Organic geochemical appraisal of hydrocarbon potential in the Danube Basin, Slovakia

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ABSTRACT: The Danube Basin is a northern marginal part of the Pannonian Basin formed in the last phase of the West Carpathian thrusting. The thickness of Neogene sedimentary basin fill in the deepest part of the central depression exceeds 6000 m. Central West Carpathian units form the pre-Tertiary basement to the north. Acid to intermediate volcanism was active during the Miocene. At a depth of 3000 m the temperature is about 133 °C in the central part and 110 °C in the northern margin of the basin. Source rock quality and maturity down to a depth of 3.5 km is characterized using Rock–Eval pyrolysis, microphotometry and, in selected samples, also by n-alkane, sterane and triterpane distribution. Basin modelling calibrated by organic maturity indicators in selected boreholes suggests the beginning of hydrocarbon generation in the Neogene at depths over 3000 m in the northern area, and over 2600 m in the central part of the basin. Simulation of maturation history in deeper undrilled parts of the basin is based on heat-flow distribution, expected lithology and types of kerogen. The hydrocarbon potential of the Danube Basin is compared with the East Slovakian and Vienna basins.

KEYWORDS: *Danube Basin, organic geochemistry, hydrocarbon potential*

INTRODUCTION

Most of the geological and geophysical exploration in the Slovak part of the Danube Basin was carried out between 1950 and 1960, and from 1970 to 1983. Several small gas fields were discovered, mainly in the northern part of the basin. In the southwestern part of the basin a gasoline-type oil was produced from the FGC-1 well. The occurrence of oil shows and bitumen impregnations in cores in some of the adjacent wells has also been reported.

The aim of this paper is to present the organic geochemistry of source rocks and a model of organic maturation and hydrocarbon generation.

GEOLOGY AND HYDROCARBON OCCURRENCES

The Slovak part of the Danube Basin (Fig. 1) represents the northern continuation of a Neogene basin, of which the southern and larger part lies in Hungary (Little Hungarian Plain). The Danube Basin is a system of sub-basins (Fig. 2), each one of them with specific evolution during the Miocene. The present shape of the basin results from young Pliocene and Quaternary tectonics which affected the geomorphology of both central and marginal parts of the basin and often masks the older Neogene geological structures.

Pre-Tertiary basement

The pre-Tertiary basement of the whole central part of the basin (Gabčíkovo Sub-basin, Fig. 2) is constructed by unknown geological–tectonic units. The basement of the western and northwestern part of the basin is represented by magmatic and metamorphic rocks of the Tatric crystalline unit of Palaeozoic age, which is related to those of the Malé Karpaty, Považský Inovec and Tríbeč Mts. In the northeastern part of the Blatné and Rišňovce depressions and the Bánovce Depression (Fig. 2), the pre-Tertiary basement is formed by Mesozoic sequences of the autochthonous Tatric Unit and the Krížna and Choč nappes. In the northern part of the Komjatice and Želiezovce depressions the basement is formed by the Late Paleozoic- Mesozoic autochthonous Veporic Unit and the Choč nappe. The Palaeozoic crystalline of the Veporic unit underlies the Neogene in the southern part of the Komjatice and Želiezovce depressions. The basement of the southwestern part of the basin comprises the Palaeozoic–Mesozoic unit of the Transdanubian/Hungarian Central Range with carbonaceous siliciclastic sediments. All the Palaeozoic units except the Transdanubian/Hungarian Central Range include intervals of igneous and metamorphic rocks. The Late Palaeozoic–Mesozoic autochthonous Veporic Unit is metamorphosed to a very low grade.

Palaeogene

The Palaeogene sediments in the Danube Basin are preserved in relatively small zones in the northernmost part of the Blatné and Rišňovce depressions and in the Bánovce Depression (Fig. 2). These Palaeogene sediments lie discordantly on the pre-Tertiary basement formed mostly by carbonates of the Choč nappe, and underlie with less discordance the Neogene sediments.

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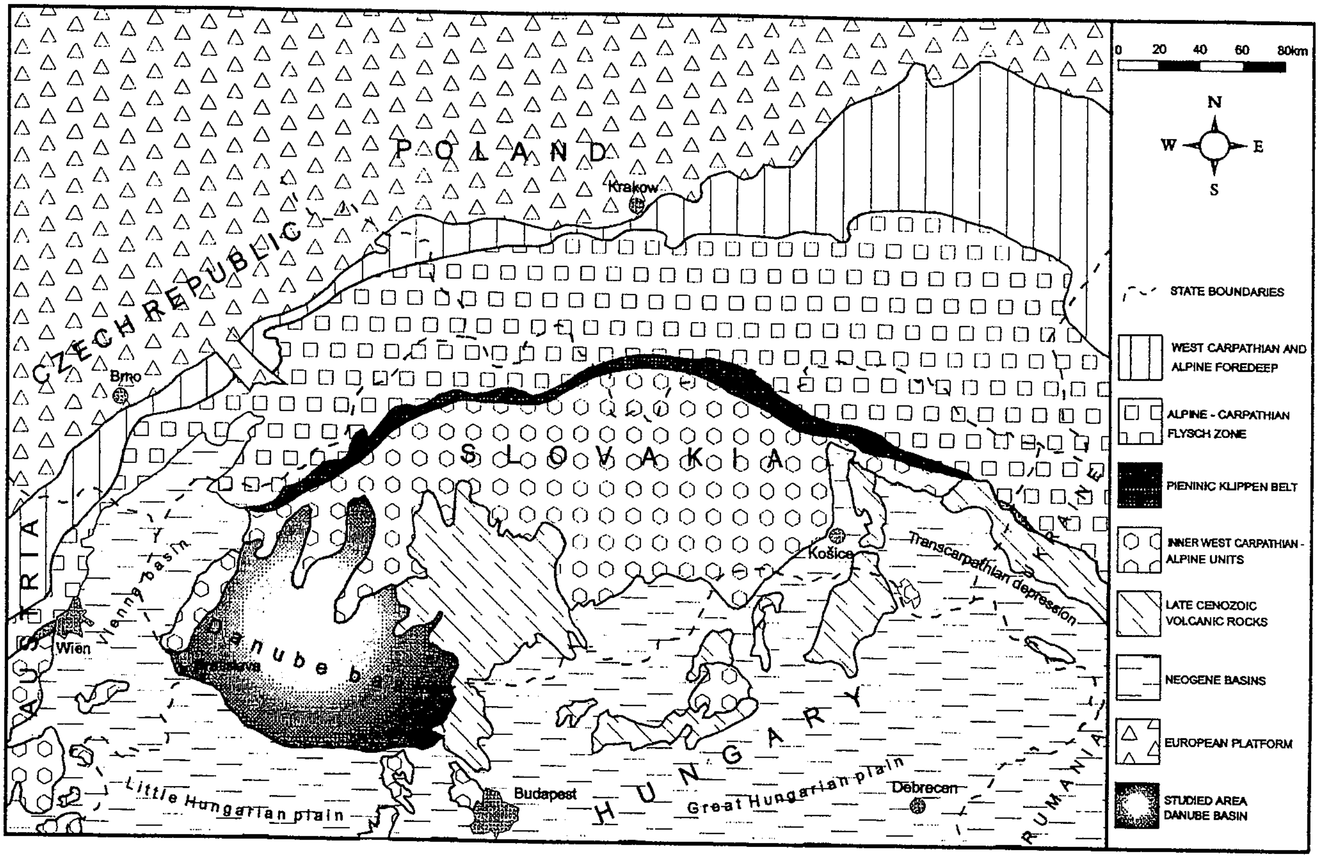

