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# ORGANIC GEOCHEMICAL FEATURES OF THE MAAR-TYPE OIL SHALES OF HUNGARY

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## ABSTRACT

In the last decade several so-called maar-type oil shales were discovered in Hungary, this type being infrequent on a world scale, as well. These were deposited in the enclosed lakes formed in volcanic rings. The composition of the biomass serving as precursor of the organic matter of the oil shales proved to be different in each bed.

The organic matter of the three beds generated under the same geological but somewhat differing biological conditions is different both from qualitative and quantitative points of view. In the Pula locality the favourable environmental conditions allowed the accumulation of the algal material, its good preservation, thus the formation of type I kerogen. The organic matter of the Várkeszõ and Gérce oil shales is heterogeneous, the precursors of the kerogens of type I and III are mixed in them. The kerogen of Várkeszõ is of type II due to the higher proportions of the humic substance. The kerogen of Gérce is transitional between the types I and II.

The organic matter content, the genetic potential, the HI, OI, $T_{max}$ values measured by Rock-Eval pyrolysis, as well as the H/C atomic ratios and diagenesis coefficients ($C_R/C_T$) of the oil shales support the classification mentioned above. To express quantitatively the type-differences the PC/TOC ratio seems to be suitable. Its value in the order of Pula, Gérce, Várkeszõ is as follows: 65, 47 and 38%. Taking the same sequence, the quantity of bitumen of the oil shales, formed during the natural evolution of the oil shales, is increasing, i. e. the activation energy of kerogen is decreasing.

## INTRODUCTION

In the last decade several oil shale beds were discovered in Hungary, their dimensions being rather small. These beds can be fundamentally divided into two groups. The first group is represented by the accumulations of the former intramontane lagoons. The second group involves the maar-type oil shales being curious also on a world scale and only of geological interest.

The maar-type oil shales of Pula, Gérce and Várkeszõ were deposited in the enclosed lakes developed in basalt craters of Western Hungary, Transdanubia (BENCE, JÁMBOR, PARTÉNYI, 1979; JÁMBOR and SOLTI, 1975, 1976). In the course of the final basalt volcanism of the Carpathian Basin, as a result of a strong eruption happening once isometric tuff-rings were developed. Their age is 3.05—5.34± ±0.93 ma (JÁMBOR, RAVASZ and SOLTI, 1982). In the oligohaline water (about 3‰ salt content) of the lakes formed in the tuff rings, the intense weathering of the basalt tuff produced favourable conditions to the growth of planctonic algae, first of all of the Botryococcus braunii. The accumulation of the organic matter was promoted by the warm-temperate climate during sedimentation (NAGY, 1976; HAJÓS, 1976) and by the anaerobic conditions prevailing in the lower horizon of the

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lakes (RAVASZ, 1976). Simultaneously, the dense vegetation at the crater margins prevented the coarse detritus to get the water.

In some strata the Pula oil shale is of excellent, but on the average of medium quality, the oil shales of Várkesző and Gérce are of medium to poor quality. The qualitative differences between the beds of the same type can probably be attributed to the fact that in the Pula crater the water of the crater lake was warmed periodically by the uprushing hot water produced by the post-volcanic activity (SOLTI, 1981). The hot water produced favourable conditions first of all to the algae, promoting thus the formation of sediment more abundant in organic matter and, of oil shale of better quality. In the composition of the biomass serving as precursor of the organic matter of the bed qualitative differences can also be observed in addition to the quantitative ones. In the Gérce oil shale the pollen analyses identified coalified vascular tissue remnants in addition to the amorphous organic matter of huge quantity (KEDVES, personal communication). In some strata of the Várkesző oil shale the coalified remnants of higher terrestrial plants can be observed macroscopically, as well. Thus, the composition of the original biomass of the beds accumulated under the same geological conditions and to be compared below slightly differs from one another. Further, as proved by the pollen analyses, the biological activities of the afore-mentioned sedimentary basins was also different (KEDVES, 1983; HETÉNYI *et al.*, 1982; HETÉNYI, 1983). The state of preservation of the Botryococcus algae and sporpmorphs of the Pula oil shale refers to biologically inactive sedimentation environment. The Várkesző bed could develop under conditions of special biological activity: the Botryococcus algae are destructed, the sporomorphs, however, being fairly well preserved. In the Gérce oil shale the quantity of Botryococcus is small and, based on the remnant composition, the deposition took place in a biologically active, probably alkaline environment (KEDVES, personal communication).

