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Organic geochemistry of Jurassic-Cretaceous source rocks and oil seeps from the profile across the Adriatic-Dinaric carbonate platform

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Abstract: Organic geochemical and stable isotope investigations were performed to provide an insight into the depositional environments, origin and maturity of the organic matter in Jurassic and Cretaceous formations of the External Dinarides. A correlation is made among various parameters acquired from Rock-Eval, gas chromatography-mass spectrometry data and isotope analysis of carbonates and kerogen. Three groups of samples were analysed. The first group includes source rocks derived from Lower Jurassic limestone and Upper Jurassic "Lemeš" beds, the second from Upper Cretaceous carbonates, while the third group comprises oil seeps genetically connected with Upper Cretaceous source rocks. The carbon and oxygen isotopic ratios of all the carbonates display marine isotopic composition. Rock-Eval data and maturity parameter values derived from biomarkers define the organic matter of the Upper Cretaceous carbonates as Type I-S and Type II-S kerogen at the low stage of maturity up to entering the oil-generating window. Lower and Upper Jurassic source rocks contain early mature Type III mixed with Type IV organic matter. All Jurassic and Cretaceous potential source rock extracts show similarity in triterpane and sterane distribution. The hopane and sterane distribution pattern of the studied oil seeps correspond to those from Cretaceous source rocks. The difference between Cretaceous oil seeps and potential source rock extracts was found in the intensity and distribution of *n*-alkanes, as well as in the abundance of asphaltenes which is connected to their biodegradation stage. In the Jurassic and Cretaceous potential source rock samples a mixture of aromatic hydrocarbons with their alkyl derivatives were indicated, whereas in the oil seep samples extracts only asphaltenes were observed.

Key words: Jurassic, Cretaceous, Adriatic-Dinaric carbonate platform, biomarkers, potential source rock, oil seep.

Introduction

The Adriatic-Dinaric carbonate platform (ADCP) (Fig. 1), developed during the Alpine evolution of the Dinaric parts of the Tethys (Pamić 1993), is composed of up to 8 km thick carbonate and shallow-water carbonate-evaporite sequences (Fig. 2).

Potential and effective source rocks in the ADCP include: (1) Carboniferous mudstones and shales and Middle Permian laminated limestones and shales; (2) Middle Triassic marls, shales and dolomicrites; (3) Upper Jurassic "Lemeš" beds — sediments deposited in a deeper bay of Tethys, represented by thin-bedded to platy limestones interbedded with cherts, in some places with rich ammonite assemblages (Furlani 1910; Chorowicz & Geyssant 1972) and (4) Lower and Upper Cretaceous carbonates. Some Lower and Middle Eocene limestone formations contain immature or early mature source rocks (Pamić 1993). Oil seeps in the ADCP were correlated to source rocks of various stratigraphic levels ranging from the Middle Triassic to the Upper Cretaceous (Moldowan et al. 1992; Jerinić et al. 1994).

This paper presents data on Rock-Eval pyrolysis, the stable isotopic composition of carbonates ($\delta^{13}C$, $\delta^{18}O$) and kerogen ($\delta^{13}C$), as well as the molecular distribution of saturated and aromatic compounds from the Jurassic and Cretaceous potential source rocks and oil seeps, collected along the 400 km long profile in ADCP (Fig. 1).

The aim of this paper is geochemical characterization of the depositional environments and maturation history of the organic matter (OM) in carbonate deposits of the ADCP during the Jurassic and Cretaceous Periods.

Geological setting

The studied area extended along the Croatian coast-line, including Hvar and Brač Islands, from Metković (43.05°N, 17.65°E) to Senj (44.99°N, 14.90°E) (Fig. 1).

The Dinarides form a complex fold, thrust and imbricate belt which developed along the northeastern margin of the Adriatic (Dewey et al. 1973) or Apulia microplate (Ricou et al. 1986; Dercourt et al. 1993). The Dinarides, which can be traced along-strike for about 700 km, merge in the north-west with the Southern Alps and in the south-east with the Hellenides (Pamić et al. 1998). The largest part of the Central Di-

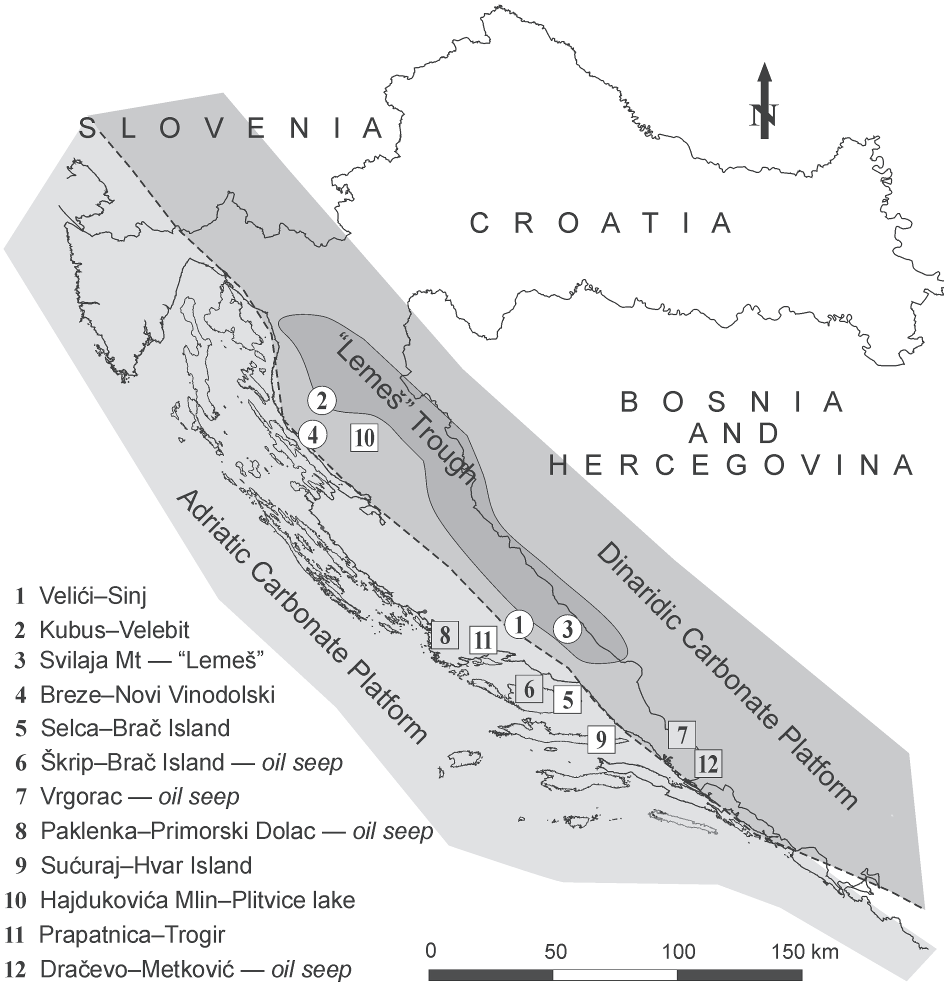

Fig. 1. Map of the Adriatic-Dinaric carbonate platform with marked localities of sampled potential source rocks and oil seeps. (□ — Cretaceous potential source rock; ■ — Cretaceous oil seep; ○ — Jurassic potential source rock).

narides, despite their complex fold, thrust and imbricate structure, is characterized by a regular zonal pattern in the spatial distribution of characteristic Mesozoic–Paleogene tectonostratigraphic units developed during the Alpine evolution in the Dinaric parts of the Tethys (Pamić et al. 1998). From the south-west to the north-east, that is from the Adriatic microplate towards the Pannonian Basin, the following tectonostratigraphic units, originating in different Tethyan environments, can be distinguished: (1) Adriatic-Dinaric carbonate platform (ADCP) — the External Dinarides (Fig. 1); (2) carbonate–clastic sedimentary rocks, in some places with flysch signatures, of the passive continental margin of the Dinaric Tethys; (3) ophiolites associated with genetically related sedimentary formations (the Tethyan open-ocean realm); (4) sedimentary, igneous and metamorphic units of the Euroasian active continental margin; (5) Paleozoic–Triassic nappes, which are thrust onto the Internal Dinarides units; their frontal parts directly overlying the northeastern margin of the ADCP. The tectonostratigraphic units 2 to 4 define the Internal Dinarides.

