volume.
- KRUGE, M. A., SOLECKI, A. & STANKIEWICZ, B. A. 1991. Molecular organic geochemistry of black shales and related strata, Carpathian Mountains, Southeastern Poland. In: Manning, D. A. C. (ed.) Organic Geochemistry: Advances and Applications in the Natural Environment. Manchester University Press, Manchester, 59–62.
- LADWEIN, H. W. 1988. Organic geochemistry of Vienna Basin: Model for hydrocarbon generation in overthrust belts. AAPG Bulletin, 72, 586–599.
- ——, SEIFERT, P. & SCHMIDT, F. 1989. Reife-modeling und Kohlenwasserstoff-Genese im alpinen Überschiebungsbereich. Erdöl, Erdgas Kohle, 105, 204–205.
- ——, SCHMIDT, F., SEIFERT, P. & WESSELY, G. 1991. Geodynamics and generation of hydrocarbons in the region of the Vienna basin, Austria. In: Spencer, A. M. (ed.) Generation. Accumulation, and Production of Europe's Hydrocarbons I. Oxford University Press, Oxford, 289–305.
- LAFARGUE, E., ELLOUZ, N. & ROURE, F. 1994. Thrust-controlled exploration plays in the outer Carpathians and their foreland (Poland, Ukraine and Romania). First Break, 12, 69–79.
- LEYTHAEUSER, D., SCHAEFER, R. G., CORNFORD, C. & WEINER, B. 1979. Generation and migration of light hydrocarbons (C<sub>2</sub>-C<sub>-</sub>) in sedimentary basins. Organic Geothemistry, 1, 191–204
- MACKENZIE, A. S. 1984. Application of biological markers in petroleum geochemistry. In: Brooks, J. & Welte, D. H. (eds) Advances in Petroleum Geochemistry 1. Academic Press, London, 115–214.
- MILIČKA, J., MASSAULT, M. & FRANCU, J. 1994. Carbon and hydrogen isotopes in four natural gases from the Slovak and Czech part of the Vienna Basin. Geologica Carpathica, 45, 379–382.
- ——, PERESZLÉNYI, M., FRANCÚ, J. & VITÁLOŠ, R. 1996. Organic geochemical appraisal of hydrocarbon potential in the Danube Basin, Slovakia. This volume.

- MILOTA, K., KOVÁCS, A. & GALICZ, ZS. 1995. Petroleum potential of the North Hungarian Oligocene sediments. Petroleum Geoscience, 1, 81–87.
- MOLDOWAN, J. M., FAGO, F. J., CARLSON, R. M. K., YOUNG, D. C., VAN DUYNE, G., CLARDY, J., SCHOEL, M., PILLINGER, C. T. & WATT, D. S. 1991. Rearranged hopanes in sediments and petroleum. *Geochimica et Cosmochimica Acta*, 55, 3333–3353.
- MÜLLER, P. & KREJĆÍ, O. 1992. Gas and oil prospects in the deeper-lying platform slopes of the Bohemian Massif. *Geologický Přítzkum*, 34, 236–241 (in Czech).
- PETERS, K. E. & MOLDOWAN, J. M. 1993. The Biomarker Guide. Prentice Hall, Englewood Cliffs, New Jersey.
- RADKE, M. 1987. Organic geochemistry of aromatic hydrocarbons. In: Brooks, J. & Welte, D. H. (eds) Advances in Petroleum Geochemistry Vol. 2. Academic Press, London, 141–207.
- —— 1988. Application of aromatic compounds as maturity indicators in source rocks and crude oils. Marine Petroleum Geology, 5, 224–236.
- & WELTE, D. H. 1983. The Methylphenanthrene Index (MPI): A maturity parameter based on aromatic hydrocarbons. In: Bjoroy, M. (ed.) Advances in Organic Geochemistry. Wiley, Chichester, 504–512.
- ——, SITTARDT, H. G. & WELTE, D. H. 1978. Removal of soluble organic matter from rock samples with a flow-through extraction cell. *Analytical Chemistry*, **50**, 663–665.
- ——, WILLSCH, H. & WELTE, D. H. 1980. Preparative hydrocarbon group type determination by automated medium pressure liquid chromatography. *Analytical Chemistry*, **52**, 406–411.
- ROTH, Z. & HANZLİKOVÁ, E. 1982. Palaeotectonic and palaeo-ecological position of the Menilite Formation in the Carpathian Mts. Casopis pro mineralogii a geologii, 27, 113–126.
