

## Search for source rocks of the crude oils of the Drmno depression (southern part of the Pannonian Basin, Serbia)

B. JOVANČIĆEVIĆ<sup>1,2#</sup>\*, H. WEHNER<sup>3</sup>, G. SCHEEDER<sup>3</sup>, K. STOJANOVIĆ<sup>2,4</sup>, A. ŠAINOVIĆ<sup>1</sup>, O. CVETKOVIĆ<sup>2#</sup>, M. ERCEGOVAC<sup>5</sup> and D. VITOROVIĆ<sup>2#</sup>

<sup>1</sup>Faculty of Chemistry, University of Belgrade, P. O. Box 158, YU-11001 Belgrade, <sup>2</sup>ICTM-Center of Chemistry, P. O. Box 815, YU-11001 Belgrade, <sup>3</sup>Federal Institute for Geosciences and Natural Resources, P. O. Box 510153, Hannover, Germany, <sup>4</sup>Department of Medicine, University of Belgrade, Višegradska 26, YU-11000 Belgrade and <sup>5</sup>Faculty of Mining and Geology, University of Belgrade, Džušina 7, Belgrade, Serbia, Yugoslavia

(Received 11 April 2002)

*Abstract:* In a search for source rocks of the crude oils of the Drmno depression (southern part of the Pannonian Basin, Serbia), based on bulk and specific organic geochemical parameters, six out of eight Sirakovo, Bubušinac and Bradarac sedimentary core samples were found to possess typical source rock characteristics. By comparing the results observed for these sedimentary samples with the corresponding properties of the crude oils from the Sirakovo and Bradarac oil-gas fields, a positive organic geochemical oil-source rock correlation was experienced for the first time within this basin. This finding may be considered as an important step towards the ultimate organic geochemical/geological interpretation of the Drmno depression.

*Keywords:* source rocks, crude oils, Drmno depression, organic geochemical correlation, biological markers.

### INTRODUCTION

In oil and gas exploration studies, the identification of petroleum source rocks and their relationship with oils originating from known oil fields (organic geochemical oil-source rock correlation) is one of the most important tasks. Following the petroleum system concept of Magoon and Dow,<sup>1</sup> exploration of any oil field should not be considered complete until the location of source rocks has been identified and the source rock potential has been estimated.

Petroleum source rocks are characterized by three basic parameters.<sup>2,3</sup> Firstly, they must contain a certain amount of organic matter (total organic carbon, TOC), generally above 0.5 %. Secondly, the maturity of a source rock has to be sufficiently high, *i.e.*, close

# Serbian Chemical Society active member.

\* Corresponding author.

to the maturity of the crude oil itself. Finally, the source rock kerogen should preferably be of type I and/or type II, these two kerogen types being characterized by a high liquid hydrocarbon potential.

The exact location of the source rocks of the oils obtained from the Drmno depression oil fields (the district of the so-called Stig, Serbia), is not yet fully and reliably known. Hence, this locality has not yet been completely explored. Up-to-date organic geochemical investigations were comprised mainly of correlations of the oils from the discovered oil fields, or correlations of these oils with oils from other neighbouring oil or oil-gas fields. It was shown that the Drmno depression crude oils, according to their origin (higher participation of terrestrial precursor biomass) and to their maturity (mainly of somewhat lower maturity), differed from the crude oils from Banat and North Bačka depressions (Vojvodina) oil fields.<sup>4-7</sup> On the other hand, among the Drmno depression crude oils themselves, some minor variations concerning the type of precursor organic matter and the degree of thermal maturity were observed.<sup>8</sup>

Sedimentary samples originating from the Sirakovo, Bubušinac and Bradarac boreholes (all from Drmno depression locations) were examined in this paper. Organic geochemical methods were used for their investigation (TOC, bitumen and hydrocarbons; distribution and abundance of biological markers such as *n*-alkanes, isoprenoid aliphatic alkanes, triterpanes and steranes). They were aimed at estimating their oil potential. The observed organic geochemical parameters were correlated with the same parameters determined for the crude oils from two nearby localities (Sirakovo and Bradarac; these comparative results were published in one of our recent papers<sup>8</sup>). The correlations were expected to show whether a genetic relationship exists between the examined sediments and the mentioned crude oils, *i.e.*, whether a positive oil-source rock correlation between them may be assumed.

## EXPERIMENTAL

### *Samples*

Eight samples of sedimentary rocks from the localities of the Sirakovo (Sir-), Bubušinac (Bub-) and Bradarac (Bra- and Bra-Malj-) boreholes were investigated. A list of these samples, including the corresponding depths and stratigraphic data, is given in Table Ia. The sedimentary samples were correlated with the crude oils from the Sirakovo and Bradarac oil-gas fields (Table Ib<sup>8</sup>).

