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TYPE AND EVOLUTION STAGE OF HUNGARIAN OIL SHALE KEROGENS

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ABSTRACT

The insoluble organic matter of some Hungarian oil shales (Upper Pannonian, maar type: Pula, Gérce, Várkesző, and Miocene, lagoon-type: Mecsek, Várpalota, Mátraszele) were investigated.

In spite of the same age and similar formation processes the maar-type oil-shale kerogens are different: the Pula kerogen proved to be an algal-derived organic matter of type I, of high conversion and H/C ratio, and good petroleum potential. On the contrary, the organic matter of Várkesző oil shale corresponds to type II and can be interpreted by presence of terrestrial plant remnants in the precursor material. The considerable difference between the Pula and Várkesző oil shales during the thermal decomposition in the evolution paths, apparent activation energy (Pula: 146 $kJmol^{-1}$ and Várkesző 75 $kJmol^{-1}$) and in the ratio of the gas and oil phases formed can be interpreted by the presence of terrestrial plant remnants in the precursor material of the Várkesző oil shale. The kerogen of Gérce oil shale can be considered as a transition between type I and II.

The lagoon-type oil chales contain kerogen of type II. The Corgcontent and petroleum potential, as well as the H/C atomic ratio and the HC-yield of the Várpalota oil shale is fairly high. During the pyrolysis it generates considerable amount of oil. The petroleum potential of oil shales from Mecsek and Mátraszele corresponds rather to a source rock of good quality.

INTRODUCTION

In Hungary two types of oil shale formations had been found by the Hungarian Geological Survey (BENCE, JÁMBOR, PARTÉNYI, 1979; JÁMBOR and SOLTI, 1975, 1976; JÁMBOR, RAVASZ and SOLTI, 1982; SOLTI, 1980, 1985):

1. Maar-type oil shale beds generated as fillings in volcanic craters, and
2. Lagoon-type oil shale beds deposited in intramontane lagoons.

The maar-type oil shale formations were discovered in the course of investigating the tuff rings of Upper Pannonian basalt areas in Transdanubia (Hungary). The beds are of small size and medium to poor quality as compared to the international scale and they are insignificant as sources for energy and raw materials, respectively. Nevertheless, these oil shales serve as excellent model to investigate the characteristics of different organic matters and to study their artificial evolution (HETÉNYI, 1979, 1980, 1983; HETÉNYI, TÓTH, MILLEY, 1982). These provide the possibility to seak for relationships between the depositional environments, the composition of the precursor biomass and the type of the generating kerogen.

In the development of maar-type occurrences the isolation of the crater lake from the inland sea as well as the warm to temperate climate played an important role.

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The intense weathering of the crater wall and thus the abundance of the crater lake in nutriments promoted the accumulation of the organic matter (Bence *et al.*, 1979; Hajós, 1976; Nagy, 1976).

The oil shales in the intramontane basins are of poor quality. Their formation was influenced mainly by their isolation from the open sea and from the main sediment transporting currents. These are usually related to coal beds (Solti, 1982).

To analyse in detail the pecularities of the organic matter, three samples were chosen from both environments. These are: those of maar-type from Pula, Gérce and Várkesző, and those of lagoon-type from Várpalota, Mecsek Mountains and Mátraszele.

EXPERIMENTS

The oil shale samples were ground to grain size of 0,05—0,15 mm, the bitumen was extracted in a Soxhlet extractor by chloroform and by benzene-acetone-methanol mixture of 70:15:15 ratio.

Kerogen was isolated first by physical method, the remaining mineral components were destructed by means of chemical procedures.

The organic carbon content was determined at 1000 °C in oxygen atmosphere.

The CR/CT ratio was measured on the basis of the ASTM standard (Cummins *et al.*, 1972).

Experimental evolution was carried out between 300 and 500 °C under nitrogen atmosphere. Products were collected on a cooled trap and oil was separated from the water. The solid matter remained was extracted.

The organic matter of the oil shales as well as that of the degradation products and unconverted organic matter were characterized by the H/C atomic ratio and by Rock Eval pyrolysis (Espitalié *et al.*, 1977).

The shale oil was checked by IR and NMR method (Pápay, 1982).