From the Liassic period to the Middle Eocene, the ADCP was an isolated platform surrounded by the Tethys Ocean. The final disintegration of the ADCP started in the Senonian with regional tectonic movements resulting in uplift, partial regression and flysch deposition (Pamić et al. 1998). Tangential tectonics reduced transversally the area of the ADCP to the about 700 km long and 50–250 km wide thrust belt commonly named the External Dinarides (Velić et al. 2001). From the Late Triassic to the Middle Eocene, for almost 150 million years, the ADCP was a relatively stable, shallow-marine platform; global sea-level changes and synsedimentary tectonics influenced both platforms periodically but not contemporaneously, generating about 5 to 8 km thick carbonate sequences. The carbonate rocks and carbonate-evaporite shallow-water deposits in the ADCP include effective and potential source rocks, oil seeps, and ore deposits associated with organic matter of different ages starting from the Carboniferous and continuing up to the Paleogene.

Samples and methods

Sampling and geochemical analysis

A total of 13 Jurassic and 23 Cretaceous samples of potential source rocks and oil seeps were collected from fresh rock surface exposures at 12 localities along a profile in the ADCP (Fig. 1). The studied Jurassic and Cretaceous potential source rock samples are represented by carbonates which contain autochthonous organic matter, kerogen and associated bitu-

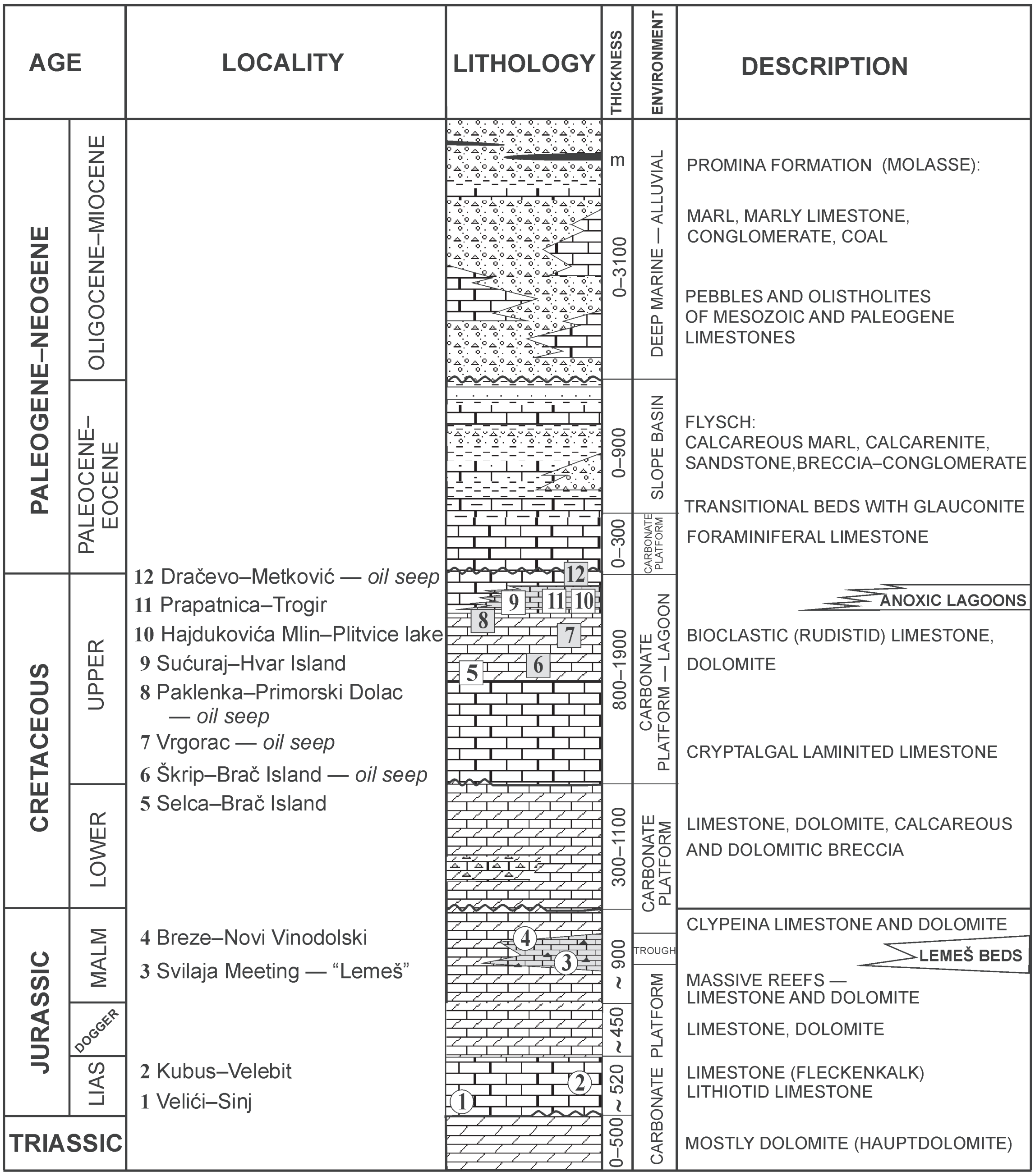

Fig. 2. Stratigraphic column of Cretaceous and Jurassic carbonate deposits in the Adriatic-Dinaric carbonate platform. (☐ — Cretaceous potential source rock; ■ — Cretaceous oil seep; ○ — Jurassic potential source rock).

men. The Cretaceous oil seep samples are represented by carbonates with pores, fissures and cavities filled with migrated bitumen.

Samples were chosen based on the literature and knowledge accumulated at the Croatian Oil Company INA in order to represent carbonate formations of different depositional environments developed during the Jurassic and Cretaceous Periods.

To remove superficial contamination from handling and weathered material, the rock samples were cut into slabs with a water cooled saw, washed with deionized water and distilled ethanol and dried at 50 °C for 48 h. The cleaned samples were milled in an agate ball-mill, and analysed for distribution of hydrocarbons and isotopic composition of carbonates and kerogen according to the procedure described by Spangenberg & Macko (1998).

All the samples were subjected to TOC and Rock-Eval analysis in order to investigate basic potential source rock properties and select a reduced number of samples for further detailed analysis. Rock powders were submitted to total organic carbon (TOC) and Rock-Eval analysis at the Humble Geochemical Services Division (Humble, TX 77347).