In this paper the organic geochemical features of three maar-type oil shales of Hungary (Pula, Gérce, Várkesző) will be compared, the oil shales being formed under the same geological but somewhat different biological conditions. It could be assumed that due to the somewhat different character of the sedimentation environment, the organic matter of the beds would differ from one another both from the qualitative and from the quantitative points of view.

## EXPERIMENTAL

The oil shale samples were ground to the grain size of 0.05—0.15 mm, the bitumen was extracted in a Soxhlet extractor in two steps: first by chloroform (Bit-A), then by benzene-acetone-methanol mixture of 70:15:15 ratio (BAM-bitumen).

Kerogen was enriched first by specific gravity differences, the remaining mineral components were destroyed by means of chemical procedures.

The determination of the $C_{org}$ content was carried out at 1000 °C under intense oxygen flow, by means of combusting in a Carmhograph-8 equipment.

The H and C contents were measured in CHN-analysator.

The determination of the maximal hydrocarbon generation temperature ($T_{max}$), of the genetic potential ($S_1+S_2$), of the H- and O-indices was performed by Rock-Eval pyrolysis (ESPITALIE *et al.*, 1977).

The $C_R/C_T$ ratio was measured on the basis of the ASTM standard (CUMMINS *et al.*, 1972).

## RESULTS

As it has been usual, the characterization of the organic matter was made according to the organic carbon content. The quantity of the organic carbon is extremely high in the Pula bed, especially in some strata where the above-mentioned conditions favoured the accumulation and preservation of the algal material. The average organic carbon content of the samples between 4.5 and 39.5 m (sampling interval 0.5 to 1.0 m) is 13.4% (Table 1). In some layers (*e.g.* 24.5—26.0 m and 14.0—17.0 m) the organic carbon content is as high as 30 to 50% (HETÉNYI *et al.*, 1977). This periodicity can be most probably attributed to the hydrochemical changes, to the periodical geyser activity. In harmony with the sedimentation, the organic carbon content of the Gérce and Várkesző oil shales is much lower than in the Pula oil shale, i.e. 15.5 and 18.7%, respectively.

TABLE 1

*Quantitative characterization of the organic matter of the maar-type oil shales*

| Characteristics | Locality | | |
|---|---|---|---|
| | Pula | Gérce | Várkesző |
| Depth (m) | 4.5—39.5 | 4.0—68.3 | 55.0—70.5 |
| Organic carbon content (%) | 0.3—45.7 | 0.1—15.5 | 3.2—18.7 |
| Soluble organic matter (%) | 2.47 | 3.50 | 4.79 |
| Bit-A (%) | 1.78 | 2.54 | 3.30 |
| BAM-Bit (%) | 0.69 | 0.96 | 1.49 |
| $\beta$-coefficient (%) | 18.4 | 53.0 | 36.8 |

Bit-A = soluble organic matter extracted by chloroform
BAM-Bit = soluble organic matter extracted by benzol: acetone: metanol = 70:15:15
$\beta$-coefficient = 100 × soluble organic matter/organic carbon content

Based on the genetic potential being the most important quantitative index from the hydrocarbon genetic point of view, the Pula oil shale can be fairly well distinguished from that of Gérce and Várkesző. In case of the Pula oil shale the genetic potential is 70—80 kg HC/t rock on the average, the extreme values being 40 and 260 kg HC/t rock. The genetic potential of the Gérce and Várkesző oil shales is 40—60 and 40—50 kg HC/t rock, the extreme values being 10 and 115 kg HC/t rock in the Gérce, 10 and 88 kg HC/t rock in the Várkesző oil shales.