RESULTS

From economic point of view the most important features of the organic matter-bearing sedimentary rocks, among others that of the oil shales, are the quantity and chemical composition of hydrocarbons generated from them either by natural evolution or by experimental thermal degradation. Based on the organic matter content of the sediments and on the type and evolution stage of kerogen, the values of these characteristics can be estimated.

1. Quantity of organic matter

The organic matter content is usually characterized by the organic carbon content. Based on the average values of the Hungarian oil shales of medium to poor quality, their organic carbon contents vary between 10—13% and 2—7%, respectively (Table 1).

2. Evolution stage of kerogen

As it has been expected, the maturity of the kerogen of the oil shales studied corresponds to the zone of diagenesis (Table 2). The ratio of the diagenesis coefficient and the H/C atomic ratio of the kerogen concentrates (CR/CT equals to 0,1—0,5, the atomic ratio from 1,3 to 1,7) refer to this fact. As compared to the heteroatomic

TABLE 1

Organic carbon content of the different Hungarian oil shales

Age	Locality	Depths (m)	C_{org} (%) average	C_{org} (%) min.—max.
Upper Pannonian	Pula Gérce Várkesző	4.5—39.5 4.0—68.3 55.0—70.5	13.4 6.6 13.0	0.3—45.7 0.1—15.5 3.2—18.7
Badenian	Várpalota	3.1—14.0	10.9	4.1—26.3
Carpathian	Mecsek	surface exposure	4.3	—
Ottnangian	Mátraszele	234.7—236.1	2.8	1.8—4.5

TABLE 2

Evolution level of the Hungarian oil shale kerogens

Locality	CR/CT	H/C atomic ratio	S2/S3	T_{max}	HI mgHC/gTOC
Pula	<0.10	1.7	15.7	442	745
Gérce	0.20	1.6	8.7	429	500
Várkesző	0.43	1.3	6.4	425	390
Várpalota	0.36	1.5	6.7	425	460
Mecsek	0.36	1.5	9.2	432	440
Mátraszele	0.53	1.3	6.8	428	370

products (S3), the quantity of hydrocarbon (S2) measured by Rock Eval pyrolysis is higher than five. The ratio indicates that the changes describing the main phase of hydrocarbon generation, that is the catagenesis, did not start yet. When plotting the maximal temperature of hydrocarbon generation (T_{max}) against the H-index being in good correlation with the H/C atomic ratio, it can be seen that the samples are in the immature zone *(Fig. 1).*

The immaturity of this kerogen is evidenced by the position of the samples on the evolution path as well as the fact that by means of experimental degradation nearly the complete evolution path can be reproduced. *Fig. 2* illustrates the artificial evolution paths of different types of kerogen obtained by experimental thermal degration.

3. *Type of kerogen*

The evolution paths are suitable to determine the most important characteristic of kerogen, i.e. its type. As it can be seen in *Fig. 2,* based on the evolution paths the lagoon-type oil shale kerogens belong to type II. Nevertheless, considerable differences can be observed between the samples of the Mecsek Mountains, Mátraszele and the Várpalota samples. The latter starts with a higher H-index than the previous ones. Consequently, during its artificial evolution, as well as during the corresponding natural evolution under suitable conditions, this can or could produce

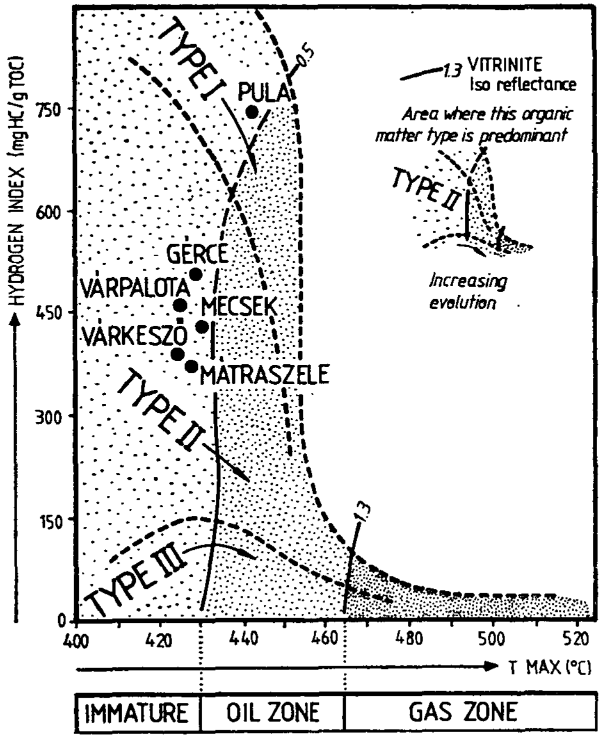

Fig. 1. Classification of the kerogens of the different Hungarian oil shales and characterization of their maturity in general HI—T_{max} diagram