Fig. 1. Position of the Danube Basin within the West Carpathians.

The Palaeogene in the Štúrovo area (Fig. 2) represents a part of the Hungarian (Buda) Palaeogene. The sedimentation ranges from the Eocene (Lutetian) to Early Miocene (Egerian). The maximum preserved thickness is about 850 m. The lithology comprises siliciclastic sediments, breccias, conglomerates, sandstones and shales with organic limestones. Sediments were deposited in a bathyal to shallow-water environment. Marine complexes alternate with brackish to freshwater sediments with coal seams and freshwater limestones (Vass *et al.* 1992 unpublished report). The present distribution of the Palaeogene sediments represents only a relict of the original sedimentary area directly connected with the open sea.

Neogene

Lower Miocene sedimentation began with the Eggenburgian transgression in the northern part of the Danube Basin. The thickness of the mainly siliciclastic sediments, conglomerates, breccias and sandstones is about 50 m. In the Bánovce Depression shales are also developed in the upper part of the section.

Ottnangian sediments comprise siltstones, shales, and locally conglomerates at the base. The dark colour of the sediments and the presence of pyrite indicate that sedimentation took place in a restricted or anaerobic environment.

Karpatian sediments transgressed locally upon the pre-Neogene basement, and in the basin conditions the sedimentation progressed continuously from the Ottnangian to the Karpatian. The high energy of the sedimentary environment in marginal parts is expressed by many graded cycles of conglomerates, breccias, sandstones, siltstones and shales. Alternation of sandstones, siltstones and shales is dominant in more deep-water conditions. The maximum thickness of Karpatian sediments is about 700 m and they are also developed mostly in the northern part of the Danube Basin. A few remnants of most probably Lower Miocene sediments exist in the southern part of the Danube Basin in the Transdanubian/Hungarian Central Range area, and these are connected with the Lower Miocene development in Hungary.

The Badenian was the main period of formation of the Danube Basin. Lower Badenian sediments lie transgressively on the Hungarian (Buda) Palaeogene in the Štúrovo area, and on pre-Tertiary sediments and crystalline rocks in the Želiezovce Depression. At the eastern and northern part of the depression, basal clastics represented by polymict conglomerates covered by volcanosedimentary rocks occur. Bioherms, sandstones, shaly sandstones and siltstones are present in the centre. Lower Badenian clastic sediments probably also occur in the Blatné Depression lying discordantly upon pre-Tertiary rocks. The maximum thickness of the Lower Badenian sediments is about 600 m. The Middle and Upper Badenian was the period of intensive sedimentation in local depressions. The greatest extent and subsidence occurred in the Blatné Depression (Fig. 2) where the entire thickness of the Badenian sediments is about 2700 m, while in the Rišňovce and Komjatice depressions it is about 1000 m, and in the Želiezovce Depression it is less than 1000 m. Basal sediments are represented by coarse clastics, and in a few cases by organic limestones, which pass vertically into sandy and calcareous siltstones and shales. In the uppermost part sandstones occur, locally up to 400 m thick. The Middle Badenian sediments in the Želiezovce Depression comprise andesitic and

