East Herzegovina is located in the southeast part of Bosnia and Herzegovina and geologically belongs to the External Dinarides (Hrvatović, 2006; Fig. 1). The area investigated is in the High Karst zone of the Adriatic Carbonate Platform that extends along the Adriatic seashore from Italy to Albania and is one of the largest Mesozoic carbonate platforms in the Perimediterranean region (Juračić and Palinkaš, 2004; Vlahović et al., 2005).

There has been interest for petroleum exploration in the area for a long time and several oil companies undertook modest geological and geochemical prospecting. The main exploration risk in the area, in terms of the petroleum system, is uncertainty about the existence of efficient seals. There has been no drilling for oil and gas so far, but there is a well-known bitumen seep east of Ljubinje (Mišljen, Fig. 1C – on the left border) in the Cretaceous limestone. The Mišljen occurrence has been moderately exploited by mining in a dozen excavated holes (wells), about 15 m deep, in the middle of the 20th century.

Documented petroleum source rocks in the broader area are organic matter-rich limestones, deposited in the intra-platform basins during the Late Triassic and Early Jurassic (Novelli and Demaisano, 1988; Bosellini et al., 1999; Masseti et al., 2012), as well as Cretaceous limestones and dolomites (Velaj, 2011; Prifti and Muska, 2013; Cazzini et al., 2015). Strong tectonic deformation from Oligocene to Pleistocene led to the formation of structural traps, such as anticlinal belts in Albania: Berati, Kurveleshi and Cika (Velaj, 2011; Cazzini et al., 2015). Petroleum deposits in the area are found at relative depths of more than 5,000 m (Velaj, 2011).
The main petroleum reservoirs are Triassic and Jurassic dolomites and Cretaceous to Eocene carbonates (Albania, Italy, Croatia; Cazzini et al., 2015). The seals (caprocks) are Triassic evaporites (Kotenev, 2015) and Palaeogene shales (Velaj, 2011; Cazzini et al., 2015).

Figure 2 shows lithostratigraphic column of the Adriatic Carbonate Platform in East Herzegovina with main elements of a possible petroleum system.

The Adriatic Carbonate Platform has high thermal conductivity; the heat flow varies between 20 and 50 mW/m², and the geothermal gradient is very low - usually 10–20 °C/km (Cota and Barić, 1998; Carella, 1999; Frasheri et al., 2009; Miošić et al., 2010). According to the available data, the geothermal gradient in the territory of East Herzegovina is also very low, as in the surrounding countries (Italy, Croatia and Albania). In such conditions, the onset of the transformation...
of kerogen to petroleum ("oil window"), that is usually at temperatures 110–120 °C (Philippi, 1965; Cooles et al., 1986), it could have taken place at depths greater than normal.

The thermal maturation profile and depth of the oil window in East Herzegovina have not been evaluated so far. There are no published data either on thermal maturity or on possible source rocks in the area. Since one of the first steps in petroleum exploration is to determine possible source rocks, their thermal maturity and burial history, the present study focused on the investigation of organic matter type and thermal maturity of outcropping sedimentary rocks that are possible source rocks in the regional petroleum system. Thermal maturity was studied by means of Rock-Eval pyrolysis and vitrinite reflectance measurements.

GEOLOGICAL SETTING

The Dinarides are located in the central area of the Mediterranean system of orogens (Fig. 1A). Their evolution was determined by the collisional processes of large-scale continental units (either belonging to Europe-derived or Adriatic-derived components) and the domains of the Neotethys Ocean (Pamić et al., 1998; Robertson et al., 2009; Van Unen et al., 2019; Schmid et al., 2020). The study area encompasses the SE part of the external Dinarides (Fig. 1B), which represents the fold-and-thrust belt of several units of Adriatic affinity, i.e., the Pre-Karst, High Karst, and Budva-Cukali, and the Dalmatian units (Fig. 1B; Schmid et al., 2020). In more detail, this study covers the Mesozoic–Cenozoic sedimentary succession of the High Karst Unit, which is thrust towards the southwest over the Dalmatian Unit (also partially over the Budva-Cukali Unit), while it is overthrust by the Pre-Karst Unit towards the NE (Fig. 1D). In a palaeogeographic sense, this region belonged to the realm of the Adriatic Carbonate Platform (Vlahović et al., 2005). The Adriatic Carbonate Platform passed through several stages of development during its long and eventful history, starting with the platform basement, epeiric platform, and isolated platform, etc. (Vlahović et al., 2005) and reflected in a variety of deposited rock types that can be observed in East Herzegovina (Fig. 1C).
The oldest stratigraphic unit in the area is the mixed siliciclastic-carbonate succession of the Late Triassic, exposed in the core of the Lastva Anticline (Fig. 1C). These sediments are represented by Carnian limestones, dolomites, conglomerates, sandstones, and thin coal beds, followed by Norian and Rhaetian dolomites (Hrvatović, 2006).