An aliquot of selected samples (150–200 g) was extracted with dichloromethane (DCM) (200 ml) for 6 days, with a change of solvent after the first 48 h in the case of samples with low TOC (< 1 %), or Soxhlet extracted (ca. 50 g of sample) for 72 h with DCM in the case of samples with high TOC (> 1 %). The extractable organic matter (EOM) was desulphurized with activated Cu (24 h, room temperature). The extracts were fractionated by silica-alumina liquid chromatography into saturated, aromatic and polar compounds. Prior to liquid chromatography asphaltenes were precipitated from oil seeps and potential source rock extracts with TOC > 2 wt. % with hexane at room temperature. Chemical characterization of saturated and aromatic hydrocarbons was performed with an Agilent Technologies 6890 GC coupled to an Agilent Technologies 5973 quadrupole mass selective detector (gas chromatography-mass spectrometry — GC/MS) using a HP-ULTRA-2 fused-silica capillary column (50 m×0.20 mm i.d. coated with 0.11 μm cross-linked 5%-diphenyl-95%-dimethyl siloxane as stationary phase) and He as carrier gas. The samples were injected splitless at 280 °C. After an initial period of 1 min at 70 °C, the column was heated to 280 °C at 5 °C/min followed by an isothermal period of 20 min. The MS was operated in the electron impact mode at 70 eV, source temperature of 250 °C, emission current of 1 mA and multiple-ion detection with a mass range from 50 to 700 amu. Compound identifications are based on comparison of standards, GC retention time, mass spectrometric fragmentation patterns and literature mass spectra.

Isotope analysis of kerogen

The insoluble organic matter (kerogen) was obtained by acidification of the extracted sample with 6 N HCl for 24 h and HF for 48 h. The oven-dried residues (consisting mostly of kerogen, a little quartz and clay) were analysed for carbon isotopic composition by using a Carlo Erba 1108 EA connected to a Finnigan MAT Delta S IRMS via a Conflo II split interface (EA/IRMS). The isotopic composition is reported in delta (δ) notation as the per mil (‰) deviation relative to the Vienna Pee Dee Belemnite (V-PDB). The reproducibility of the EA/IRMS analyses, assessed by replicate analyses of a laboratory standard (glycine (–25.8‰), urea (–43.1‰ $\delta^{13}C$) and USGS24 (–15.9‰ $\delta^{13}C$)), was better than 0.1‰.

Isotope analysis of carbonates

Thirty-six carbonates were separated for stable isotope analyses. Extraction of CO_2 from the carbonates was done by reaction with 100% phosphoric acid (4 h, 50 °C) in a closed reaction vessel (McCrea 1950). Carbon and oxygen isotopic compositions were measured via dual inlet on a Thermoquest/Finnigan Delta S mass spectrometer. The results were corrected for carbonate-phosphoric acid fractionation using the factors of 1.010600 for dolomite (Rosenbaum & Sheppard 1986) and 1.009311 for calcite (Friedman & O'Neil 1977). The stable C and O isotope ratios are reported in delta (δ) notation as the per mil (‰) deviation relative to the V-PDB international standard. Analytical uncertainty, assessed by replicate analyses of the laboratory standard (Carrara marble, $\delta^{13}C = +2.1‰$ and $\delta^{18}O = +29.4‰$), is less than ±0.05‰ for $\delta^{13}C$ and ±0.1‰ for $\delta^{18}O$.

Results

Total organic carbon and Rock-Eval pyrolysis

The total organic carbon (TOC) values of Lower and Upper Jurassic carbonates range from 0.04 to 0.13 % (Table 2). For Upper Cretaceous and Cretaceous-Paleocene samples higher values were recorded, up to 3.1 % and 6.0 %, respectively (Table 3).

The Rock-Eval pyrolysis data (S_1, S_2, and S_3) are used to assess the temperature of maximum hydrocarbon generation (T_{max}) and to determine the hydrogen (HI), oxygen (OI) and production (PI) indices for chemical characterization of primary in situ sedimentary organic matter (Peters 1986). The results of Rock-Eval pyrolysis are presented in Table 2 and Table 3, conventional HI vs. OI (Fig. 3) and HI vs. T_{max} (Fig. 4) plot.

Acyclic hydrocarbons

In gas chromatograms of all fractions of saturated hydrocarbons which did not undergo severe biodegradation, normal alkanes and acyclic isoprenoids pristane (Pr) and phytane (Ph) are the main resolvable compounds.

Table 1: Stable carbon and oxygen isotope data of the analysed carbonates.

Point	Sample	Locality	Age	$\delta^{13}C$ (‰,V-PDB)	$\delta^{18}O$ (‰,V-PDB)
1	HR-017	Velić near Sinj, Jabuka quarry	Lower Jurassic	0.6	–4.3
	HR-018			–1.0	–4.6
	HR-019			–0.4	–4.2
2	HR-052A	Kubus, Velebit		1.7	–4.4
	HR-052B			1.3	–5.0
3	HR-004	Svilaja Mt	Upper Jurassic	1.0	–2.2
	HR-005			0.0	–1.8
	HR-006	Svilaja Mt		–3.9	–4.0
	HR-007A	Lemeš beds		–3.1	–4.0
	HR-007B			–3.2	–1.2
4	HR-072	Breze, Novi Vinodolski		3.7	–2.6
	HR-073			4.2	–2.8
	HR-074			4.3	–2.1
5	HR-036	Selca, Brač Island	Upper Cretaceous	2.4	–1.0
	HR-037			2.3	–1.5
7*	HR-020	Vrgorac		1.3	–1.5
	HR-021			–2.1	–2.6
	HR-022			1.2	–2.5
8*	HR-049	Paklenka, Primorski Dolac		3.0	–3.7
	HR-050			3.6	–2.9
	HR-051			1.3	–4.5
9	HR-031	Sućuraj, Hvar Island		0.9	2.6
	HR-032			1.0	3.2
	HR-033			1.1	4.2
	HR-034			–0.7	3.3
	HR-035			0.3	3.8
10	HR-001	Hajdukovića Mlin, Plitvica lake		–5.1	–1.1
	HR-002			–10.1	–0.8
	HR-003			–5.6	–1.5
11	HR-043	Prapatnica, Trogir		3.5	–1.5
	HR-044			1.8	–2.0
	HR-045			1.9	–3.4
12*	HR-028A	Dračevo, Metković	Cretaceous Paleocene	0.8	1.4
	HR-028B			0.9	1.6
	HR-029			0.9	1.7
	HR-030			0.8	2.7

* — *oil seep*

Table 2: The Rock-Eval pyrolysis parameters of the analysed Jurassic potential source rock samples.

Point	Sample	Locality	Age	Lithology	TOC (%)	T_{max} (°C)	S_1 (mg HC/g rock)	S_2 (mg HC/g rock)	S_3 (mg CO_2/g rock)	HI	OI	PI
1	HR-017	Velić near Sinj,	Lower	limestone	0.05	–	0.02	0.00	0.15	0	315	1.00
	HR-018	Jabuka querry	Jurassic		0.06	–	0.04	0.26	0.84	365	1178	0.13
	HR-019				0.04	–	0.01	0.00	0.08	0	189	1.00
2	HR-052A	Kubus, Velebit		limestone	0.13	322	0.01	0.02	0.22	83	596	0.33
	HR-052B				0.05	427	0.02	0.06	0.43	–	–	0.25
3	HR-004	Svilaja Mt	Upper		0.07	–	0.02	0.00	0.16	0	236	1.00
	HR-005		Jurassic		0.10	431	0.02	0.02	0.11	200	–	0.50
	HR-006	Svilaja Mt,		Lemeš	0.09	–	–	–	–	0	–	–
	HR-007A	Lemeš beds		beds	0.06	–	0	0	–	0	283	–
	HR-007B				0.07	–	0	0	–	0	288	–
4	HR-072	Breze,		limestone	0.10	–	–	–	–	–	–	–
	HR-073	Novi Vinodolski			0.05	–	–	–	–	–	–	–
	HR-074				0.06	–	–	–	–	–	–	–

TOC (%) — total organic carbon; Tmax — temperature of maximum production of pyrolysed hydrocarbons; S_1, S_2 — mg of hydrocarbons per gram of rock; S_3 — mg of carbon dioxide per gram of rock; OI — oxygen index (OI=S3×100/TOC); HI — hydrogen index (HI=S2×100/TOC); PI — production index (PI=S1/(S1+S2)); Note: "–" — indicates not measured or meaningless ratio.