TABLE I. A list of the investigated sediments (a) and crude oils (b)

a)			
No.	Sample	Depth (m)	Age/complex
1	Sir-1	1995.1	Eggenburgian/"Red series"
2	Bub-3	1911.8	Ottangian-Carpathian/B1
3	Bra-1	2290.1	Badenian
4	Bra-4	2194.5	Eggenburgian/"Red series"
5	Bra-5	2159.2	Ottangian-Carpathian/C2

TABLE I. Continued

No.	Sample	Depth (m)	Age/complex
6	Bra-8	2018.8	Ottningian-Carpathian/C2
7	Bra-Malj-2	2174.2	Ottningian-Carpathian/C2
8	Bra-Malj-7	2293.2	Ottningian-Carpathian/C2
b)			
1	Sir-1	1782–1778	Ottningian-Carpathian
2	Sir-2	1704–1701	Ottningian-Carpathian
3	Sir-18	1548–1544	Ottningian-Carpathian
4	Sir-19	1436–1429	Ottningian-Carpathian
5	Sir-20	1444–1440	Ottningian-Carpathian
6	Bra-Malj-2	2307–2302	Ottningian-Carpathian/partly "Red series"
7	Bra-Malj-4	2170–2156	Prebadenian/"Red series"
8	Bra-Malj-5	1989–1985	Badenian
9	Bra-Malj-10	1808–1804	Badenian

#### Analytical methods

Following the elimination of carbonates from the powdered samples (< 0.063 mm) with dilute hydrochloric acid (1:4), the content of organic carbon, TOC, was determined by the Coleman method. The amount of bitumen was determined by Soxhlet extraction for 36 h, using the azeotropic dichloromethane-methanol mixture as solvent. The bitumen content was calculated relative to dry sediment (ppm) and relative to TOC (mg/g).

The proportion of hydrocarbons in the isolated bitumen fractions was determined by column chromatography (the adsorbents used were silica gel and alumina). The saturated hydrocarbons were eluted with petroleum ether and the aromatic hydrocarbons with benzene. The total hydrocarbon content was calculated relative to sediment (ppm) and relative to bitumen (%) (Table II).

*n*-Alkanes, the isoprenoid alkanes pristane and phytane, the steranes and triterpanes, as constituents of the saturated hydrocarbon fractions, were analyzed by a Hewlett Packard 5890, Series II gas chromatograph fitted with a capillary column coated with HP-5MS, coupled to a Hewlett-Packard 5972 MSD operated at 70 eV, using helium as the carrier gas (flow rate 1 cm<sup>3</sup>/min). The *n*-alkanes and isoprenoids, as the dominant constituents, were identified from the Total Ion Current (TIC). The steranes and triterpanes were identified using the single ion monitoring method (SIM), from the *m/z* 217 and *m/z* 191 fragmentograms.

The analytical procedure used for crude oils was described in one of our recent papers.<sup>8</sup>

## RESULTS AND DISCUSSION

### Source rock potential of the investigated sediments

**Bulk parameters.** The content of organic matter (TOC), together with the observed numerical values of bulk parameters generally used for the estimation of the maturity of sedimentary organic matter, are presented in Table II. For comparison, numerical values of the same parameters typical for source rocks<sup>3</sup> are also shown in Table II.

The content of TOC in six out of the eight examined samples was found to be above 0.5 %. The sample Bra-8 contained a marginal amount of TOC, 0.46 % and the sample Bra-4 just 0.24 % (parameter 1, Table II).

TABLE II. Bulk parameters of the analyzed sediments

No.	Sample	TOC (%)	Bitumen		Hydrocarbons	
			(ppm of sediment)	(mg/g C <sub>org</sub> )	(ppm of sediment)	(% of bitumen)
1	Sir-1	1.31	2162	165.0	322	51.0
2	Bub-3	1.22	2816	230.8	276	57.1
3	Bra-1	2.07	2306	111.4	306	59.8
4	Bra-4	0.24	353	147.1	144	40.9
5	Bra-5	3.01	2054	68.2	222	43.2
6	Bra-8	0.46	475	103	152	42.0
7	Bra-Malj-2	2.54	3086	121.5	315	57.0
8	Bra-Malj-7	1.11	2264	204.0	423	74.5
Source rock standards:		>0.5	300–3000	50–200	>100–260	20–60
Parameter:		1	2a	2b	3a	3b

The amounts of bitumen and hydrocarbons in sedimentary rocks serve primarily as a basis for an estimation of the maturity of the organic matter. By comparing the observed

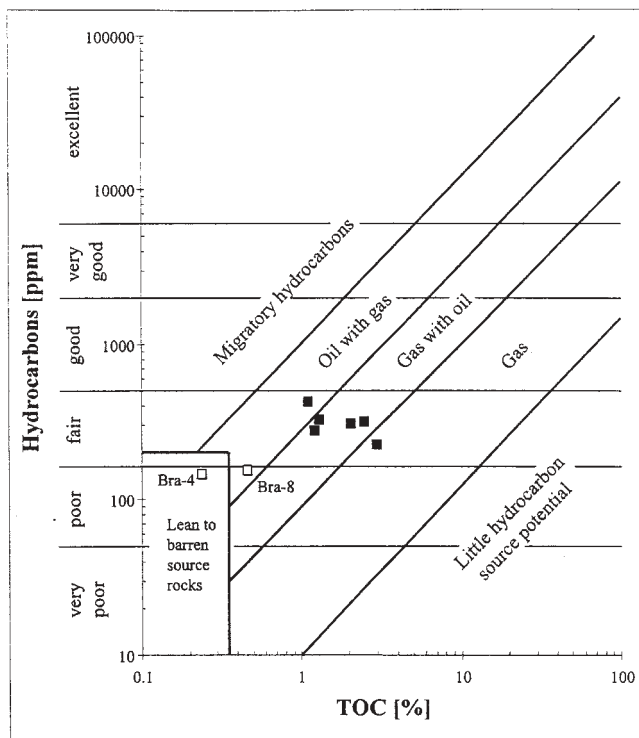


Fig. 1. Evaluation of the crude oil potential of the investigated sediments based on the amount of hydrocarbons (ppm, relative to sediment) and the content of organic carbon, TOC (%), relative to sediment), according to the source rock criteria proposed by Landais and Connan.<sup>9</sup>