The Late Triassic dolomites and the Early Jurassic lithoid limestones within the same structure (Natević and Petrović, 1970; Vujisić, 1975) constitute the exposed basement of the Adriatic Carbonate Platform, similar to other localities in the Dinarides (Vlahović et al., 2005). The Middle and Late Jurassic strata are composed of oolithic limestones, reef and lagoonal shallow-water limestones, and dolomites (Natević and Petrović, 1970; Mirković, et al., 1974). Similar rocks of Cretaceous age cover larger parts of the study area (Mojčević and Laušević, 1965; Natević and Petrović, 1970). The Middle Jurassic to Late Cretaceous sedimentary cycle marks the main carbonate production period of the Platform, reflected in large quantities of carbonate rocks of predominantly shallow-water type (of up to 3.5 to 5 km in thickness; Vlahović et al., 2005). The end of the Adriatic Carbonate Platform was a result of regional emersion at the end of the Late Cretaceous, which was due to the collisional processes and uplift of the Dinarides (Van Unen et al., 2019). This led to the deposition of tectonically controlled turbidites near Nevesinje (Eocene carbonates and siliciclastics similar to the Promina Beds; Vlahović et al., 2012; Fig. 1C), while carbonate sedimentation continued only sporadically. The youngest sediments in East Herzegovina belong to the intramountain system of lake deposition during Neogene times (i.e., in the Gacko Basin; Fig. 1C; Mandić et al., 2011).

MATERIALS AND METHODS

Samples

Twenty representative outcrop samples from twelve locations in East Herzegovina, between Nevesinje and Gacko in the north and Trebinje and Lastva in the south, were collected for the study (Fig. 1C). The main sampling criteria were to include all outcropping stratigraphic units in the area from the oldest (Triassic) to the youngest (Miocene), focusing on sedimentary rocks, rich in organic matter. For the thermal maturation study, the preferred organic matter type was coaly, since it is more reliable for vitrinite reflectance measurements. Whenever possible, roadcut sites were selected for sampling, in order to minimize the effect of weathering on the organic matter (Petsch et al., 2000).

Samples of the oldest, Upper Triassic, rocks (Carnian) were collected from two adjacent localities in the Lastva Anticline: Klobuk, and Župa (Fig. 1; Table 1). Samples were

| Sample No. | Age | Locality | TOC | S1 | S2 | S3 | HI | T max |
|------------|-----|----------|-----|----|----|----|----|-------|
| 1          | T   | Klobuk   | 3.74| 0.06| 14.00| 2.34| 374 | 437   |
| 2          | T   | Klobuk   | 2.81| 0.05| 9.35 | 3.17| 333 | 439   |
| 3          | T   | Župa     | 0.83| 0.08| 4.19 | 0.36| 505 | 424   |
| 4          | T   | Župa     | 1.05| 0.08| 5.62 | 0.42| 535 | 421   |
| 5          | J   | Necvijeće| 2.07| 0.02| 0.70 | 3.00| 34  | 434   |
| 6          | J   | Avtovac  | 1.23| 0.07| 1.92 | 0.68| 156 | 424   |
| 7          | J   | Avtovac  | 1.11| 0.03| 1.80 | 0.80| 162 | 424   |
| 8          | K   | Bogdašići| 0.79| 0.21| 5.93 | 0.19| 751 | 411   |
| 9          | K   | Bogdašići| 1.36| 0.27| 8.97 | 0.51| 660 | 414   |
| 10         | K   | Bogdašići| 0.94| 0.31| 5.89 | 0.43| 627 | 420   |
| 11         | K   | Pridvorci| 4.47| 1.70| 35.76| 0.96| 800 | 394   |
| 12         | K   | Pridvorci| 5.87| 2.19| 47.04| 1.46| 801 | 400   |
| 13         | K   | Todorići| 0.85| 0.21| 6.95 | 0.33| 818 | 406   |
| 14         | K   | Todorići| 3.08| 1.81| 25.46| 0.90| 827 | 397   |
| 15         | K   | M. Gruda | 0.90| 0.17| 6.58 | 0.40| 731 | 424   |
| 16         | K   | M. Gruda | 0.45| 0.33| 2.81 | 0.31| 624 | 423   |
| 17         | K   | Bugovina | 1.93| 0.54| 14.68| 0.76| 761 | 415   |
| 18         | K   | Čepelica | 0.93| 0.28| 5.64 | 0.33| 606 | 423   |
| 19         | E   | Kljen    | 3.37| 0.02| 1.26 | 3.44| 37  | 433   |
| 20         | M   | Gacko    | 51.03| 2.41| 48.97| 34.00| 96  | 411   |