Table 3: The Rock-Eval pyrolysis parameters of the analysed Cretaceous potential source rock and oil seep samples.

Point	Locality	Sample	Age	Lithology	TOC (%)	T_{max} (°C)	S_1 (mg HC/g rock)	S_2 (mg HC/g rock)	S_3 (mg CO_2/g rock)	HI	OI	PI
5	HR-036A	Selca,	Upper	limestone	2.74	392	0.81	9.08	0.33	296	11	0.08
	HR-036B	Brač Island	Cretaceous		1.34	398	0.35	3.26	0.33	255	26	0.10
6*	HR-038A	Škrip.		limestone	1.39	404	0.16	2.24	0.05	361	8	0.07
	HR-038B	Brač Island			1.50	425	0.49	4.67	0.23	313	15	0.09
	HR-040				0.37	379	0.08	0.10	0.27	34	93	0.44
	HR-041				2.54	425	1.82	16.65	0.18	737	8	0.10
	HR-042				3.07	425	7.52	54.02	0.59	730	8	0.12
7*	HR-020	Vrgorac		limestone	0.11	370	0.00	0.01	0.00	9	0	0.00
	HR-021				0.85	407	0.08	0.53	0.69	62	81	0.13
8*	HR-049	Paklenka,		limestone	0.02	392	0.01	0.04	0.08	224	447	0.20
	HR-050A	Primorski Dolac			0.01	389	0	0.04	0.01	400	100	0.00
	HR-050B				0.01	–	0	0.04	0.00	100	0	0.00
9	HR-031	Sućuraj,		limestone	0.37	431	0.20	1.17	0.21	688	124	0.15
	HR-032	Hvar Island			0.38	432	0.18	1.10	0.33	688	206	0.14
	HR-033				0.40	430	0.19	1.05	0.30	656	188	0.15
	HR-035A				0.62	422	0.22	2.35	0.10	534	23	0.09
	HR-035B				0.31	428	0.08	1.12	0.16	437	67	0.07
10	HR-001	Hajdukovića Mlin		stromatolitic	0.39	423	0.14	1.78	0.18	685	69	0.07
	HR-002	Plitvica lake		dolomite	0.31	424	0.11	1.25	0.21	543	91	0.08
	HR-003				0.96	434	0.37	4.70	0.28	540	32	0.07
11	HR-043	Prapatnica,		limestone	0.04	–	0	0	0.13	0	363	0.01
	HR-044	Trogir			0.17	420	0.01	1.00	0.30	588	176	0.01
	HR-045				0.04	–	0.01	0	0.17	0	456	1.00
12*	HR-028	Dračevo,	Cretaceous	limestone	6.00	424	3.53	41.95	0.32	699	5	0.08
	HR-029	Metković	-Paleocene		2.95	422	0.48	17.18	0.56	767	150	0.03
	HR-030				5.84	427	2.53	42.35	0.32	698	23	0.06

* — oil seep; TOC (%) — total organic carbon; Tmax — temperature of maximum production of pyrolysed hydrocarbons; S_1, S_2 — mg of hydrocarbons per gram of rock; S_3 — mg of carbon dioxide per gram of rock; OI— oxygen index (OI=S3×100/TOC); HI — hydrogen index (HI=S2×100/TOC); PI — production index (PI=S1/(S1+S2)); Note: "–" — indicates not measured or meaningless ratio.

In Jurassic potential source rock extracts the *n*-alkanes are easily noticed in C_{12}–C_{31} range, maximized at *n*-C_{16-18} (Fig. 5). Phytane is generally dominant over pristane with Pr/Ph ratio values between 0.59 and 0.82. The only exception is the sample from Velić (Lower Jurassic) with Pr/Ph = 2.34. The ratios between acyclic isoprenoids (Pr and Ph) and their neighbouring *n*-alkanes *n*-C_{17} and *n*-C_{18} range from 0.24 to 0.92 for Pr/*n*-C_{17} ratio and from 0.46 to 1.09 for Ph/*n*-C_{18} ratio.

In Upper Cretaceous potential source rock extracts the *n*-alkanes are found to be present in the C_{11}–C_{25} range. In samples from Sućuraj, Hvar Island and Selca, Brač Island *n*-alkanes exhibit a bimodal distribution maximizing at *n*-C_{13} and *n*-C_{18-19}, whereas in samples from Hajdukovića Mlin and Prapatnica (Fig. 5) *n*-alkanes maximize at *n*-C_{21} and *n*-C_{18}, respectively. The Pr/*n*-C_{17} (0.59–2.38) and Ph/*n*-C_{18} (0.78–3.10) ratio values are higher then for Jurassic samples with Pr/Ph ratios ranging from 0.32 to 0.99.

In oil seep extracts from Vrgorac (Upper Cretaceous), Paklenka (Upper Cretaceous) and Dračevo (Cretaceous-Paleocene) no *n*-alkanes were identified. Only oil seep samples

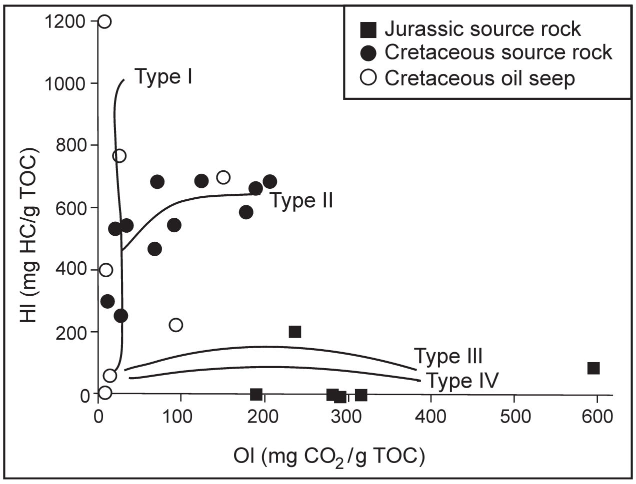

Fig. 3. Hydrogen index (HI) vs. oxygen index (OI) plot of the analysed samples.

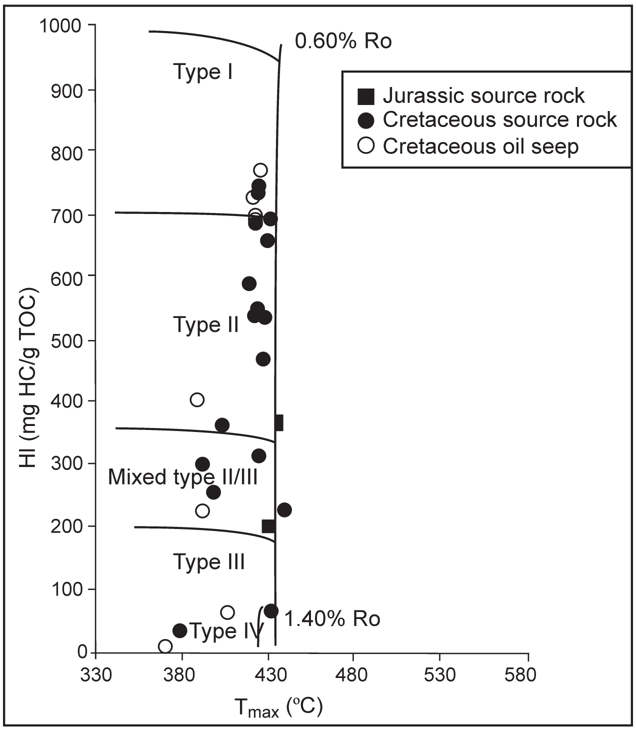

Fig. 4. Hydrogen index (HI) vs. T_{max} plot of the analysed samples.