more hydrocarbons than the kerogen of the Mecsek or Mátraszele samples. Thus, under the same geological conditions the type of the organic matter of oil shales accumulated in intramontane lagoons is the same but due to smaller differences within the given type, these samples are of different economic values.

Among the oil shales generated in volcanic tuff rings the differences are much more emphasized. The kerogen of Pula can be ranged to type I, whereas the kerogen of Várkesző belongs to type II. The kerogen of Gérce seems to be transitional between them (HETÉNYI, 1985).

As a comparison, the experimental evolution paths of the sedimentary samples containing kerogen of type III, are also demonstrated in *Fig. 2.* These samples are sediments from the neighbourhood of the Mátraszele bed presumed formerly as oil shale indications but these cannot be considered to be oil shales due to their organic geochemical features, for example due to the type of organic matter.

The value which can be measured by Rock-Eval pyrolysis as well as the value which can be calculated from it are also suitable to characterize the type of the organic matter. Consequently, as to our opinion the type of kerogen of similar stage being at the beginning of evolution can be expressed numerically by the PC/TOC ratio (HETÉNYI, 1983). The ratio shows the proportion of the total organic carbon to that pyrolizable by Rock Eval method. Based on the organic carbon content of 65% to be pyrolized by Rock Eval, the kerogen of the Pula oil shale belongs unambiguously

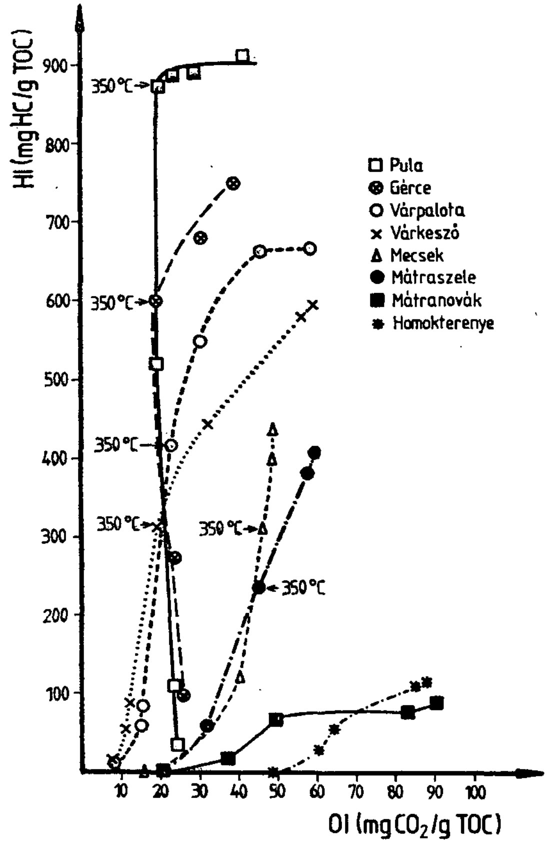

Fig. 2. Artificial evolution paths of the different Hungarian oil shales

to type I. The PC/TOC value of the samples of type III, varying between 12 and 13, considerably differs from this value. This is a medium value and shows some closeness in case of the kerogens of lagoon type oil shales and of the Várkesző oil shale kerogens, varying between 32 and 40 per cent. Based on this value, the kerogen of the Gérce oil shale seems to be transitional between the type I and II, but closer to type II having 47% PC/TOC value (Table 3).

When plotting the H-index as a function of T_{max} *(Fig. 1)*, all the oil shales are found in the field characterized by the organic matter of type II, except the Pula oil shale which, on the basis of these values, contains organic matter of type I.