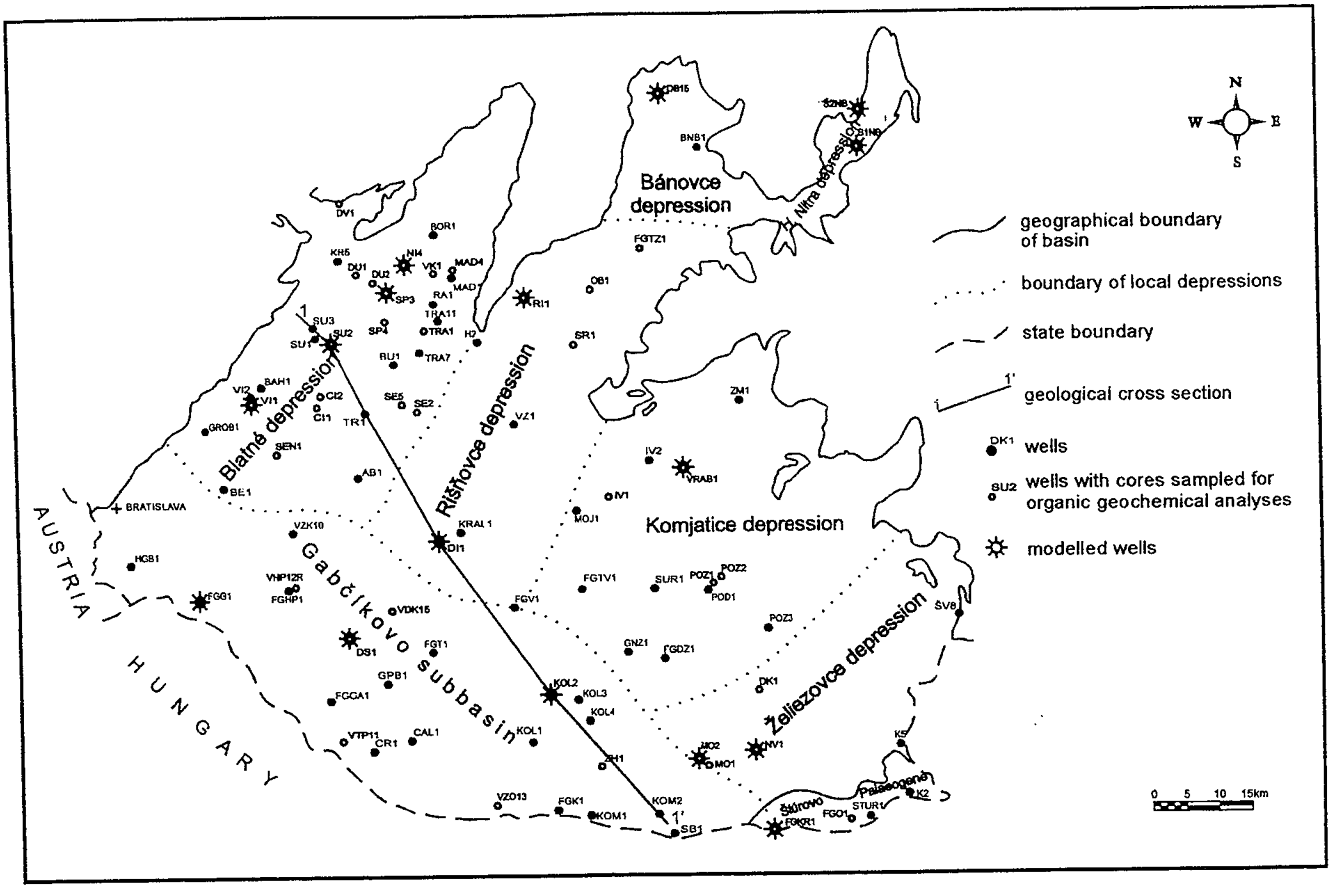

Fig. 2. Location of wells and geological cross-sections.

acid volcaniclastics. The deposition of Badenian sediments occurred generally in shallow water, but locally (in the centres of depressions) in deep water.

The Sarmatian sediments, whose greatest thickness is about 1600 m, in the Rišňovce Depression, (Fig. 2), mostly lie discordantly on the Badenian or, locally, on the pre-Neogene basement. Volcanic activity influenced the sedimentation at the eastern and southeastern margin of the basin. Lignite seams are locally present in the upper part. Deposition occurred in shallow water. The drying-up of the shallow marine environment is characteristic of the latest Sarmatian.

The main feature of the Pannonian is the change of the tectonic subsidence style to that of thermal subsidence. The centre of the subsidence migrated from the northern to the southern part of the basin to form the Gabčíkovo Sub-basin (Fig. 2). Pannonian fine clastic sediments, about 2000 m thick, are distributed over the whole Danube Basin except along the northernmost margins. The shallow marine environment changed everywhere to a limnic one. In the northern marginal areas, deltaic and marsh sediments with lignite are present.

During the Pontian, Dacian and Romanian, thermal subsidence and limnic–fluviatile deposition of clastics continued. The maximum thickness of these sediments exceeds 1000 m.

A maximum of 300 m of Quaternary gravels were deposited mainly in the centre of the Gabčíkovo Sub-basin.

Tectonics

The tectonic structure of the Danube Basin is quite complicated. The pre-Tertiary basement is folded, thrusted, faulted and strongly eroded. Block faulting took place along distinctive tectonic lines, e.g. the Hurbanovo–Rába Line.

The Neogene tectonics can be subdivided into two main stages. The older, pre-Lower Pannonian stage, including the pre-rifting and synrifting stages with a dominant role of strike-slip deformation, combined with synsedimentary normal faulting. During this period Lower Miocene and Badenian sedimentary basins were formed. During the younger postrifting stage of basin formation, downwarping played the dominant role. The post-Sarmatian strike-slip faulting in the central part of the basin and normal faulting at the margins was of minor significance.

Hydrocarbon occurrence

Hydrocarbon gases with a high methane content (85–98%) were discovered in the Blatné Depression. These gases are trapped in sandy horizons of the Middle Badenian. The total volume of effectively exploitable gas is estimated to be approximately 800×10^6 m^3.

Natural gases with a predominance of inorganic gases, carbon dioxide and nitrogen are known from other parts of the Danube Basin. The reserves of these gases are estimated to be 6×10^9 m^3.

Oil accumulations are restricted to a small amount of condensate from the geothermal well FGČ 1 in the southwestern part of the basin, and to some core impregnations.

SOURCE-ROCK STUDY

Core samples from a depth of 3500 m were analysed using Rock–Eval pyrolysis, microphotometry, gas chromatography,

Table 1. *Summary of selected organic geochemical characteristics of the Danube Basin sediments*

Stratigraphy	TOC (weight %)	S1 (mgHC/g rock)	S2 (mgHC/g rock)	HI (mgHC/g TOC)	T_{max} (°C)	R_0 (%)	Kerogen type
Pliocene–Pontian	0.0X–0.70	0.0X–0.20	0.0X–0.50	30–95	425–435	0.24–0.35	III
Upper + Middle Pannonian	0.12–0.81	0.0X–0.30	0.13–0.70	26–100	427–440	0.35–0.60	III
Lower Pannonian	0.32–1.20	0.0X–0.55	0.34–4.80	50–409	435–445	0.35–0.69	III–II
Sarmatian	0.11–1.00	0.0X–0.16	0.0X–1.58	30–222	425–445	0.30–0.76	III
Upper Badenian	0.0X–0.88	0.0X–0.16	0.11–0.89	28-100	430–446	0.35–0.82	III
Middle Badenian	0.35–1.12	0.0X–0.18	0.21–1.40	40–233	427–444	0.30–0.78	III
Lower Badenian	0.10–0.81	0.0X–0.23	0.15–1.28	60–250	430–435	0.30–0.51	III
Lower Miocene	0.28–1.94	0.0X–0.12	0.20–2.23	20–227	425–444	0.28–0.61	III
Palaeogene	0.0X–1.45	0.0X–0.23	0.12–5.86	62–404	427–444	0.33–0.80	III–II
Pre-Tertiary basement	0.0X–1.40	0.0X–0.42	0.0X–1.78	10–110	440–530	0.78–1.80	?

S1, S2, HI, T_{max}: Rock–Eval pyrolysis parameters.
TOC, total organic carbon; R_0, vitrinite reflectance.
Kerogen type: III–II, mixed marine–terrestrial; III, terrestrial.