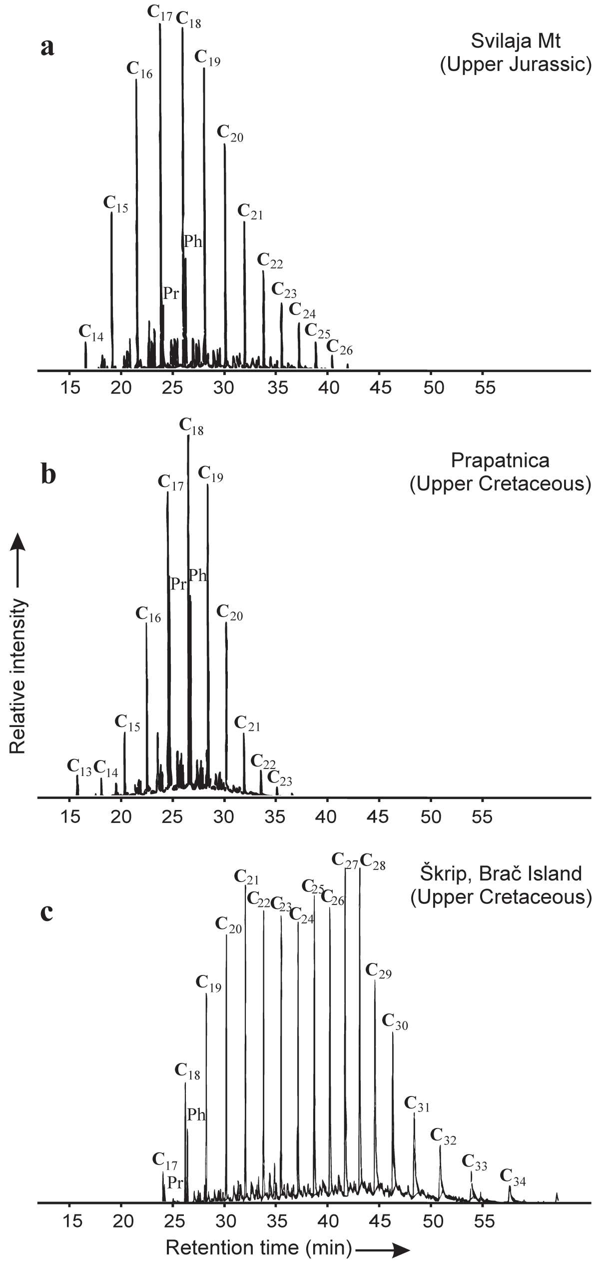

Fig. 5. Ion chromatograms showing the distribution of alkanes (*m/z* 71) in potential source rock (**a**,**b**) and oil seep (**c**) samples. Peak identifications: $\mathbf{C_x}$ = *n*-alkanes with x carbon number; **Pr** = pristane; **Ph** = phytane.

from Škrip, Brač Island (Upper Cretaceous) contained *n*-alkanes displaying a bimodal distribution in the range of C_{16}–C_{35} with a major mode centred at *n*-C_{21} and a secondary mode centered at *n*-C_{27} (Fig. 5).

Cyclic hydrocarbons

In all potential source rock extracts, triterpanes ($m/z = 191$) (Fig. 6) and steranes ($m/z = 217$) (Fig. 7) show a similar distribution pattern. The *m/z* 191 mass chromatograms are dominated by three groups of pentacyclic terpanes: Tm, norhopanes and hopanes (Fig. 6). The tricyclic terpanes are found only in source rock samples from Velić (Lower Jurassic) and Svilaja Mt (Upper Jurassic) and two oil seep samples from Vrgorac (Upper Cretaceous) and Dračevo, Metković (Cretaceous–Paleocene). When present, tricyclic terpanes are found in the C_{19}–C_{24} range, maximized at $C_{23.}$ Among pentacyclic terpanes C_{31} and C_{32} 17α(H)-homohopanes are found and characterized with predominance of 22S over 22R epimers. The concentrations of homohopanes decrease with an increase of their molecular mass which is characteristic for suboxic conditions during OM deposition (Peters & Moldowan 1991). The applied lower final GC oven temperature (280 °C) resulted in peak broadening and height lowering, causing the difference to the results published by Moldowan et al. (1992). All Jurassic samples have C_{29} hopane as the most abundant hopane, while in Upper Cretaceous potential source rock extracts C_{30} hopane is dominant (Fig. 6).

Regarding regular steranes predominantly composed of C_{27} and C_{29} homologs (Fig. 7), Jurassic extracts are characterized by dominant content of C_{27}, while in Cretaceous extracts C_{29} regular sterane is the most abundant (Fig. 7). In potential source rock extracts from the Velić (Lower Jurassic) and Svilaja Mt (Upper Jurassic) (Fig. 7) a remarkable amount of pregnanes is found.

The Cretaceous oil seeps can be divided into two subgroups based on their hopane and sterane distribution pattern (Fig. 6 and Fig. 7). Hopane (*m/z* 191) mass fragmentograms of oil seep extracts from Vrgorac (Upper Cretaceous), Škrip, Brač Island (Upper Cretaceous) and Dračevo, Metković (Cretaceous-Paleogene) are characterized by C_{27}–C_{30} 17α(H)-hopanes maximized at C_{29} and presence of C_{31} and C_{32} 17α(H)-homohopanes with predominance of 22S diastereomers. Regular steranes in samples from Vrgorac (Upper Cretaceous) are below the detection limit. In oil seep extracts from Paklenka (Upper Cretaceous) hopane distribution is characterized by C_{27}–C_{30} 17α(H)-hopanes maximized at C_{30} and again with C_{31} and C_{32} 17α(H)-homohopanes 22S diastereomers predominating. Sterane distribution in all oil seep samples is similar to those of Cretaceous potential source rocks comprising predominantly C_{27} and C_{29} homologs maximized at C_{29}. All oil seep extracts have one feature in common, they all contain pregnanes (Fig. 7).

Aromatic hydrocarbons

The aromatic hydrocarbon fractions of all potential source rocks are dominated by alkyl derivatives of naphthalene, phenantrene and dibenzothiophene. The methylphenantrene index (MPI-1) values obtained from GC/MS data of aromatic hydrocarbons are listed in Table 4. In oil seep extracts only asphaltenes were observed.

Isotopic composition of carbonates and kerogen

The $\delta^{13}C$ values of Lower Jurassic carbonates range between −1.0 ‰ and 1.7 ‰ V-PDB (Table 1). The $\delta^{13}C$ values of Upper Jurassic carbonates display higher scatter ranging between −3.9 ‰ and 4.3 ‰ V-PDB. The whole set of Jurassic $\delta^{13}C$ isotopic values falls within those documented for marine limestones (Marshall 1992; Mahboubil et al. 2002).