Kerogen was isolated from the maar-type oil shale (Pula sand Várkesző) containing organic matter of two different types (type I and II), and from the most important lagoon-type bed (Várpalota) (Table 4). Isolation was carried out from the strata being most abundant in organic matter. In case of the Várkesző oil shale containing greater amounts of coalified plant remnants, organic matter-rich strata were chosen which contained greater quantities of plant remnants. As to our opinion the difference between the Pula and Várkesző kerogens can be attributed to the different

TABLE 3

Characterization of the type of the organic matter in Hungarian oil shales and oil shale indications

Locality	Type of organic matter	PC/TOC %	T_{max} °C	HI mgHC / g TOC
Pula	Type I	65	442	745
Gérce	Type(I)—II	47	429	500
Várkesző	Type II	38	425	390
Várpalota	Type II	40	425	460
Mecsek	Type II	38	432	440
Mátraszele	Type II	32	428	370
Mátranovák	Type III	13	432	140
Homokterenye	Type III	12	431	130

TABLE 4

Characterization of the kerogens isolated from Hungarian oil shales

Locality	Oil shale formation	H/C atomic ratio	CR/CT	Type of kerogen
Pula	maar-type	1.7	<0.10	Type I
Várkesző	maar-type	1.3	0.43	Type II
Várpalota	lagoon-type	1.5	0.36	Type II

proportion of mixing of the algal material constituting the biomass and of the higher plant remnants in the two samples (HETÉNYI, 1985).

As to the pollen analyses (NAGY, 1978; KEDVES, 1983) Botryococcus remnants are abundant in both beds, but the Pula oil shale shows extreme abundance. This is caused by the conditions favourable to the accumulation of Botryococcus braunii K. in the Pula oil shale. The uprushing water with carbonic acid produced by the subvolcanic activity warmed the crater lake, producing favourable living conditions to the algae. The conservation of the huge amount of algal material accumulated in this manner was assured by the lack of destructive organism. The higher concentration and good preservation of the algae produced aliphatic polimer rich in hydrogen, that is the kerogen of type I. The organic matter of the Várkesző oil shale contains also large colonies of Botryococcus, the amount of it, however, being less than in the case of Pula. Further, the colonies are destructed due to the biologically active sedimentation environment. At the same time, the occasionally macroscopically identifiable higher plant remnants constitute the major part of the organic matter, being the precursors of the kerogen of type III. The mixing of the two extreme kerogen types, that is type I and III, resulted in kerogen which can be qualified as type II (HETÉNYI, 1983).

4. *Experimental simulation of the catagenesis*

The different types of kerogen, that is the different precursor biomasses can be recognized in the course of the experimental evolution, as well.

Based on the experimental simulation of the catagenesis the apparent activation energy of the Pula and Várkesző kerogens shows a ratio of two-to-one (Table 5).

The composition of the precursor matter is reflected also in the quantities and qualities of the hydrocarbons formed during the kerogen evolution. The Pula oil shale generated 688 mg shale oil to 1 g organic carbon. The maar-type oil shale of Várkesző and the lagoon-type oil shale of Várpalota generated 400—450 mg shale oil to 1 g organic carbon (Table 5).

TABLE 5

Artificial evolution of kerogens isolated from maar-type oil shales

Locality	Pula	Várkesző
Type of kerogen	Type I	Type II
Temperature of degradation (°C)	500	500
Degradation-period (hours)	5	5
Oil yield (mg/g TOC)	688	425
Gas+water yield (mg/g TOC)	492	669
Ratio of conversion (%)	85	70
Apparent activation energy of catagenesis ($kJmol^{-1}$)	146	75

The bitumen, being intermediary product of the evolution shows better the differences in the chemical composition of the kerogens than the shale oil. The H/C atomic ratios characterizing the bitumens are ranged between the values of 1,63—1,74 and 1,31—1,50 in case of the oil shales containing organic matter of type I and type II, respectively (Table 6).

TABLE 6

H/C atomic ratio of bitumens formed by artificial evolution of the different oil shales (temperature: 350 °C)

Degradation period (hours)	Maar-type oil shales		Lagoon-type oil shales	
	Pula	Várkesző	Várpalota	Mecsek
1	1.74	1.39	1.50	1.45
5	1.64	1.38	1.46	1.36
10	1.63	1.34	1.31	1.35

Shale oil is the most significant end-product generated during the pyrolysis. In case of the two maar-type kerogens the average length of the paraffin chain is very different in the shale oils. The lagoon-type kerogen shows transitional characteristics,