GC MS and isotopic analyses. All the Neogene stratigraphic units, the Palaeogene, the autochthonous Mesozoic Unit as well as Mesozoic nappes were investigated. Prediction of catagenetic stages in deeper, unpenetrated parts of the basin are based mainly on mathematical models (Yükler 1D and Matoil). Most of the geochemical analyses and modelling with Matoil software were carried out at IFP France, while carbon isotopes of methanes and vitrinite reflectance were measured at ČGÚ Prague and Brno.

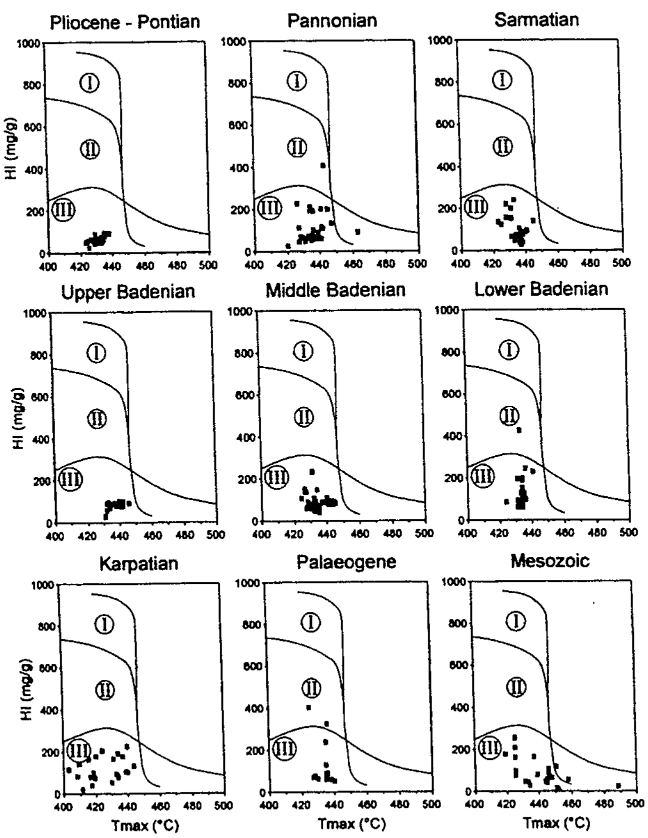

Fig. 3. Kerogen types in potential source rocks. HI, Hydrogen index.

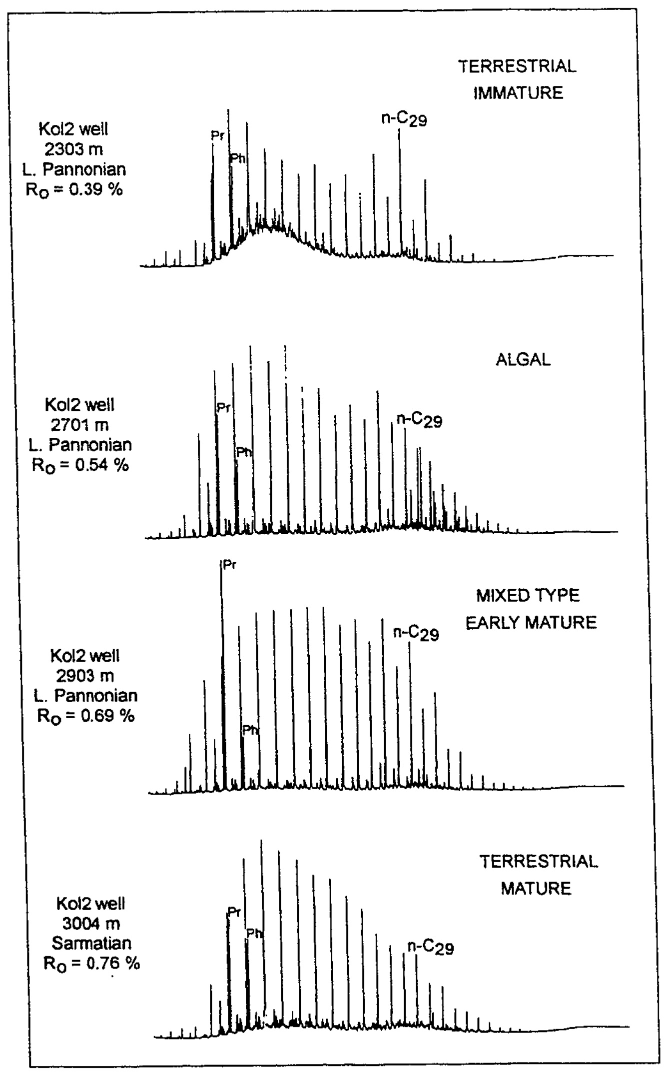

Fig. 4. Saturated hydrocarbons in source rock extracts in the Kol 2 well depth profile.

The locations of the investigated and modelled wells and the summary of basic geochemical analyses are shown in Fig. 2 and Table 1.

Source-rock quality

The total organic carbon (TOC) content and hydrocarbon potential of the pre-Tertiary basement is generally poor and exhausted to a considerable extent, except for a few samples from the northwestern part of the basin near the edge of the Malé Karpaty Mountains from the DV 1 well. These sediments belong to the Reifling Formation of Middle Triassic (Masaryk *et al.* 1993), and according to their maturity (R_o = 1.14%) at a depth of 689 m they are in a passive maturation stage. The present state of knowledge makes it difficult to reconstruct sedimentation and tectonic processes and kerogen alteration in nappe units of the pre-Tertiary basement. According to the vitrinite reflectance there is a jump in alteration grade of organic matter between the pre-Tertiary basement and the Palaeogene, as well as between the Palaeogene and Neogene sediments. The difference in vitrinite reflectance values between the base of the Tertiary sediments and the basement is about 0.4% or more (Fig. 6). It is supposed that the present degree of organic matter alteration (R_o = 1–2%) of the basement was reached before the Tertiary, most probably during the Middle and Upper Cretaceous. However, strong erosion of the pre-Tertiary basement must be taken into account. This erosion would have been followed by overthrusting of nappes, further erosion and subsequent deposition of Tertiary rocks. An alternative explanation is that the pre-Tertiary basement was subjected to a weak metamorphism, i.e. the autochthonous Veporic Unit of Late Palaeozoic to Mesozoic age is metamorphosed to very low grade. Features of metamorphism to very low grade are recognizable in other sedimentary sequences of the basement at various localities.