For Upper Cretaceous carbonates $\delta^{13}C$ values range from −2 ‰ to 3.6 ‰ V-PDB. The $\delta^{13}C$ values from −2.5 ‰ to 2.5‰ have been interpreted as characteristic of Cretaceous marine limestones and dolomitic limestones (Hudson 1977; Moss & Tucker 1995), although relatively higher $\delta^{13}C$ values were also documented for marine carbonates (Anderson & Arthur 1983). The significant scatter of these values, up to 5.6 ‰, likely reflects the primary compositional variability in the $\delta^{13}C$ of organic matter (i.e. variable contribution from marine plankton, bacteria and algae) and variations in the productivity

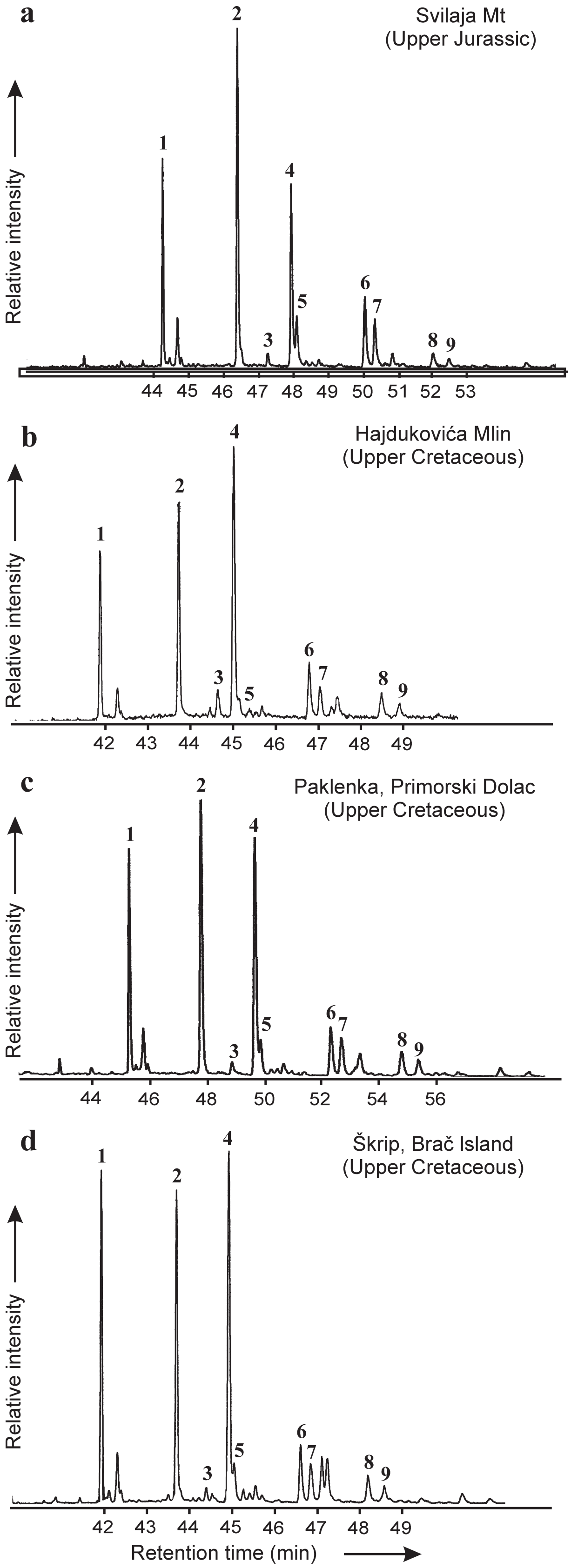

Fig. 6. Ion chromatograms showing the distribution of hopanes (*m/z* 191) in potential source rock (**a**,**b**) and oil seep (**c**,**d**) samples. Identification of the labeled compounds is given in Table 6.

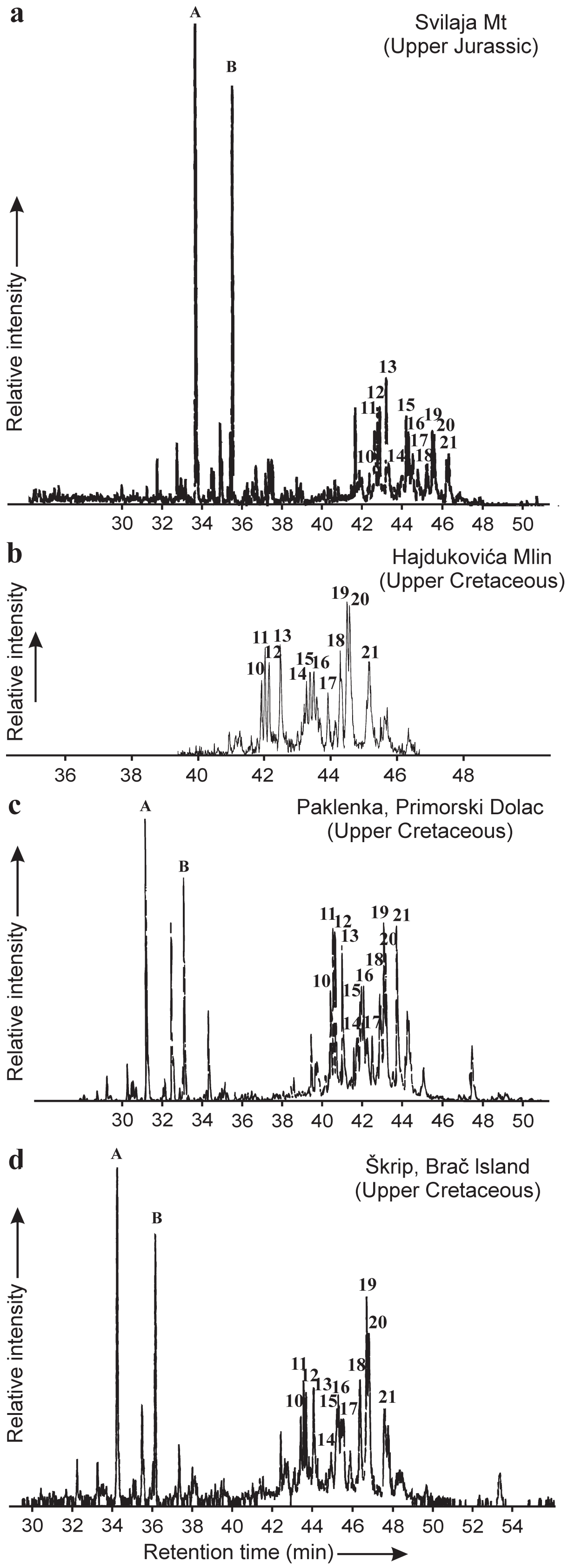

Fig. 7. Ion chromatograms showing the distribution of steranes (*m/z* 217) in potential source rock (**a**,**b**) and oil seep (**c**,**d**) samples. Identification of the labeled compounds is given in Table 6.

rate during deposition (Hollander & McKenzie 1991; Fogel & Cifuentes 1993).

However, samples from Hajdukovića Mlin, Plitvice Lake (Upper Cretaceous) which display values between –10 ‰ and –5 ‰ were also recorded. The ^{13}C-depleted dolomite interbedded with shale from Hajdukovića Mlin, Plitvice lake most likely indicate a contribution from biogenic carbon sources.