The determination of the primordial feature of the organic matter, i.e. of the type, bear great possibility of error. In most measurement methods a peculiarity is traced which changes as a function of the type and maturity stage of the organic matter. Considering the fact that the organic matter of the oil shale is in the initial stage of evolution and thus samples of the same evolution stage are compared, the value of the indices will depend unambiguously on the type. The mineral components, however, mean further problems. The inorganic ingredients constituting the major part of the sedimentary rocks impede the determination of the adjoining organic matter. When isolating the kerogen the following circumstance should be taken into account: a part of kerogen will be lost; certain chemical changes will follow in the organic matter in the course of isolation. These error possibilities thought to be decreased by making measurements both in the oil shales and in the kerogens isolated from them.

Some samples representing the average of the three beds were chosen and Rock-Eval pyrolysis were made. The most important data measured in this manner are shown in Table 2. In addition to the differences in the genetic potential, the type I and II can be distinguished also after the H- and O-indices, and the transition between the two types can be observed, respectively *(Fig. 1)*. When plotting the H-index as a function of the maximal hydrocarbon generation temperature the type and evolution state of the organic matter can be determined together (ESPITALIE *et al.*, 1977). As it is seen in *Fig. 2*, the organic matter of the Pula oil shale is assigned unambiguously to the type I, that of the Várkeszõ oil shale to the type II. The organic matter of the Gérce oil shale shows values usually characteristic of the type II, but in certain layers it approches the type I on the basis of all the characteristics. As a whole, it can be considered to be transitional between the types I and II.

To characterize the type differences the PC/TOC ratio seems to be suitable describing the pyrolysable part of the organic carbon content of the samples under definite experimental conditions (the measurement of PC was carried out by Rock-Eval pyrolysis). Based on the average values of the ratio the organic matter of type I (PC/TOC=65%) and of type II (PC/TOC=38%) can be fairly well distinguished, and the transitional character of the Gérce oil shale (PC/TOC=47%) can also be demonstrated, as well (Table 3). The PC/TOC seems to be useful not only to distin-

TABLE 2

*Characterization of the organic matter of the maar-type oil shales by Rock-Eval pyrolysis*

| Depth (m) | $T_{max}$ (°C) | $S_1+S_2$ kg HC/t oil shale | $S_2/S_3$ | HI mg HC/g TOC | OI mg $CO_2$/g TOC |
|---|---|---|---|---|---|
| | | PULA | | | |
| 9.5—10.0 | 440 | 40.08 | 8.18 | 556 | 67 |
| 10.0—10.5 | 440 | 81.13 | 10.44 | 671 | 64 |
| 16.0—16.5 | 437 | 71.63 | 8.79 | 560 | 63 |
| 19.5—20.0 | 439 | 77.22 | 14.89 | 749 | 50 |
| 25.0—25.5 | 440 | 258.53 | 22.21 | 840 | 37 |
| | | GÉRCE | | | |
| 14.0—14.5 | 434 | 39.40 | 9.18 | 407 | 44 |
| 21.0—22.0 | 436 | 45.74 | 9.66 | 598 | 61 |
| 34.0—35.0 | 425 | 35.34 | 6.95 | 372 | 53 |
| 43.0—44.0 | 432 | 69.57 | 10.94 | 646 | 59 |
| 58.0—59.0 | 426 | 57.39 | 7.01 | 426 | 60 |
| | | VÁRKESZŐ | | | |
| 55.0—56.0 | 421 | 47.94 | 7.74 | 397 | 51 |
| 58.0—59.0 | 434 | 48.62 | 5.02 | 354 | 70 |
| 69.0—69.5 | 422 | 43.65 | 4.61 | 330 | 71 |
| 70.0—70.5 | 431 | 88.12 | 8.42 | 461 | 54 |