Table 1

Main output parameters of the Rock-Eval pyrolysis of the samples analysed.

T – Triassic; J – Jurassic, K – Cretaceous, E – Eocene, M – Miocene; TOC – total organic carbon (wt.%), HC – hydrocarbons, S1 – free HC (mg HC/g rock) released at 300 ºC; S2 – HC generated during pyrolysis (mg HC/g rock) from 300 to 650 ºC; S3 – amount of CO₂ generated from oxygenated functional groups (mg CO₂/g rock); HI – hydrogen index = (S2 x 100)/TOC; mg HC/g TOC; T max – temperature of peak HC generation (ºC).

N. ALEKSIĆ ET AL.
taken from the black, layered, carbonaceous marls and shales that occur in a sequence of dark grey limestones.

Samples of Lower Jurassic rocks were taken from two distant locations, where a series of bituminous limestones and marls was observed: Necvijeće, in the south (east of Trebinje), and Avtovac, in the north (east of Gacko). Samples are represented by limestone and marl with carbonaceous organic matter. Sample 5 was taken from the Lower to Middle Jurassic marls and limestones at the Avtovac locality (Fig. 1C). These rocks belong to a different unit (the Pre-Karst), but they were also included in the thermal maturity study, as they represent the base of the Adriatic Carbonate Platform (Vlahović et al., 2005).

The Cretaceous sedimentary rocks, prevalent in the area, were sampled at six localities, where they outcrop. All samples belong to Turonian sequences. Samples from the Middle Turonian were taken close to Bileća (Bogdašići, in the north, and Cepelica, in the south), and near Trebinje (Pridvorci and Todorići, in the south), and are all from thin-layered brown limestone, with a significant, visible content of organic matter (resembling microbial mats). As a good example, the Pridvorci site consists of thin-bedded, laminated limestones, rich in organic matter (Fig. 3), with a bed thickness of 1–6 cm. The predominant laminated mudstones are made up of alternating laminae of carbonate composition and laminae of organic matter. The carbonate laminae are often bent and broken (Fig. 3, red arrow indicating “broken lamina”) and recrystallized to microsparry calcite. The other type of limestone at the outcrop are biomicrites (wackstones), rich in organic matter. The upper Turonian rocks were sampled near Trebinje (Bugovina, in the south) and between Bileća and Gacko (Meka Gruda), in outcrops with layers of grey limestone with organic-rich laminae.

The Eocene sedimentary rocks were sampled in the west, near Nevesinje (Kljen in the southeast), in a series consisting of brown and grey to dark grey, layered limestone banks, interbedded with carbonaceous marl. The sample was taken from the carbonaceous marl.

The youngest sediments (Middle Miocene) were sampled near the Gacko coal mine. A piece of clean coal was taken from the main coal seam, formed on top of light grey marl. The Gacko main coal seam has a thickness of 9 to 24 m (Mirković et al., 1974) and it was deposited during the Langhian, about 15.5 Ma ago (Mandić et al., 2011).

All samples collected were washed, dried at room temperature, crushed, and pulverized. The crushed fraction (<2 mm) was used for preparing petrographic “whole rock” specimens (polished block), and the pulverized rock (0.10–0.25 mm) was used for Rock-Eval pyrolysis.