The Palaeogene sediments analysed come mainly from the southern part of the basin (Štúrovo Palaeogene) and generally indicate moderate source potential and organic matter of terrestrial origin. Locally a mixed marine-terrestrial kerogen type (HI about 400 mg/g) occurs. The most recently analysed samples from the northern part of the Bánovce Depression show fairly good source rock properties (TOC over 4%, HC potential to 4 kgHC per ton, HI over 500; Milička *et al.* 1993 and new unpublished data); however, the number of samples is too small to drawn regional conclusions. The prospectivity of the Palaeogene sediments in the Danube Basin is restricted by their relatively small areal distribution and shallow depth of burial. In other words, practically all the Palaeogene sediments except for a small area around the NV 1 well in the southeastern part of the basin are at present in the passive maturation stage.

The average TOC content of the Neogene basin fill reaches at most 1%, with higher values for the Lower Pannonian, Sarmatian, Middle Badenian and Lower Miocene sediments (Table 1). According to the results of Rock–Eval pyrolysis the organic matter is mostly of continental type III (Espitalié *et al.* 1986; Fig. 3). The same is indicated by the predominance of higher n-alkanes in gas chromatograms of the C_{12+} fraction and the presence of oleanane in the samples investigated. Locally, in the

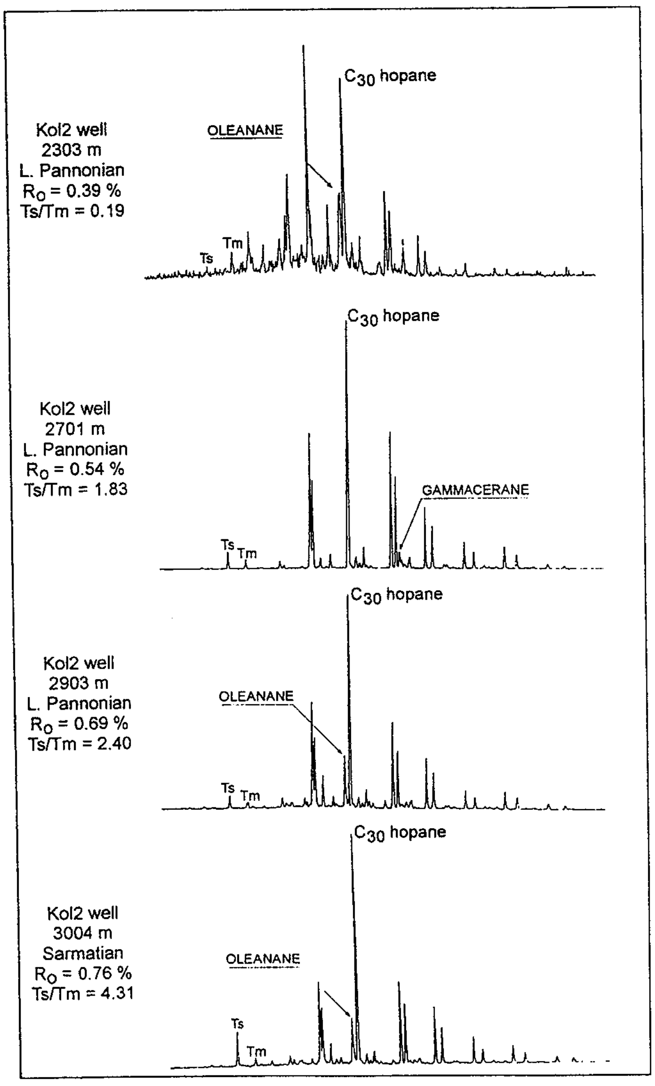

Fig. 5. Triterpanes (m/z 191) in Kol 2 well depth profile.

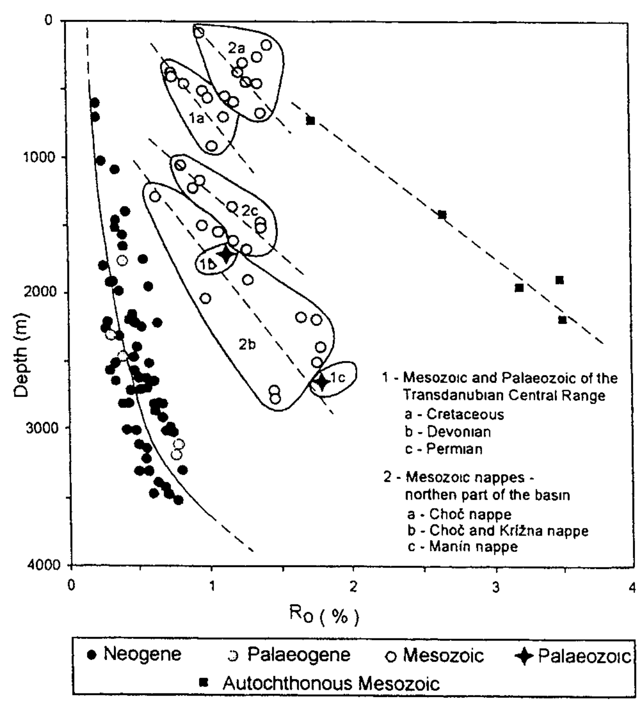

Fig. 6. Vitrinite reflectance characteristics of Tertiary and pre-Tertiary rocks.