TABLE 7

Characteristic values of shale oil yielded by thermal degradation of kerogens isolated from Hungarian oil shales (temperature: 500 °C)

Locality	Type of kerogen	Length of the average paraffinic carbon skeleton *	H in the different carbon skeleton*		
			aliphatic %	alicyclic %	aromatic %
Pula	Type I	C_{16}	60	30	10
Várkesző	Type II	C_{10}	48	31	21
Várpalota	Type II	C_{13}	55	27	18

* Measured by NMR records

in this respect, too. The proportion of the aromatic compounds refers also to the similarity of the Várpalota and Várkesző organic matters. The proportion of the aromatic compounds amounts to about twenty percent in these cases, but only about ten percent in case of the Pula shale oil (Table 7).

REFERENCES

Hajós, M. (1976): Diatom flora in Upper Pannonian sediments of borehole Put—3 at Pula village (Transdanubia, Hungary). — Annual Report of the Hungarian Geological Institute of 1974 Budapest, p. 263—486.

Hetényi, M. (1979): Thermal degradation of the oil shale kerogen of Pula (Hungary) at 473 and 573 K. — Acta Miner., Petr. Szeged, **XXIV/1**, p. 99—111.

Hetényi, M. (1980):Thermal degradation of the organic matter of oil shale of Pula (Hungary) at 573—7.73 K. — Acta Miner. Petr., Szeged, **XXIV/2**, p. 301—314.

Hetényi, M., Tóth, I. and Milley, Gy. (1982): On the role of temperature and pressure in the artificial evolution of organic matter of the Pula oil shale (Hungary). — Acta Miner. Petr., Szeged, **XXV/2**, p. 131—146.

Hetényi, M. (1983): Experimental evolution of oil shales and kerogens isolated from oil shales. — Acta Miner. Petr., Szeged, **XXVII/1**, p. 73—85.

Hetényi, M. (1985): Organic geochemical features of maar-type oil shales of Hungary. — Acta Miner. Petr., Szeged, **XXVII**, p. 145—152.

Jámbor, Á. and Solti, G. (1975): Geological conditions of the Upper Pannonian oil shale deposit recovered in the Balaton Highland and at Kemeneshát, — Acta Miner. Petr., Szeged, **XXII**, p. 9—28.

Jámbor, Á. and Solti, G. (1976): Geological conditions of the Upper Pannonian oil shale deposit recovered in the Balaton Highland and at Kemeneshát (Transdanubia, Hungary). — Annual Report of the Hungarian Geol. Institute of 1974, Budapest, p. 193—220.

Jámbor, Á., Ravasz, Cs. and Solti, G. (1982): Geological and lithological characteristics of oil shale deposits in Hungary. — 3rd All Union Meeting on the Geochemistry of Oil Shales, Tallinn.

Kedves, M. (1983): Étude paleobotanique sur les schistes pétrolifere du tertiaire supérieur de Hongrie. —
Revue de Micropaléontologie, **26/1**, p. 48—53.

Nagy, E. (1976): Palynological investigation of Transdanubian oil shale exploratory boreholes. — Annual Report of the Hungarian Geological Institute of 1974, Budapest, p, 247—262.

Pápay, L. (1982): IR and NMR characterization of oil generated from some Hungarian oil shale at 773 K. — Acta Miner. Petr.. Szeged, **XXV/2**, p. 147—156.

Solti, G. (1980): The oil shale deposit of Várpalota. — Acta Miner. Petr., Szeged, **XXIV/2**, p. 289—300.

Solti, G. (1981): The geyserite of Pula. — Annual Report of the Hungarian Geological Institute of 1970, Budapest. p. 241—247.

Solti, G. (1985:) Alginite (oil shale) exploration and utilization possibilities in Hungary.—Földtani Kutatás, **XXVIII**, p. 11—20.

Tissot, B., Durand, B., Espitalié, J. and Combaz, A. (1974): Influence of the nature and diagenesis of organic matter in formation of petroleum. — Am. Assoc. Petr. Geol. Bull., **58**, p. 499—506.

Tissot, B. P. and Welte, D. H. (1978): Petroleum formation and occurrence.—Springer Verlag.

Tissot, B. P. (1084): Recent advences in petroleum geochemistry applied to hydrocarbon exploration. — Am. Assoc. Petr. Geol. Bull., **68**, p. 545—563.

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