**Methods**

In this study, common analytical methods were used: Rock-Eval pyrolysis and organic petrographic investigations, including vitrinite reflectance. All investigations were carried out at the University of Belgrade, Faculty of Mining and Geology, in the Department of Economic Geology.

Rock-Eval pyrolysis was performed using a Rock-Eval 6, Standard analyser. About 100 mg (25 mg for coal sample) of the pulverized fraction (0.10–0.25 mm) were used, along with IFP 160000 calibration standard. The entire process was managed by “RockSix” software (Vinci Technologies). For ten representative Mesozoic samples, the extraction of bitumen was also performed in order to test Rock-Eval parameters before and after extraction. The usual dichloromethane/methanol azeotrope (88:12) solvent was used for 32 hours (Schwarzbauer and Jovančićević, 2020).

Pyrolysis is the process of thermal decomposition of kerogen in the absence of oxygen and is particularly important for source-rock evaluation. Rock-Eval pyrolysis (Espitalié et al., 1977, 1985; Lafargue et al., 1998) has many output parameters that provide useful information not only on the quantity and quality of organic matter (total organic carbon – TOC, mg hydrocarbons/g rock, etc.), but also on thermal maturity (Peters and Cassa, 1994; Behar et al., 2001; Dembicki, 2017; Bechtel et al., 2018).

For maturity determination, the main parameter used is $T_{\text{max}}$, the temperature corresponding to the peak of hydrocarbon generation. $T_{\text{max}}$ values, expressed in °C, generally increase with increasing thermal maturity. However, the exact values that correspond to the oil window depend on the kerogen composition and other factors (Espitalié and
Bordenave, 1993; Yang and Horsfield, 2020). $T_{\text{max}}$ values for the onset of oil generation vary with the type of kerogen but are generally in the range of 430–445 °C (Espitalié and Bordenave, 1993; McCarthy et al., 2011). The onset of significant gas generation is associated with a $T_{\text{max}}$ value of about 460 °C. Because kerogen type I has a very narrow temperature range for the oil window, $T_{\text{max}}$ is not a reliable maturity indicator for sediments with kerogen type I. $T_{\text{max}}$ is also not suitable for source rocks containing kerogens that generate petroleum at a lower level of maturity (Tegelaar and Noble, 1994; Hunt, 1996; Yang and Horsfield, 2020) or for low-TOC sediments (TOC <0.4%; Peters and Nelson, 1994; Peters and Nelson, 1992). Along with $T_{\text{max}}$, the production index (PI), the ratio between free and total hydrocarbons $[S1/(S1+S2)]$, also is usually employed as a maturity indicator, where PI > 0.1 indicates sufficient thermal maturity. However, since there is significant reduction and alteration of free HC in weathered samples, the PI was not a suitable maturity indicator for the outcropping sedimentary rocks analysed in this study.

An organic petrographic investigation including vitrinite reflectance was done with a Zeiss Axios Imager 2 microscope with an oil immersion objective 50x in incident non-polarized light at a wavelength of 546 nm (Taylor et al., 1998) and in incident fluorescence-mode illumination. A digital camera and Fossil software were used for the acquisition of reflectance measurements. The results of vitrinite reflectance are presented as mean random reflectance values (% $R_r$), the number of measurements on a representative population, and the standard deviation. Depending on the abundance of autochthonous vitrinite/huminite, 14–456 points per sample were measured. Standard deviations ranged from 0.038 in a coal sample to 0.061 in a sample with the finest-grained dispersed particles.

Vitrinite reflectance, as a well standardized method, is a key diagnostic tool for assessing thermal maturity (ICCP, 1963–1975, 1998; Mukhopadhyay, 1994; ISO 7404-5, 2009; McCarthy et al., 2011; Hackley et al., 2015). Vitrinite is the main coal maceral, formed through the thermal alteration of the remains of higher plants, and dispersed vitrinite particles are present in almost all sedimentary rocks from Devonian times onwards, i.e., since the evolution of the vascular plants. Vitrinite reflectance is one of the most widely used and accepted maturity indices, as it reliably covers the entire maturity range and is the only standardized method for the determination of thermal maturity determination. As the temperature increases, huminite (the immature equivalent of vitrinite; < 0.50% $R_r$), and later vitrinite (with a higher rank; > 0.50% $R_r$), undergo complex, irreversible aromatization reactions that increase the reflectance (Van Gijzel, 1981; Peters and Casa, 1994; Peters et al., 2005), which therefore represent a kind of a geothermometer.