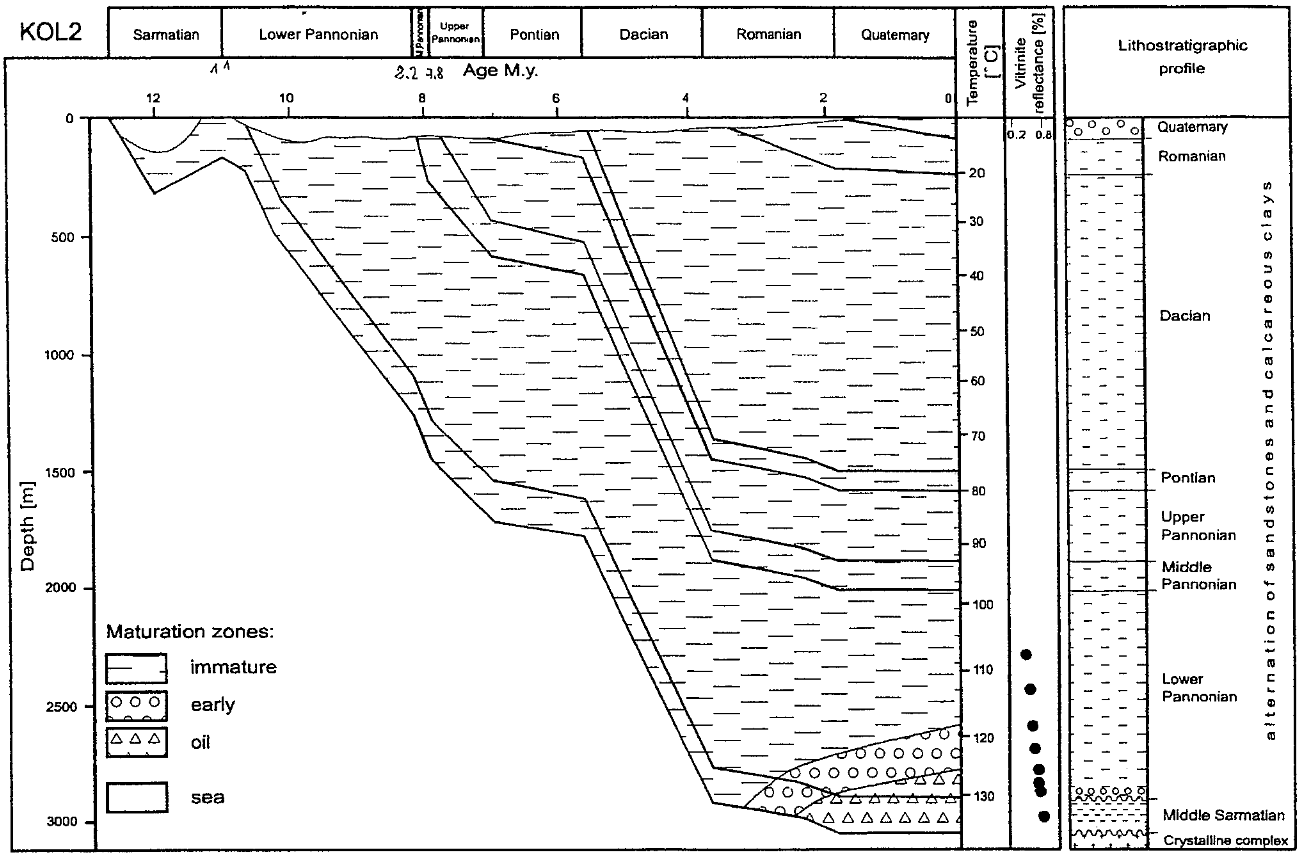

Fig. 7. Burial history plot and hydrocarbon generation zones in Kol 2 well.

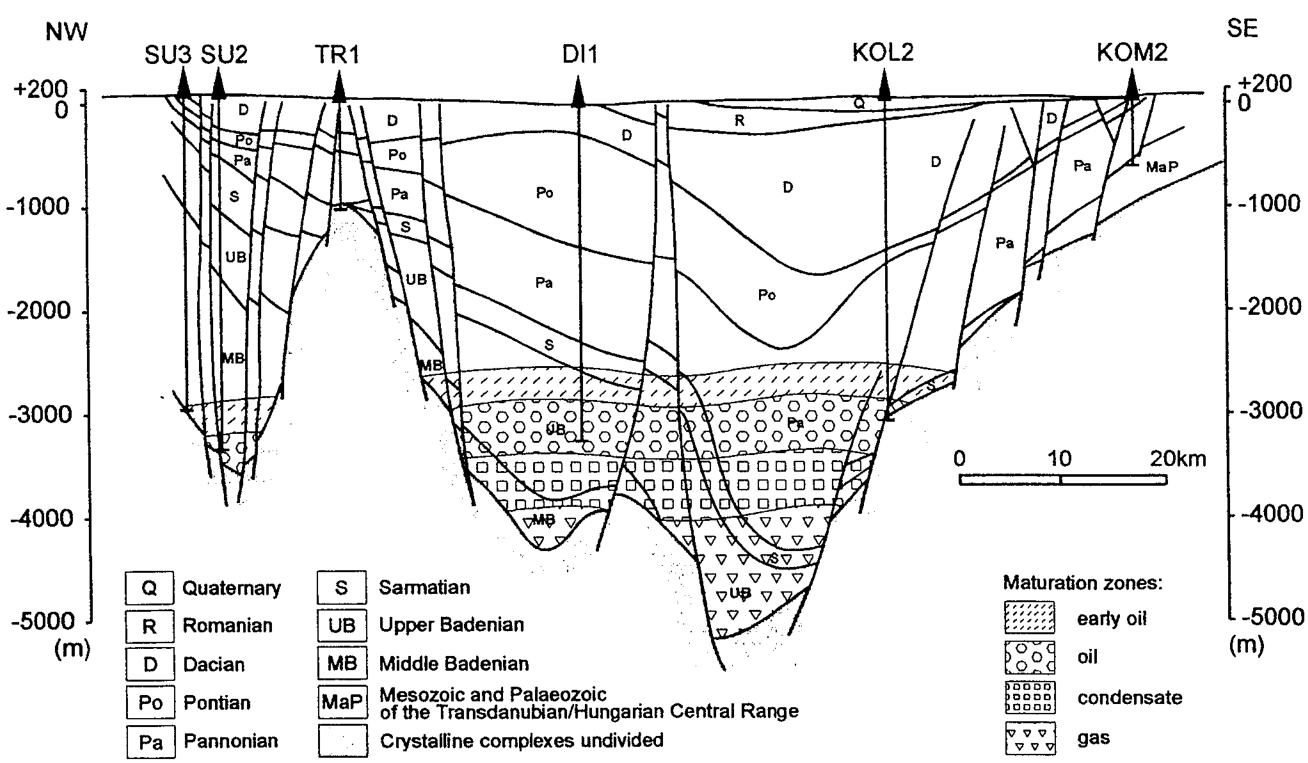

Fig. 8. Geological cross-section with hydrocarbon generation zones based on mathematical modelling.