quantities of bitumen and hydrocarbons (parameters 2a and 2b, and 3a and 3b, respectively, Table II) with the ranges typical for source rocks,<sup>3</sup> the maturity of the organic matter of the investigated sediments was shown to be equal with the maturity of the organic matter of source rocks. The sample Bra-Malj-2, as well as the sample Bra-Malj-7, contained somewhat higher amounts of bitumen compared to the amounts typical for source rocks (*i.e.*, 3086 *vs.* 3000 ppm, parameter 2a, and 204 mg/g *vs.* 200 mg/g, parameter 2b, respectively, Table II). The quantity of hydrocarbons in sample Bra-Malj-7 was also somewhat higher compared to the maximum amount typical for source rocks (*i.e.*, 74.5 % *vs.* 60 %, parameter 3b, Table II). Theoretically, these exceptions might suggest that parts of this organic matter are allochthonous, *i.e.*, represent a migration product. However, the location of these two samples in a diagram proposed by Landais and Connan (Fig. 1),<sup>9</sup> based on TOC and hydrocarbon contents, did not corroborate such a presumption. Namely, according to the parameter ranges

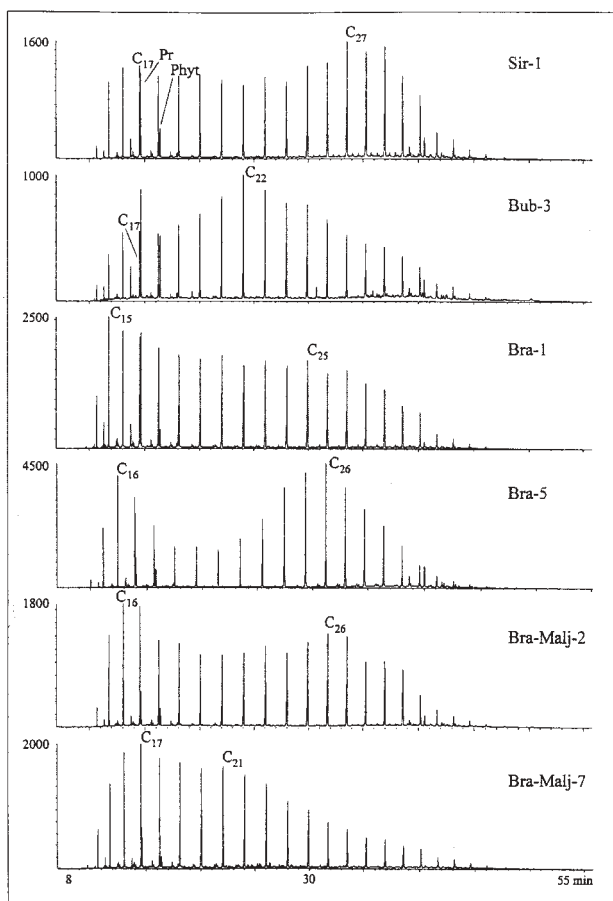


Fig. 2. Distribution of *n*-alkanes, observed in the TICs during the GC-MSD analyses of the alkane fractions from six samples of sedimentary rocks which had been classified into the category of source rocks on the basis of their bulk parameters.

indicated in this diagram, six out of the eight investigated samples demonstrated the characteristics of source rocks. The exceptions were again samples Bra-4 and Bra-8, containing less than 0.5 % TOC and insufficient amounts of bitumen and hydrocarbons (parameters 1–3, Table II; Fig. 1). Hence, only samples Bra-4 and Bra-8 were excluded from the group of potential crude oil source rocks and were not analyzed in more detail.

*Specific maturity parameters (n-alkanes, steranes and triterpanes).* The distribution of *n*-alkanes, as well as of the isoprenoid alkanes pristane and phytane (TICs in GC-MSD analyses of the alkane fractions), in the sediments which, according to their bulk parameters, were indicated as source rocks are shown in Fig. 2. The corresponding parameters are presented in Table III.

TABLE III. Alkane molecular parameters of the analyzed sediments

No	Sample	Most abundant <i>n</i> -alkane	CPI*	Pr/Phyt
1	Sir-1	C <sub>17</sub> ; C <sub>27</sub>	1.11	2.94
2	Bub-3	C <sub>17</sub> ; C <sub>22</sub>	1.00	1.79
3	Bra-1	C <sub>15</sub> ; C <sub>25</sub>	1.13	6.78
4	Bra-5	C <sub>16</sub> ; C <sub>26</sub>	1.00	1.60
5	Bra-Malj-2	C <sub>16</sub> ; C <sub>26</sub>	1.15	2.11
6	Bra-Malj-7	C <sub>17</sub> ; C <sub>21</sub>	1.07	3.40
Source rock standards:		–	0.80–1.20	–
Parameter:		1	2	3

\*CPI was calculated for the full range of *n*-alkanes.<sup>3</sup>

The chromatograms of all the samples were characterized by a more or less distinct bimodal distribution of the *n*-alkanes (Fig. 2). Consequently, the corresponding chromatograms showed two maxima (parameter 1, Table III). The distributions of the odd and even carbon number *n*-alkanes were pretty smooth. The calculated CPI values (CPI = 1.00–1.15, parameter 2; Table III) were within the source rock range (0.80–1.20). Hence, the *n*-alkane distributions were further proof of the source rock characteristics of the six investigated samples.