The mean random vitrinite reflectance (%$R_r$) in oil immersion, often referred to as %Ro (“o” for oil), which corresponds to the oil window, varies with the type of organic matter, but also with the heating rate (Welte, 1989). The onset of oil generation mostly corresponds to reflectance values of 0.50–0.60% $R_r$ (Tissot and Welte, 1978; Sweeney et al., 1990; Kostić, 2000, 2012). However, there are also source rocks containing kerogen that generates petroleum at lower or higher values, up to ± 0.15% $R_r$ (Cook, 1982; Welte, 1989; Espitalié and Bordenave, 1993; Tegelaar and Noble, 1994; Hunt, 1996; Pickel et al., 2017). Empirical conversions between vitrinite reflectance and $T_{\text{max}}$ were published by Teichmüller and Durand (1983) and Tissot et al. (1987).

### RESULTS AND INTERPRETATION

**Rock-Eval pyrolysis analyses**

The main output parameters of Rock-Eval pyrolysis, including maturity parameter $T_{\text{max},*}$ are shown in Tables 1, 2 and Figure 4.

The total organic carbon (TOC, wt.%) content is over 0.45% in all samples analysed. The Triassic samples (No. 1–4)

| Locality | Age* | Sample | TOC (%) | $S_1$ (mg HC/g rock) | $S_2$ (mg HC/g rock) | HI (mg HC/g TOC) | $T_{\text{max}}$ (°C) | $\Delta T_{\text{max}}$ (°C) |
|----------|------|--------|---------|---------------------|---------------------|-----------------|-----------------------|--------------------------|
| Klobuk   | T    | 1      | 3.74    | 3.63                | 0.06                | 0.05            | 14.00                 | 13.55                    | 374                      | 373                      | 437 | 437 | 0 |
| Župa     | T    | 3      | 0.83    | 0.72                | 0.08                | 0.02            | 4.19                  | 3.36                     | 505                      | 467                      | 424 | 426 | 2 |
| Avtovac  | J    | 6      | 1.23    | 1.20                | 0.07                | 0.01            | 1.92                  | 1.88                     | 156                      | 156                      | 424 | 424 | 0 |
| Bogdašići | K   | 8      | 0.79    | 0.65                | 0.21                | 0.03            | 5.93                  | 4.63                     | 751                      | 712                      | 411 | 414 | 3 |
| Bogdašići | K   | 10     | 0.94    | 0.80                | 0.31                | 0.05            | 5.89                  | 4.69                     | 627                      | 586                      | 420 | 421 | 1 |
| Pridvorci| K    | 11     | 4.47    | 3.60                | 1.70                | 1.08            | 35.76                 | 28.82                    | 800                      | 801                      | 394 | 396 | 2 |
| Todorici | K    | 13     | 0.85    | 0.75                | 0.21                | 0.10            | 6.95                  | 5.97                     | 818                      | 796                      | 406 | 410 | 4 |
| M. Gruda | K    | 15     | 0.90    | 0.84                | 0.17                | 0.07            | 6.58                  | 5.98                     | 731                      | 712                      | 424 | 424 | 0 |
| M. Gruda | K    | 16     | 0.45    | 0.24                | 0.33                | 0.03            | 2.81                  | 1.35                     | 624                      | 562                      | 423 | 429 | 6 |
| Ćepelica | K    | 18     | 0.93    | 0.86                | 0.28                | 0.07            | 5.64                  | 4.94                     | 606                      | 574                      | 423 | 423 | 0 |

* T – Triassic; J – Jurassic, K – Cretaceous, E – Eocene, M – Miocene
have TOC between 0.83% and 3.74%, with HI values ranging between 333 and 535 mg HC/g TOC. The Jurassic samples (No. 5–7) have 1.11–2.07% TOC, with rather low HI values (34–162 mg HC/g TOC). The samples from Cretaceous rocks (No. 8–18) show the highest petroleum potential in terms of HI (606–827 mg HC/g TOC) and TOC (up to 5.87%). The Eocene sample (No. 19) has a high TOC (3.37%), but a very low HI (37 mg HC/g TOC), and the Miocene sample (No. 20) is coal (TOC > 50%) with HI of 96 mg HC/g TOC. According to the T_max values, most samples correspond to an immature stage of thermal maturation (< 430–435 °C).