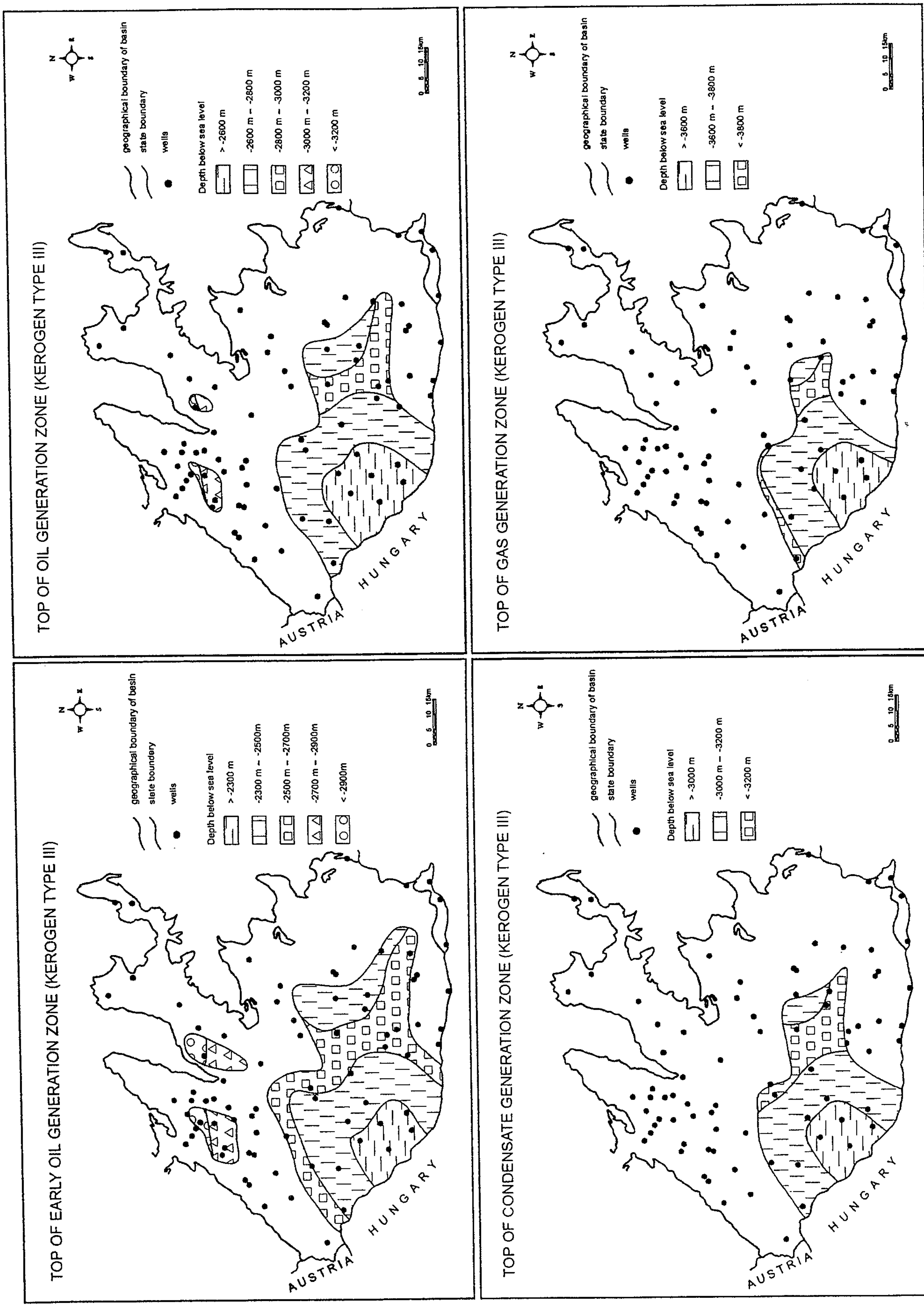

Fig. 9. The distribution of hydrocarbon generation zones in the Danube Basin.

Lower Pannonian sediments, mixed terrestrial–marine kerogen type III–II was found. A characteristic depth profile of n-alkane distribution in Lower Pannonian sediments is shown on Fig. 4. The absence of oleanane in the sample investigated from 2701 m in the same depth profile (Fig. 5) indicates the dominant input of marine organic matter. The hydrocarbon potential of the Neogene sediments is generally rather poor (up to 2 kg hydrocarbons per ton) but it is fairly good in some of the Lower Pannonian sediments. The maturity level of the Neogene sediments is deduced in some cases from the T_{max} parameter, but mainly vitrinite reflectance was used. The continuous increase of maturity with depth in the Neogene is documented on Fig. 6. The increase in geothermal conditions is stronger in the central part in the Gabčíkovo Sub-basin compared with the 'colder' northern part of the basin in the Blatné and Rišňovce depressions.

MODEL OF CATAGENETIC ZONALITY

The principal stages of oil and gas generation were determined using mathematical models mainly in the deeper, undrilled parts of the basin. Calculated maturity parameters in all the modelled wells (Fig. 2) were compared with the measured ones (Fig. 7). The catagenetic zonation for kerogen type III in the Danube Basin is based on mathematical modelling as well as measured maturation parameters (Figs 8, 9, 10):

(a) The base of the immature zone or the top of the early oil generation zone lies at about 3000 m in the northern and western part of the basin, while it is at about 2600 m in the central part.
(b) The main phase of oil generation in the northern part is below 3300 m, and even the kerogen at the base of the Neogene sediments did not reach higher maturity levels in this area. In the warmer and deeper central part the main oil generation zone ranges from 2800 m to 3200 m. The free hydrocarbon quantity increases and the residual source potential decreases.
(c) The top of the condensate zone was established only by mathematical modelling at a depth below 3200 m.
(d) The dry gas zone is expected to begin at a depth of about 4000 m in the central part of the basin.

According to these results the best conditions for hydrocarbon formation in the Danube Basin can be expected in the central part of the Gabčíkovo Sub-basin in Neogene shales.

GAS ANALYSES

The origins of 14 samples of methane from natural gases in various parts of the Danube Basin (Fig. 10) were deduced from the chemical compositions of the hydrocarbon gases and the carbon isotopic composition of the methane (Fig. 11). Two main groups (i.e. thermogenic and mixed methanes) can be distinguished. According to the modelling the former most probably originates in the deeper parts of the Gabčíkovo Sub-