TABLE 3

*Quantitative characterization of the different types of oil shale kerogen*

| Pula | | Gérce | | Várkesző | |
|---|---|---|---|---|---|
| Depth (m) | PC/TOC % | Depth (m) | PC/TOC % | Depth (m) | PC/TOC % |
| 9.5—10.0 | 60 | 14.0—14.5 | 39 | 55.0—56.0 | 42 |
| 10.0—10.5 | 51 | 21.0—22.0 | 54 | 58.0—59.0 | 33 |
| 16.0—16.5 | 77 | 34.0—35.0 | 38 | 69.0—69.5 | 35 |
| 19.5—20.0 | 65 | 43.0—44.0 | 63 | 70.0—70.5 | 43 |
| 25.0—25.5 | 72 | 58.0—59.0 | 42 | | |
| Average: | 65 | | 47 | | 38 |

guish the type but to make distinction between the sub-types. This ability is shown by the fact that the value of this ratio proved to be between 30 and 40% in case of other three oil shales generated under different geological conditions and containing organic matter of type II. At the same time, the sediments of organic matter of type

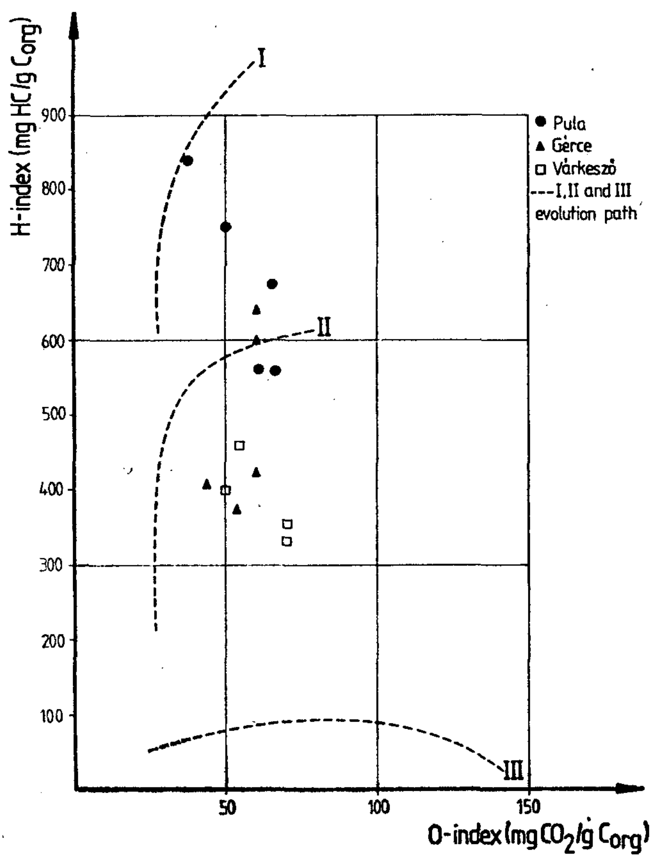


*Fig. 1.* Classification of the kerogens of the different Hungarian oil shales in a hydrogen index/oxygen index diagram

III and of the same evolution state could be characterized by PC/TOC values of 12 to 13% (HETÉNYI, unpublished data).

As it has been shown by the measurement data, there are considerable differences between the organic matter of the three oil shale beds accumulated in the same geological environment. It is highly probable that these differences can be attributed to the composition of the initial biomass. The differences between the organic matter of the Pula and Várkesző oil shales can be attributed to the different ratio of mixing of the algal material constituting the biomass and of the higher terrestrial plants. In the organic matter of the Várkesző oil shale the latter is of higher proportion. This biopolymer being the precursor of the organic matter of type III of somewhat greater quantity produced an essentially heterogeneous organic matter having mixed with the kerogen of type I.