The polycyclic alkanes of the triterpane and sterane types were also analyzed (GC-MSD; SIM). The fragmentograms *m/z* 191 and *m/z* 217 are shown in Fig. 3.

The observed distributions resemble typical crude oil distributions.<sup>10</sup> For example, in the case of the triterpanes, besides oleanane and gammacerane (O and G, Fig. 3), the thermodynamically most stable hopanes (*i.e.*, peaks a, c and the isomer 22*S* of peak e) and their less stable isomers (*i.e.*, peaks b, d and the isomer 22*R* of peak e) were found in ratios characteristic of crude oils. Moreover, with the sterane fractions, besides the biolipid isomers C<sub>27</sub>-C<sub>29</sub> αα (20*R*) (peaks 2, 3 and 6), geolipid isomers were also found, like diasteranes, as well as C<sub>27</sub>-C<sub>29</sub> steranes with the hydrogen atoms at C<sub>14</sub> and C<sub>17</sub> in the β-position and *S*-configuration at C<sub>20</sub> (peaks 1, 4 and 5). Hence, the triterpane and sterane fingerprints themselves also suggest that the organic matter in these sediments is on the level of source rock as well as crude oil maturities.

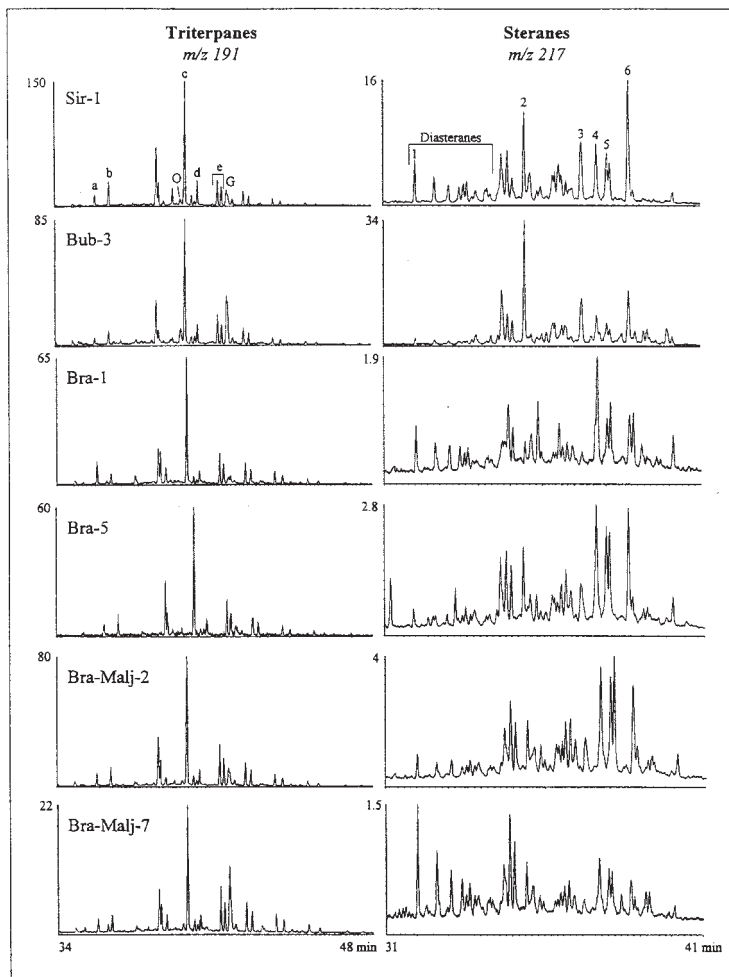


Fig. 3. Fragmentograms of triterpanes ( $m/z$  191) and steranes ( $m/z$  217) in the alkane fractions of the investigated sediments. a –  $C_{27}$ -18 $\alpha$ (H)-22,29,30-trisnorhopane (Ts); b –  $C_{27}$ -17 $\alpha$ (H)-22,29,30-trisnorhopane (Tm); c –  $C_{30}$ -17 $\alpha$ (H),21 $\beta$ (H) hopane; d –  $C_{30}$ -17 $\beta$ (H),21 $\alpha$ (H) moretane; e –  $C_{31}$ -17 $\alpha$ (H),21 $\beta$ (H) homohopanes (22*S* and 22*R*); O – oleanane; G – gammacerane; 1 –  $C_{27}$ -13 $\beta$ (H),17 $\alpha$ (H) diasterane (20*S*); 2 –  $C_{27}$ -14 $\alpha$ (H),17 $\alpha$ (H) sterane (20*R*); 3 –  $C_{28}$ -14 $\alpha$ (H),17 $\alpha$ (H) sterane (20*R*); 4 –  $C_{29}$ -14 $\alpha$ (H),17 $\alpha$ (H) sterane (20*S*); 5 –  $C_{29}$ -14 $\beta$ (H),17 $\beta$ (H) sterane (20*R*); 6 –  $C_{29}$ -14 $\alpha$ (H),17 $\alpha$ (H) sterane (20*R*). (The detailed identification of the corresponding peaks was discussed in our previous papers).<sup>5,6</sup>