- SACHSENHOFER, R. F. 1994. Petroleum generation and migration in the Styrian Basin (Pannonian Basin system, Austria): an integrated geochemical and numerical modelling study. *Marine and Petroleum Geology*, 11, 684–701.
- SAJGÓ, CS. 1984. Organic geochemistry of crude oils from south-east Hungary. *Organic Geochemistry*, **6**, 569–578.
- SCHAEFER, R. G. 1992. Zur Geochemie niedrigmolekularer Kohlenwasserstoffe im Posidonienschiefer der Hilsmulde: Kohlenwasserstoffbildung und Reifeaspekte. Erdöl und Kohle Erdgas-Petrochemie/Hydrocarbon Technology, 45, 73–78.
- ——, POOCH, H. & LEYTHAEUSER, D. 1984a. Automatic headspace gas chromatography of C<sub>1</sub>–C<sub>7</sub> hydrocarbons in sedimentary rocks. Application in Petroleum geochemistry. *Chromatographia*, 19, 377–381.
- ——, WELTE, D. H. & POOCH, H. 1984b. Geochemistry of low molecular weight hydrocarbons in two exploration wells of the Elmworth gas field. *Organic Geochemistry*, 6, 695–701.
- SCHOELL, M. 1984. Wasserstoff und Kohlenstoffisotope in Organischen Substanzen, Erdölen und Erdgasen. *Geologisches Jahrbuch*, **D** 67, 1–164.
- ŠIMÁNEK, V. 1977. Geochemie der Erdöle und Genese der Erdöllagerstätten des Tschechoslowakischen Teils des Wiener Beckens. Nänka o Zemi, Seria Geologica, 11, 1–69.
- ——, ADAMOVÁ, M. & STRNAD, M. 1981. Geochemical characteristics of the Menilite Fm. in the Czechoslovak Carpathians. Zemni Phyn Nafia, 26, 101–111 (in Czech).
- SZALAY, A. & KONCZ, I. 1991. Genetic relations of hydrocarbons in the Hungarian part of the Pannonian basin. In Spencer, A. M. (ed.) Generation, Accumulation, and Production of Europe's Hydrocarbons I. Oxford University Press, Oxford, 317–322.
- TEN HAVEN, H. L., LAFARGUE, E, & KOTARBA, M. 1993. Oil/oil and oil/source rock correlations in the Carpathian Foredeep and Overthrust, south-east Poland. Organic Geochemistry, 20, 935–959.
- THOMPSON, K. F. A. 1983. Classification and thermal history of petroleum based on light hydrocarbons. Geochimica et Cosmochimica Acta, 47, 303–316.
- —— 1987. Fractionated aromatic petroleums and the generation of gas-condensates. Organic Geochemistry, 11, 573–590.
- TISSOT, B. & ESPITALIÉ, J. 1975. L'évolution thermique de la matiere organique des sédiments. Applications d'une simulation mathématique. Revue de l'Institut Français du Pétrole, 30, 743-777.
- —— & WELTE, D. H. 1984. Petroleum Formation and Occurrence (2nd edn). Springer Verlag, Berlin.
- VETÖ, I. 1987. An Oligocene sink for organic carbon: upwelling in the Paratethys? Palaeogeography, Palaeoclimatology, Palaeoecology, 60, 148–153.
- WEHNER, H. & KUCKELKORN, K. 1995. Zur Herkunft der Erdöle im nördlichen Alpen-/Karpatenvorland. Erdöl. Erdgas Koble, 111, 1–7.
- WELTE, D. H., KRATOCHVIL, H., RULLKÖTTER, J., LADWEIN, H. & SCHAEFER, R. G. 1982. Organic geochemistry of crude oils from the Vienna Basin and an assessment of their origin. *Chemical Geology*, 35, 33–68.
- ——, YÜKLER, M. A. RADKE, M. & LEYTHAEUSER, D. 1981. Application of organic geochemistry and quantitative basin analysis to petroleum exploration. In: Atkinson, G. & Zuckerman, J. (eds) Origin and Chemistry of Petroleum. Pergamon Press, 67–88
- ZIMMER, W. & WESSELY, G. 1996. Exploration results in thrust and subthrust complexes in the Alps and below the Vienna Basin in Austria. This rolume.