The $\delta^{18}O$ values of the Lower Jurassic samples show a higher scattering than the $\delta^{13}C$ values, from –4.0 ‰ to –1.2 ‰ V-PDB (Table 1). The $\delta^{18}O$ values of Upper Jurassic carbonates cover a narrower range, from –5 ‰ to –4.2 ‰ V-PDB.

The oxygen isotope behaviour of the Cretaceous samples exhibits a considerable scatter with $\delta^{18}O$ values ranging from –4.5 ‰ to 4.2 ‰ V-PDB. Positive $\delta^{18}O$ values are characteristic of samples from Dračevo, Metković (Cretaceous-Paleocene) and Sućuraj, Hvar Island (Upper Cretaceous). Since these values are too high to have formed from normal sea water these heavy carbonates must have been precipitated from fluids enriched in O^{18}, probably as a result of evaporation (Gill et al. 1995).

The $\delta^{13}C$ values of kerogens and asphaltenes from Upper Cretaceous carbonates (Table 5) vary between –26.2 ‰ and –20.4 ‰ V-PDB and –26.9 ‰ and 22.3 ‰ V-PDB, respectively, whereas the analysed Jurassic carbonates display slightly lower values for kerogens in the range –27.9 ‰ to –24.0 ‰ V-PDB. The significant scatter of these values is most likely due to changes in the source of organic matter during deposition.

Discussion

By combining geochemical and isotope analyses of selected potential source rock and oil seep samples, especially the correlation of certain biomarker compounds, we have attempted to determine the depositional environments, origin and maturity of the OM from the Jurassic and Cretaceous carbonates of the ADCP.

The source and deposition of environment indicators

The $\delta^{13}C$ and $\delta^{18}O$ values of Lower and Upper Jurassic, as well as Upper Cretaceous carbonates fall within the range characteristic of marine limestone and dolomitic limestone. The distinctive scatter of obtained values reflects variability in the primary composition of organic matter (algae and/or bacteria) in the Jurassic and Cretaceous sedimentary environments.

The low organic matter content (TOC < 0.13 %) is a general characteristic of the Jurassic sediments. Higher TOC values were detected in Upper Cretaceous (up to 3.1 %) and Cretaceous-Paleocene (up to 6.0 %) sediments. The wide range of obtained values (Table 2 and Table 3) is indicative of facies variability of investigated Jurassic and Cretaceous potential source rocks.

The pristane/phytane (Pr/Ph) ratio is an indicator of the redox potential of the depositional environment (Didyk et al. 1978; Chappe et al. 1982), affected by source input, maturity

Table 4: Distribution of molecular parameters determined from GC/MS analyses.

Point	Sample	Locality	Age	Pr/Ph	Pr/n-C_{17}	Ph/n-C_{18}	hopanes C_{31} 22S/(22S+22R)	steranes C_{27} 20S/(20S+20R)	steranes C_{29} 20S/(20S+20R)	MPI 1	Rc%
1	HR-019	Velić near Sinj	Lower Jurrasic	2.34	0.84	0.74	0.56	–	–	0.23	0.54
2	HR-052B	Kubus, Velebit		0.82	1.34	1.09	–	–	–	–	–
3	HR-004	Svilaja Mt	Upper Jurassic	0.59	0.24	0.47	0.57	0.32	0.68	0.33	0.60
	HR-005			0.65	0.33	0.57	0.52	0.32	0.58	–	–
	HR-006	Svilaja Mt, Lemeš beds		0.59	0.64	1.01	–	–	–	0.22	0.53
4	HR-073	Breze, Novi Vinodolski		0.82	0.91	0.81	–	–	–	–	–
	HR-074			0.69	0.92	0.87	–	–	–	–	–
5	HR-037	Selca, Brač Island	Upper Cretaceous	0.84	1.36	1.02	–	–	–	2.31	0.52
6*	HR-038A	Škrip, Brač Island		0.43	0.59	0.80	0.53	0.39			
	HR-040			0.32	0.78	0.78	–	–	–	–	–
7*	HR-020	Vrgorac		–	–	–	0.56	–	–	–	–
8*	HR-046	Paklenka, Primorski Dolac		–	–	–	0.56	0.41	0.48		
9	HR-034	Sućuraj, Hvar Island		0.85	1.09	0.88	0.59	–	–	–	–
10	HR-001	Hajdukovića Mlin		0.59	0.39	3.11	0.61	0.34	0.48	–	–
11	HR-044	Prapatnica, Trogir		0.95	1.03	0.82	–	–	–	–	–
	HR-045			0.99	1.09	0.79	–	–	–	–	–
12*	HR-029	Dračevo, Metković	Cretaceous-Paleocene	–	–	–	0.59	–	–	–	–

* — oil seep; Pr/Ph — Pristane (Pr) to Phytane (Ph) ratio; Pr/n-C_{17} — ratio between Pristane and neighbouring n-alkane C_{17}; Ph/n-C_{18} — ratio between Phytane and neighbouring n-alkane C_{18}; C_{31} 22S/(22S+22R) — ratio of C_{31} hopane; MPI 1 — Methylphenantrene Index (MPI 1=1.5×(2-MP+3-MP)/(P+1-MP+9-MP); P = phenantrene; MP = methylphenantrene); Rc (%) — calculated vitrinite reflectance (Rc(%)= 0.40+0.60×MPI 1); Note: "–" — indicates not measured or meaningless ratio.

Table 5: Stable carbon isotope data of kerogen and asphaltenes from the analysed samples.

Point	Sample	Locality	Age	$\delta^{13}C$	STD
kerogen					
1	HR-019	Velić	Lower Jurassic	–26.0	0.0
3	HR-004	Svilaja Mt	Upper Jurassic	–24.0	0.5
	HR-005			–27.9	0.0
asphaltens					
5	HR-037	Selca	Upper Cretaceous	–20.9	0.1
6*	HR-038	Škrip		–23.8	0.0
	HR-041			–22.3	0.2
	HR-042			–26.3	0.2
	HR-042			–22.8	0.1
7*	HR-021	Vrgorac		–23.4	0.2
8*	HR-050	Paklenka		–20.4	0.0
11	HR-045	Prapatnica		–23.9	0.1
12*	HR-028B	Dračevo	Cretaceous–Paleocene	–26.9	0.1

* — oil seep

and salinity (Goosens et al. 1984; ten Haven et al. 1987). The low Pr/Ph ratio (0.32–0.99) found in all samples is considered to reflect the carbonate lithology and low TOC content (Hughes et al. 1995). The only exceptions are the samples from the Velić (Lower Jurassic) with a Pr/Ph ratio of 2.34 suggesting a different depositional environment.

The distribution of n-alkanes with predominance in the C_{14}–C_{19} range indicates a dominant marine algal source of OM for all Cretaceous and Jurassic potential source rocks. The absence of n-alkanes in oil seep extracts from Vrgorac (Upper Cretaceous), Paklenka (Upper Cretaceous) and Dračevo (Cretaceous–Paleocene) can be attributed to biodegradation of migrating hydrocarbons in these samples (Peters & Moldowan 1993).

Table 6: Assignation of compounds in the *m/z* 191 and *m/z* 217 mass fragmentograms shown in Fig. 6 and Fig. 7.