The calculated numerical values of the maturation parameters were even more convincing as far as the degree of maturity of the analyzed organic matter was concerned (Table IV). This refers, in the first place, to the terpane maturation parameters (marked as parameters 2 and 3 in Table IV) the numerical values of which for almost all the samples indicated that equilibrium had been attained in the  $C_{31}$  hopane epimerization reaction  $22R \rightleftharpoons 22S$  (0.57–0.62<sup>11</sup>), as well as the  $C_{30}$  terpane epimerization reaction moretane  $\rightleftharpoons$  hopane, *i.e.*,

TABLE IV. Triterpane and sterane maturation parameters of the analyzed sediments

No.	Sample	Ts/Ts+Tm	22S/22S + 22R C <sub>31</sub> hopanes	Moretane/Hopane C <sub>30</sub>	$\beta\beta/\beta\beta + \alpha\alpha$ C <sub>29</sub> steranes	20S/20S + 20R C <sub>29</sub> steranes	C <sub>27</sub> dia/dia + ster
1	Sir-1	0.34	0.59	0.19	0.28	0.31	0.33
2	Bub-3	0.32	0.60	0.15	0.26	0.32	0.01
3	Bra-1	0.71	0.60	0.10	0.47	0.47	0.68
4	Bra-5	0.38	0.57	0.11	0.47	0.50	0.21
5	Bra-Malj-2	0.40	0.60	0.12	0.51	0.53	0.34
6	Bra-Malj-7	0.45	0.60	0.12	0.55	0.60	0.71
Equilibrium values:		/	0.57–0.62	0.05–0.10–0.15	0.67–0.71	0.52–0.55	/
Parameter:		1	2	3	4	5	6

Ts - 18 $\alpha$ (H)-22,29,30-trisnorneohopane; Tm - 17 $\alpha$ (H)-22,29,30-trisnorhopane; Dia - C<sub>27</sub> diasterane  $\beta\alpha$ (20S); Ster - C<sub>27</sub> sterane  $\alpha\alpha$ (20R).

TABLE V. Triterpane and sterane source parameters of the analyzed sediments

No.	Sample	O/H × 100	G/H × 100	$\alpha\alpha R$ steranes		
				%C <sub>27</sub>	%C <sub>28</sub>	%C <sub>29</sub>
1	Sir-1	4.5	12.1	32.9	21.5	45.6
2	Bub-3	12.3	39.2	55.1	20.8	24.1
3	Bra-1	0.0	6.06	25.8	16.9	57.3
4	Bra-5	0.2	8.3	32.4	16.7	50.9
5	Bra-Malj-2	0.3	13.7	28.1	20.8	51.1
6	Bra-Malj-7	0.6	52.3	48.0	15.3	36.7
Parameter		1	2	3		

O - oleanane; G - gammacerane; H - C<sub>30</sub> hopane



$17\beta(\text{H}), 21\alpha(\text{H}) \rightleftharpoons 17\alpha(\text{H}), 21\beta(\text{H})$  (0.05–0.10–0.15<sup>12</sup>). An exception was observed with the sample Sir-1 (parameter 3, Table IV).

The sterane maturation parameters (parameters 4 and 5, Table IV) showed that equilibrium reactions  $20R \rightleftharpoons 20S$  and  $14\alpha(\text{H})17\alpha(\text{H}) \rightleftharpoons 14\beta(\text{H})17\beta(\text{H})$  had not yet been attained. However, this observation is not unexpected, since it is known that these equilibria are attained only at high levels of maturity of the sedimentary organic matter ("oil generation peak"), corresponding to vitrinite reflectances in the range  $R_r = 0.80 - 0.90\%$ . Moreover, even for a number of crude oils the equilibria in these reactions were found not to have been attained.<sup>11</sup> On the other hand, equilibria in the terpane epimerization reactions are generally attained somewhat earlier ( $R_r = 0.60 - 0.70\%$ ), but, nevertheless, within the stage defined as "early oil generation".<sup>11</sup> Consequently, the organic matter of the sediments investigated in this paper seems to be in the "oil generation" phase.

Maturation parameters 3 and 5 from Table IV may also be used to corroborate the estimated maturity of the organic matter. Namely, it was shown earlier that the isomerization reactions moretane  $\rightarrow$  hopane (parameter 3, Table IV) and  $20R \rightarrow 20S$  steranes (parameter 5, Table IV), in addition to heat dependence, generally demonstrate a dependence on the geological time as well.<sup>13</sup> Investigation of a great number of crude oil and sediment samples showed that samples of pre-Tertiary age are characterized by moretane/hopane parameter values lower than 0.10, and by those of parameter  $20S/20S+20R$  C<sub>29</sub> steranes higher than 0.50. On the basis of parameters 3 and 5 from Table IV, as well as the corresponding boundary values, the sediments were classified into the group of Tertiary age sediments.