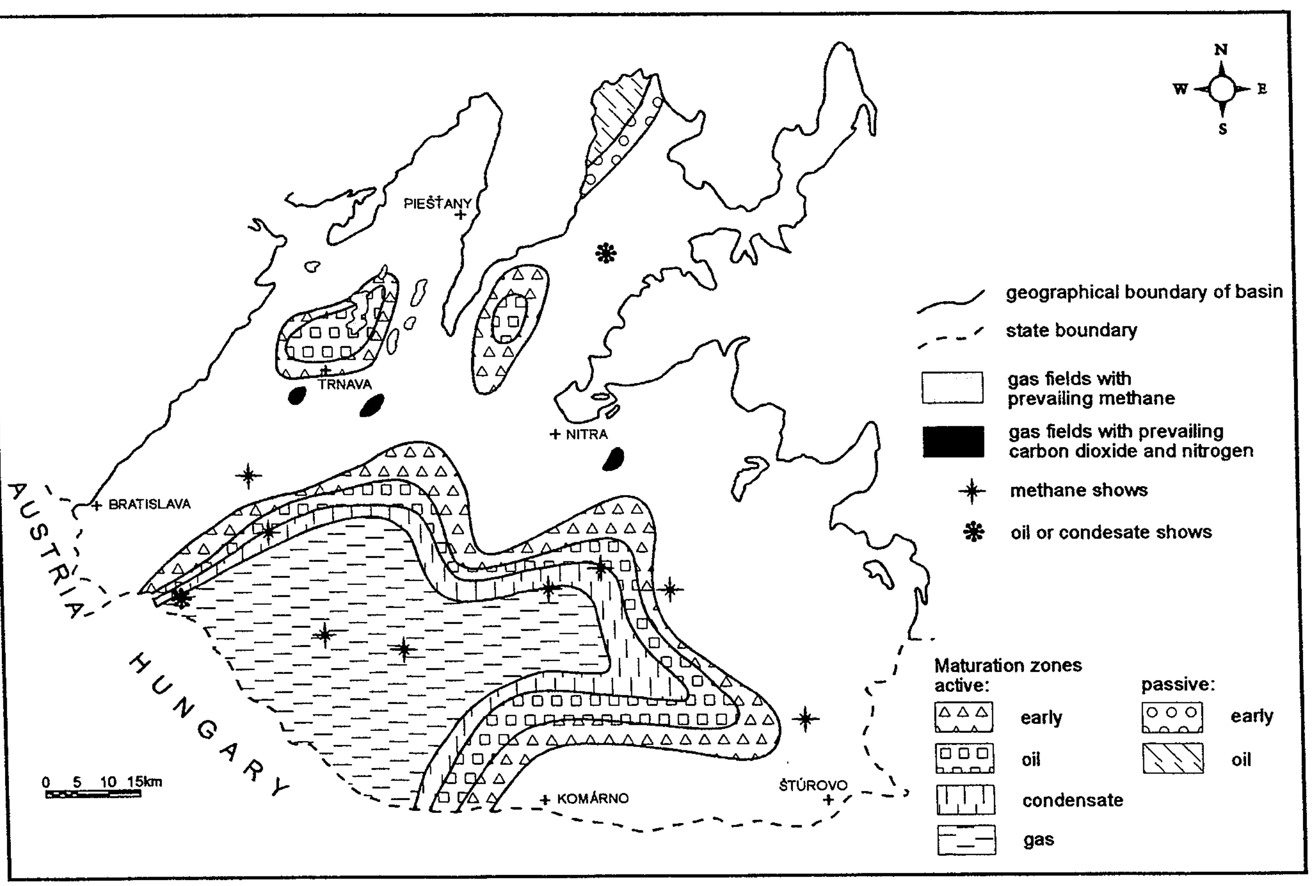

Fig. 10. Maturation zones at the base of the Neogene, gas fields and hydrocarbon shows.

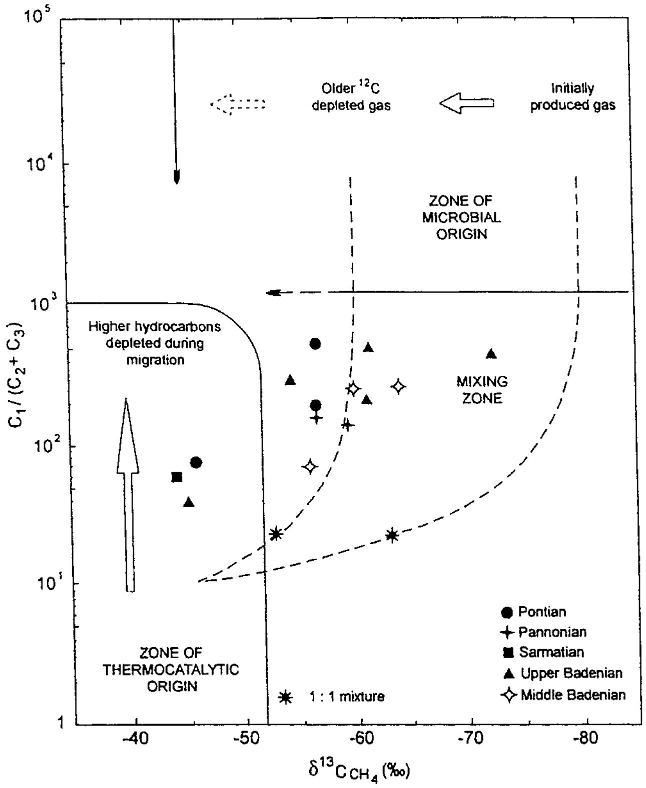

Fig. 11. Chemical and isotopic classification of methanes from the Danube Basin using the scheme of Bernard *et al.* (1976).

basin (Fig. 9). Mixed thermogenic–biogenic methanes are characteristic of the Blatné Depression. The contribution of higher hydrocarbons (C_{2+}) is most probably connected with the oil generation zone in the Blatné Depression around the Su 2 well.

CONCLUSIONS

The principal results of this study are summarized as follows:

(1) The Palaeogene, Lower Badenian and Lower Pannonian formations include fairly good source-rock intervals with mixed algal and terrestrial kerogen.
(2) Organic maturity (R_o, T_{max}, biomarkers) increases with depth continuously in the Neogene. Possible deeper burial and uplift of pre-Neogene units is indicated by a maturity jump.
(3) The absence of oleanane in a part of the Lower Pannonian sediments may be explained by the dominant input of marine organic matter. The same is indicated by n-alkanes and pyrolytic data.
(4) The application of modelling, calibrated on measured maturity data, shows that the burial depth and the temperature were sufficient for source-rock maturation and hydrocarbon generation in the Neogene. The present oil generation zone occurs at a depth of more than 3000 m in the northern part and 2600 m in the central part of the basin.
(5) Quantitative assessment of the amount of hydrocarbons generated, expelled and possibly preserved, suggests that the source potential of the Danube Basin greatly exceeds the quantity of hydrocarbons discovered so far.

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