Peak number	Compound assignation
m/z 191	
1	17α(H)-22,29, 30-trinorhopane (Tm);
2	C_{29} — 17 α(H), 21β(H)-30-norhopane;
3	C_{29} — 17β(H), 21α(H)-30-norhopane;
4	C_{30} — 17α(H), 21β(H)-hopane;
5	C_{30} — 17β(H), 21α(H)-hopane;
6	C_{31} — (22S) 17α(H), 21β(H)-29-homohopane;
7	C_{31} — (22R) 17α(H), 21β(H)-29-homohopane;
8	C_{32} — (22S) 17α(H), 21β(H)-29-bishomohopane;
9	C_{32} — (22R) 17β(H), 21α(H)-29-bishomohopane;
m/z 217	
A	pregnane;
B	homopregnane;
10	C_{27} — 5α(H), 14α(H), 17α(H) (20S) sterane;
11	C_{27} — 5α(H), 14β(H), 17β(H) (20R) sterane;
12	C_{27} — 5α(H), 14β(H), 17β(H) (20S) sterane;
13	C_{27} — 5α(H), 14α(H), 17α(H) (20R) sterane;
14	C_{28} — 5α(H), 14α(H), 17α(H) (20S) sterane;
15	C_{28} — 5α(H), 14β(H), 17β(H) (20R) sterane;
16	C_{28} — 5α(H), 14β(H), 17β(H) (20S) sterane;
17	C_{28} — 5α(H), 14α(H), 17α(H) (20R) sterane;
18	C_{29} — 5α(H), 14α(H), 17α(H) (20S) sterane;
19	C_{29} — 5α(H), 14β(H), 17β(H) (20R) sterane;
20	C_{29} — 5α(H), 14β(H), 17β(H) (20S) sterane;
21	C_{29} — 5α(H), 14α(H), 17α(H) (20R) sterane;

The composition of biomarker compounds, especially steroid and triterpenoid derivatives, are of special interest because these compounds reflect the depositional environments, origin and diagenetic/maturation history of sedimentary organic matter (Peters & Moldowan 1993; Peters et al. 2005). The relative concentration of steranes and terpanes reflects the eukaryotic and prokaryotic contributions to the organic matter of sediments (Peters et al. 2005). The higher contents of hopane over sterane in all the studied samples, Cretaceous and Jurassic, are indicative of organic matter deposited within the carbonate platform (Marynowski et al. 2000).

The relative distribution of C_{31} and C_{32} homohopanes can imply redox potential during and after deposition of carbonates (Peters et al. 2005). Presence of short-chain tricyclic terpanes is indicative of a bacterial contribution to the organic matter (Marynowski et al. 2000). High abundance of C_{23} homolog is indicative of a predominantly marine input (Peters et al. 2005).

In the *m/z* 217 mass fragmentogram of Jurassic extracts, C_{27} steranes predominate over C_{28} and C_{29} steranes due to a high contribution of algae to the organic source (Peters & Moldowan 1993). The relative abundance of C_{29} steranes in Cretaceous samples with 20S/20S+20R ratios of isomerization around 0.47 (equilibrium values=0.55) indicates a relatively low thermal maturity of samples (Yangming et al. 2005).

The overall higher proportion of pregnane relative to the sterane content can be related to backbone rearrangement catalysed by clay minerals (van Kaam-Peters et al. 1998). Diasterane to sterane ratios do not correlate with clay content but depend on the amount of clay relative to the amount of organic matter present (van Kaam-Peters et al. 1998). During early diagenesis high clay/TOC ratios may favour backbone rearrangement over reduction of steranes.

The high abundance of dibenzothiophenes in the investigated samples is considered to be the result of a sulphurization process of planktonic lipids and carbohydrates. The sulphurization of algal-derived biolipids is suggested to be an important mechanism for the selective preservation of these molecules during early diagenesis (Kohnen et al. 1990; Russel et al. 2000).

Thermal maturity

Plots of HI vs. OI as a van Krevelen-type diagram (Fig. 3) and HI vs. T_{max} (Fig. 4) were used for identification of the type of organic matter, thermal maturity and its level of secondary alteration (Kenig et al. 1994).

According to the hydrogen and oxygen indices (HI = 34–767, OI = 5–206), the organic matter of the Upper Cretaceous samples plot close to the maturation pathways typical of Type I and Type II oil prone kerogen (Fig. 3 and Fig. 4). This is in agreement with the biomarker composition data of these rocks showing that their OM consists predominantly of algal material. The low HI values obtained for oil seep samples from Škrip, Brač Island (Upper Cretaceous) and low HI and OI values for oil seep samples from Vrgorac (Upper Cretaceous), although characteristic for Type III and Type IV OM, reflect alteration of samples due to oxidation. Since relatively high abundance of benzothiophene compounds is indicated in the analysed Upper Cretaceous source rock and oil seep samples, implying high organic sulphur concentration, kerogen types might be additionally marked by S; namely Type I-S and Type II-S. The Upper and Lower Jurassic samples, according to HI (0–385) and OI (236–1178) values, plot along the thermal evolution line characteristic for Type III and Type IV organic matter (Fig. 3 and Fig. 4).

The C_{31} homohopanes 22S/(22S + 22R) ratio of the studied samples ranges between 0.52 and 0.60 (Table 4), which is below or equal to the equilibrium end point value of about 0.57–0.60 (Peters et al. 2005), indicating that these samples are near or at the beginning of the oil-generating window (Peters et al. 2005).

The MPI-1 values differ between the Jurassic and Cretaceous samples (Table 4) corresponding to a maturity range of approximately 0.44–0.55% R_c and 0.55–0.60% R_c, respectively, implying thermal immaturity or low maturity of Upper Cretaceous organic matter and the beginning of the oil-generating window for Jurassic organic matter. These low maturity levels are in agreement with the low geothermal gradients observed in that area (Cota & Baric 1998).

Since all studied kerogens contain reasonable amounts of the organically bound sulphur, as reflected in the presence of benzothiophenes, they might be expected to release hydrocarbons at relatively low maturity stage. In sulphur rich kerogen, weak S–C bonds require significantly lower activation energy during cracking, and therefore hydrocarbon generation occurs at lower maturity levels (Orr 1974; Baric et al. 1988; Cota & Baric 1998). The low T_{max} (379 to 433 °C) values observed are, therefore, probably related to the type of kerogen rather than to immaturity of the organic matter.

The data presented here are based on a rather limited number of samples and cannot be used as representative of all the processes influencing geological organic matter in the ADCP during Jurassic and Cretaceous Periods. Therefore, further more detailed research is required in order to obtain better insight into depositional environments, origin and maturation history of geological organic matter in the Jurassic and Cretaceous formations of the External Dinarides.

Conclusion

The distinctive scatter of carbon and oxygen isotope values in the studied samples is indicative of variation in the sources of the organic matter. The Rock-Eval pyrolysis and biomarker composition data characterize Upper Cretaceous organic matter in the studied potential source rock samples as Type I-S oil prone and Type II-S oil and gas prone kerogen at the immature to early mature oil-generating level. The organic matter from the Lower and Upper Jurassic potential source rocks is characterized as early mature Type III and Type IV kerogen. Low Pr/Ph ratio values in all the analysed samples mainly reflect suboxic to anoxic OM depositional environments. The biomarkers distribution indicates the predominantly algal and bacterial marine organic matter input with rare terrestrial organic matter. The sterane and triterpane maturity parameters confirm Upper Cretaceous potential source rocks as thermally immature, that is approaching or just entering the oil-generating window (corresponding to 0.45–0.52 % R_c) and Lower and Upper Jurassic potential source rocks as marginally mature with R_c values from 0.53 to 0.60 %. The high diasterane to sterane ratios found in most of the studied samples reflect the backbone rearrangement process catalysed by clay minerals. The presence of dibenzothiophenes, as dominant compounds in most of the aromatic fractions, reflects the sulphurization process of algal-derived biolipids.

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