In spite of the fact that, based on triterpane and sterane analyses, all six samples were classified as sediments of relatively high maturity, differences among them were observed. Namely, on the basis of several parameters shown in Table IV the sample Bub-3 seemed to be of the lowest, and samples Bra-Malj-7 and Bra-1 of the highest maturity. Such a conclusion is based on the already mentioned parameters 2-5 (Table IV), but also on parameters  $T_s/T_s+T_m$  and C<sub>27</sub> dia/dia+ster (parameters 1 and 6, respectively, Table IV). In spite of the well-known fact that the isomerization processes  $T_m \rightarrow T_s$  (*i.e.*,  $17\alpha(\text{H}) - 22,29,30$ -trisorhopane  $\rightarrow 18\alpha(\text{H}) - 22,29,30$ -trisorneohopane), as well as the isomerization of regular steranes into diasteranes, are mainly influenced by mineral catalysts of the silicate type (acidic sites on clays) which are constituents of source rocks,<sup>14,15</sup> the high numerical values of these parameters also corroborate the classification of samples Bra-Malj-7 and Bra-1 into the group of sediments of highest maturity.

*Specific source parameters (n-alkanes, isoprenoids, triterpanes and steranes).* The distribution of *n*-alkanes (Fig. 2), in the form of "the most abundant *n*-alkanes" and/or CPI (parameters 1 and 2, Table III), served for the estimation of the organic matter maturity of the investigated sediments. However, the domination of odd-carbon atom number *n*-alkanes (CPI = 1.00–1.15), as well as the observed noticeable amount of higher members in the *n*-alkane homologous series (*c.f.*, the "second" maximum in the bimodal distribution, C<sub>21</sub>-C<sub>27</sub>), simultaneously suggests that terrestrial precursor biomass had obviously participated in the formation of the organic substance of the investigated sediments.<sup>10,11,16</sup> The

dominance of pristane over phytane in all six analyzed samples ( $\text{Pr/Phyt} = 1.60\text{--}6.78$ ; parameter 3, Table III) corroborated such an assumption.

In the distribution of triterpanes and steranes the abundances of oleanane and gammacerane (peaks marked O and G, Fig. 3), as well as the distribution of biolipid isomers such as  $\text{C}_{27}\text{--}\text{C}_{29}$   $14(\alpha)\text{H}$ ,  $17(\alpha)\text{H}$  ( $20R$ ) regular steranes<sup>10,11,16</sup> (peaks 2, 3 and 6, Fig. 3) are most often used for the estimation of the source of the organic matter. Numerical values of the corresponding parameters are shown in Table V.

Figure 3 as well as parameter 2 from Table V show that all the examined samples contained gammacerane. On the other hand, only two samples, Sir-1 and Bub-3, contained considerable amounts of oleanane (Fig. 3 and parameter 1, Table V). The small amounts of oleanane in most of the samples were unexpected since this parameter generally indicates the terrestrial origin of sedimentary organic matter and the corresponding crude oils.<sup>10,11</sup> However, the domination of  $\text{C}_{29}$  regular sterane in four out of the six analyzed samples (peak 6 in Fig. 3, and parameter 3 in Table V) corroborated the observed noticeable participation of terrestrial precursor biomass in the formation of the organic substance of the sediments.

#### *Correlation with crude oils*

Organic geochemical investigations of Drmno depression crude oils (oil-oil correlations) have been reported in several papers published during the last fifteen years.<sup>4-8</sup> The present paper is aimed at checking, for the first time, the eventual genetic relationship of some Drmno depression crude oils with the sediments of the same basin showing source rock characteristics. For this purpose the results of organic geochemical investigations of the Sirakovo, Bubušinac and Bradarac sediments were correlated with the corresponding results observed for crude oils originating from the Sirakovo and Bradarac oil-gas fields.<sup>8</sup> The important specific maturation and source parameters for both substrates were determined using identical analytical methods.

Based on bulk and specific correlation parameters (distribution of biological markers of *n*-alkane, isoprenoid alkane, triterpane and sterane types), the Sirakovo and Bradarac crude oils were shown to be of the same origin (except Bra-Malj-10), and were characterized by a significant participation of terrestrial precursor biomass. They were also shown to have been formed in the earlier stages of the catagenetic sequence of oil formation ( $R_r = 0.70\text{--}0.80\%$ ), and to have originated from source rocks of the Tertiary age.<sup>8</sup> Certain differences were observed only in the abundance of gammacerane and particularly oleanane. The most important relevant source and maturation parameters of the crude oils, which served as a basis for the correlations, are shown in Table VI.