In order to demonstrate the type-modifying effect of the higher terrestrial plants samples were chosen from the Várkesző oil shale which showed proportions of the plant remnant higher than the average. In case of all the three oil shales, isolation was carried out from the strata most abundant in organic matter. The organic geochemical characteristics of kerogens (Table 4) fairly reflect the type difference which was generated by the biomass of different composition under the same geological conditions. Based on their H/C atomic ratios the Pula kerogen of type I and the Gérce kerogen representing the transition between types I and II differ from each other only to small extent. More remarkable is the difference when taking the $C_R/C_T$ and $T_{max}$ values. All features of the kerogen isolated from the Várkesző oil shale of highest terrestrial plant remnant quantity considerably differ from the same values of the two other kerogens (Table 4). The difference is much greater than in case of comparing the averages of the beds (Tables 2 and 3).

This type-modifying effect of the humic matter can be proved by the comparison of the kerogens and of their humin-free forms. The differences occurring in the oxidation features of the Pula and Várkesző kerogens referring to the type differences, cannot be observed in the course of oxidation of the humin-free organic matter (HETÉNYI, 1983).

The activation energy of the evolution process, thus the quantity of the degradation products of the organic matter (under the same external conditions) is closely related to the type of kerogen. The organic matter of the oil shales to be compared here is in a maturity state preceding the oil generation zone. In the course of the natural evolution different gaseous (*e.g.* $CO_2$, $H_2S$) products and bitumen were formed. The bitumen → oil transformation is insignificant yet, i.e. the end product

TABLE 4

*Characterization of kerogen isolated from Hungarian maar-type oil shales*

| | H/C | $C_R/C_T$ | PC/TOC (%) | $S_1+S_2$ kg HC/t kerogen | $S_2/S_3$ | $T_{max}$ (°C) |
|---|---|---|---|---|---|---|
| Pula | 1.72 | <0.10 | 77 | 697 | 25.7 | 444 |
| Gérce | 1.68 | 0.20 | 78 | 687 | 25.8 | 430 |
| Várkesző | 1.33 | 0.43 | 56 | 445 | 10.5 | 426 |

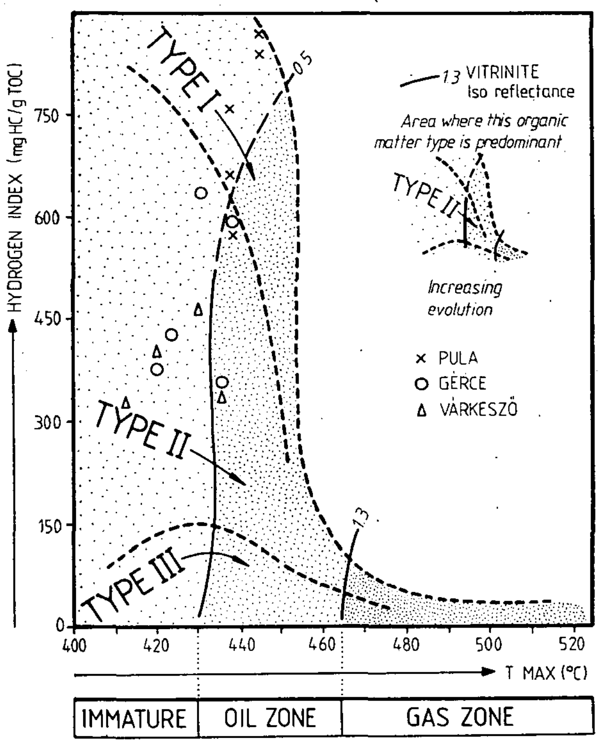


*Fig. 2.* Classification of the kerogens of the different Hungarian oil shales and characterization of their degree of evolution

of the process is the soluble organic matter in this stage. Thus, the fact that the quantity of the organic solvent soluble organic matter (bitumen) of the three oil shale beds increase in the order Pula—Gérce—Várkesző (Table 1) refers to the decreasing activation of kerogens in the same sequence. The smallest quantity of bitumen was generated in the course of natural evolution of the kerogen of type I requiring the greatest activation energy, and most considerable evolution intermediary product was formed from the Várkesző sample requiring the lowest activation energy.

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