TABLE VI. Molecular correlation parameters of the oil samples<sup>8</sup>

No.	Sample	Maturity and source parameters			Maturity parameters				Source parameters				
		Most abundant <i>n</i> -alkane	CPI	Pr/Phyt	22 <i>S</i> /22 <i>S</i> + 22 <i>R</i> C <sub>31</sub> hopanes	Moretane/ Hopane C <sub>30</sub>	ββ/ββ + αα C <sub>29</sub> steranes	20 <i>S</i> /20 <i>S</i> + 20 <i>R</i> C <sub>29</sub> steranes	O/H × 100	G/H × 100	αα <i>R</i> steranes		
											%C <sub>27</sub>	%C <sub>28</sub>	%C <sub>29</sub>
1	Sir-1	C <sub>19</sub>	1.03	1.18	0.59	0.12	0.57	0.48	7.4	6.7	35.1	19.1	45.8
2	Sir-2	C <sub>19</sub>	1.03	1.85	0.61	0.13	0.56	0.54	7.6	5.9	33.0	20.4	46.6
3	Sir-18	C <sub>19</sub>	1.03	1.85	0.61	0.11	0.56	0.46	5.7	15.4	32.7	18.4	48.9
4	Sir-19	C <sub>21</sub>	1.03	1.40	0.60	0.13	0.60	0.50	6.8	16.2	36.1	19.6	44.3
5	Sir-20	C <sub>21</sub>	1.04	1.25	0.61	0.11	0.58	0.47	6.0	16.5	34.5	19.5	46.0
6	Bra-Malj-2	C <sub>21</sub>	1.03	2.20	0.62	0.11	0.63	0.55	12.8	10.3	32.8	26.6	40.6
7	Bra-Malj-4	C <sub>25</sub>	1.06	1.17	0.61	0.13	0.39	0.44	1.9	18.8	37.0	16.5	46.5
8	Bra-Malj-5	C <sub>21</sub>	1.02	1.33	0.60	0.11	0.59	0.48	5.7	21.1	33.0	18.2	48.9
9	Bra-Malj-10	C <sub>23</sub>	1.07	1.00	0.60	0.11	0.57	0.45	3.0	9.8	20.0	28.2	51.8
	Parameter:	1	2	3	4	5	6	7	8	9	10		

O – oleanane; G – gammacerane; H – C<sub>30</sub> hopane

Comparison of the specific maturation parameters observed for the six sedimentary samples investigated in detail in this work (parameters 1 and 2, Table III; parameters 2–5, Table IV) with the corresponding crude oil maturation parameters (1, 2, 4–7, Table VI), suggested that the sedimentary organic matter and the crude oils were of similar maturity. The similarity with the examined crude oils concerned particularly the sedimentary samples Bra-1, Bra-5, Bra-Malj-2 and Bra-Malj-7. Furthermore, both the sedimentary organic matter and the crude oils could have been classified, according to maturity, into the “early oil generation” stage, corresponding to a vitrinite reflectance of  $R_r = 0.70\text{--}0.80\%$  (parameters 2–5, Table IV, for sediments; parameters 4–7, Table VI, for crude oils). Finally, the parameters  $C_{30}$  moretane/hopane and  $C_{29}$  steranes 20S/20S+20R (parameters 3 and 5, Table IV, for the sediments; parameters 5 and 7, Table VI, for the crude oils) suggest that both the sediments and the crude oils are of Tertiary age. As far as their origin is concerned, parameters such as “the most abundant *n*-alkanes”, CPI, Pr/Phyt and distribution of regular  $C_{27}\text{--}C_{29}$  steranes (parameters 1–3, Table III and parameter 3, Table V, for the sediments; parameters 1–3 and 10, Table VI, for the crude oils) suggest that terrestrial precursor biomass participated noticeably in the formation of both the sedimentary organic matter and the corresponding crude oils.

Hence, based on their maturity, age and the type of the organic matter, the core samples from Sirakovo, Bubušinac and Bradarac (Drmno depression) locations demonstrate a considerable similarity with the crude oils from the Sirakovo and Bradarac oil-gas fields of the same depression. Since according to bulk and specific organic geochemical parameters the mentioned sediments show evident source rock characteristics, a positive oil-source rock correlation is clearly demonstrated between the Drmno depression crude oils and sediments. This finding may be considered as one of the first steps in identifying the source rocks of the Drmno depression crude oil. Since the number of investigated sediments and crude oils is not considered to be fully representative of the whole depression, *i.e.*, of all potential source rocks and all discovered oil fields, respectively, further oil-source rock correlation studies, based on the same bulk and specific organic geochemical parameters, will be needed in order to be able to generalize these conclusions. Organic geochemical oil-source rock correlation studies of the Drmno depression basin should represent a basis for an ultimate organic geochemical/geological interpretation as well as further exploration studies.

#### CONCLUSIONS

Organic geochemical bulk parameters (*i.e.*, organic carbon, bitumen and hydrocarbon contents) for six out of eight sedimentary core samples from three Drmno depression boreholes (Sirakovo, Bubušinac and Bradarac) were found to possess all the criteria of source rock. Specific maturation parameters (*i.e.*, the most abundant *n*-alkane, CPI, as well as the ratios between thermodynamically more stable geo- and less stable bio-isomers of polycyclic alkanes of the triterpane and sterane types) suggest a relatively high maturity of the organic matter of these sediments, corresponding to the “oil generation” stage ( $R_r = 0.70\text{--}0.80\%$ ), as well as their origin in the Tertiary age. On the other hand, molecular

source parameters (*i.e.*, CPI, Pr/Phyt, distribution of C<sub>27</sub>-C<sub>29</sub> regular steranes) provide proof of the participation of terrestrial precursor biomass in the formation of these sediments.

Moreover, comparison of these observations with the corresponding characteristics of the Sirakovo and Bradarac (Drmno depression) crude oils suggest significant organic geochemical similarity. In this way, a positive organic geochemical oil-source rock correlation was observed for the first time with the Drmno depression. This finding will serve as a basis for further correlation and exploration studies, *i.e.*, it might be considered as a step leading to the ultimate organic geochemical/geological interpretation of this basin.

*Acknowledgements:* We thank the Alexander von Humboldt-Stiftung for supporting this research by giving a fellowship to the first author. We also thank Mrs. Angelika Vidal (Federal Institute for Geosciences and Natural Resources, Hannover, Germany) for technical help in the GC-MSD analyses. This work was supported in part by the Ministry of Science, Technologies and Development of the Republic of Serbia.

#### ИЗВОД

#### ТРАГАЊЕ ЗА ИЗВОРНИМ СТЕНАМА НАФТИ ДЕПРЕСИЈЕ ДРМНО (ЈУЖНИ ДЕО ПАНОНСКОГ БАСЕНА, СРБИЈА)

БРАНИМИР ЈОВАНЧИЋЕВИЋ<sup>1,2</sup>, HERMANN WEHNER<sup>3</sup>, GEORGE SCHEEDER<sup>3</sup>, КСЕНИЈА СТОЈАНОВИЋ<sup>2,4</sup>, АЛЕКСАНДРА ШАИНОВИЋ<sup>1</sup>, ОЛГА ЦВЕТКОВИЋ<sup>2</sup>, МАРКО ЕРЦЕГОВАЦ<sup>5</sup> и ДРАГОМИР ВИТОРОВИЋ<sup>2</sup>

<sup>1</sup>Хемијски факултет, Универзитет у Београду, б. бр. 158, Београд, <sup>2</sup>Центар за хемију ИХТМ, б. бр. 815, Београд, <sup>3</sup>Federal Institute for Geosciences and Natural Resources, P. O. Box 510153, Hannover, Germany, <sup>4</sup>Медицински факултет, Универзитет у Београду, Вишеградска 26, Београд и <sup>5</sup>Рударско-геолошки факултет, Универзитет у Београду, Бушина 7, Београд

Испитивани су седименти из бушотина које припадају локацијама Сираково, Бубушинац и Брадарак (депресија Дрмно). Примењене су органско-геохемијске методе (одређивање садржаја органског угљеника, битумена и угљоводоника, као и одређивање расподеле и обилности биолошких маркера типа *n*-алкана, изопреноидних алифатичних алкана, тритерпана и стерана) са циљем да се процени њихова нафтна потенцијалност. За шест узорака утврђен је висок степен матурираности органске супстанце, припадност "oil generation" фази ( $R_r = 0,70 - 0,80$  %), терцијарна старост и претежно терестријално порекло. Поређењем са сировим нафтама из већ откривених нафтних лежишта блиског локалитета (Сираково и Брадарак) утврђена је значајна сличност и према матурираности и према пореклу, на основу чега је између испитиваних узорака седимената и нафти, први пут када је у питању депресија Дрмно, дефинисана позитивна корелација нафта-изворна стена.

(Примљено 11. априла 2002)

#### REFERENCES

1. L. B. Magoon, W. G. Dow, *AAPG Memoir* **60** (1994) 3
2. J. M. Hunt, *Petroleum Geochemistry and Geology*, W. H. Freeman and Company, San Francisco, 1979
3. B. P. Tissot, D. H. Welte, *Petroleum Formation and Occurrence*, 2<sup>nd</sup> Ed., Springer-Verlag, Heidelberg, 1984
4. M. Šaban, B. Jovančević, S. Saračević, A. Hollerbach, D. Vitorović, *Org. Geochem.* **13** (1988) 325
5. M. Šaban, B. S. Jovančević, T. Glumičić, N. Dogović, *Rapid Communications in Mass Spectrometry* **4** (1990) 505
6. B. Jovančević, M. Šaban, T. Glumičić, E. Faber, D. Vitorović, *J. Serb. Chem. Soc.* **57** (1992) 391

7. B. Jovančičević, P. Polić, D. Vitorović, *J. Serb. Chem. Soc.* **63** (1998) 397
8. B. Jovančičević, H. Wehner, G. Scheeder, D. Plečaš, M. Ercegovac, D. Vitorović, *J. Serb. Chem. Soc.* **66** (2001) 297
9. P. Landais, J. Connan, *Bull. Cent. Rech. Explor.-Prod. Elf-Aquitaine (FRA)* **4** (1980) 709
10. R. P. Philp, *Fossil Fuel Biomarkers. Applications and Spectra*, Elsevier, Amsterdam, 1985
11. K. E. Peters, J. M. Moldowan, *The Biomarker Guide, Interpreting Molecular Fossils in Petroleum and Ancient Sediments*, Prentice Hall, New Jersey 1993
12. A. S. Mackenzie, R. L. Patience, J. R. Maxwell, M. Vandenbroucke, B. Durand, *Geochim. Cosmochim. Acta* **44** (1980) 1709
13. P. J. Grantham, *Org. Geochem.* **9** (1986) 293
14. W. K. Seifert, J. M. Moldowan, *Geochim. Cosmochim. Acta* **45** (1981) 783
15. I. Rubinstein, O. Sieskind, P. Albrecht, *J. Chem. Soc., Perkin Transactions I* (1975) 1833
16. D. Waples, *Geochemistry in Petroleum Exploration*, International Human Resources Development Corporation, Boston, 1985.