On the basis of the plot of HI vs. T_max (Fig. 4), the kerogen type is estimated for all samples analysed. According to the diagram, the Triassic samples are characterized by type II kerogen, the Jurassic samples by type III kerogen, while the kerogen of the Cretaceous sample corresponds to types I and II. The organic matter of the Eocene sample analysed contains type III kerogen, as does the Miocene coal sample from Gacko.

Ten selected Mesozoic samples (two Triassic, one Jurassic and seven Cretaceous) from eight localities were also analysed after the extraction of free hydrocarbons, in order to check the effect of bitumen. The results revealed an increase in T_max after extraction of up to 6 °C (∆T_max; Tab. 2).

Organic petrography and vitrinite reflectance

The results of organic petrographic investigations and vitrinite reflectance measurements are shown in Figures 5–7 and in Tables 3 and 4. Figure 5 shows photomicrographs of characteristic Triassic, Jurassic, Cretaceous and Eocene samples in non-polarized reflected light (on the left), with corresponding vitrinite reflectance measurement values (on the right). Maceral composition at all localities analysed is given qualitatively in Table 3. Bitumen and framboidal pyrite were observed in all samples from Triassic to Eocene, but mostly in those from the Jurassic and Cretaceous sedimentary rocks.

Observations under the blue light (fluorescence mode) showed that the organic matter of the Triassic samples contains not only vitrinite, but also liptinite (marine alginites and bituminite). The observation of Dinoflagellate cysts, some Tasmanites remains and liptodetrinite (Fig. 6) indicate high bioproductivity and good preservation potential.

### Table 3

| Locality | Age | Maceral composition |
|----------|-----|---------------------|
| Klobuk   | T   | L>V>I               |
| Župa     | T   | L>>V>I              |
| Necvijeće | J   | I>L>V               |
| Avtovac  | J   | V>>L>I              |
| Bogdašići | K   | Bit+Lam             |
| Pridvorci | K   | Bit+Lam             |
| Todorići | K   | Bit+Lam>>V+I        |
| M. Gruda | K   | Bit                 |
| Bugovina | K   | Bit+Lam>>V+I        |
| Čepelica | K   | Bit                 |
| Kljen    | E   | V>>I>L              |
| Gacko    | M   | V>>I>L              |

### Table 4

| Locality | Age    | Mean reflectance (% Rr) | Number of measurements | Standard deviation |
|----------|--------|-------------------------|------------------------|--------------------|
| Klobuk   | Triassic | 0.78                    | 73                     | 0.057              |
| Župa     | Triassic | 0.66                    | 35                     | 0.052              |
| Avtovac  | Jurassic | 0.41                    | 169                    | 0.054              |
| Todorići | Cretaceous | 0.54                  | 14                     | 0.037              |
| Bugovina | Cretaceous | 0.53                  | 61                     | 0.061              |
| Kljen    | Eocene  | 0.38                    | 456                    | 0.041              |
| Gacko    | Miocene | 0.34                    | 384                    | 0.038              |
Fig. 5. Photomicrographs of characteristic samples with representative measurement values. T – Triassic (sample 2), J – Jurassic (sample 3), K – Cretaceous (sample 17) and E – Eocene (sample 19). Oil immersion, 50x.
on a restricted shelf during the Late Triassic. The kerogen of the Jurassic (Avtovac), Eocene (Kljen) and Miocene (Gacko) samples is represented mainly by detrohumininte. The kerogen of the Cretaceous samples is composed mainly of lamalginite and bituminite (Fig. 6), typical components of the marinite type of oil shale (Hutton, 1987). Vitrinite particles are very rare in the Cretaceous samples. Thin laminae, rich in organic matter, seen at some Cretaceous outcrops, field evidence of stromatolites, as well as abundant lamalginite and bituminite observed under the microscope, strongly indicate a microbial mat origin, probably related to Cyanobacteria (Ercegovac and Kostić, 2006) and a subareal and shallow-marine depositional environment.

The predominant maceral in the Gacko coal sample is atrinite (51%), followed by densinite (39%). Other macerals, present in the sample in only small quantities, are corpohuminite (5%) and to a lesser extent textinite, ulminite, fusinite and semifusinite.

Correlating maceral composition with HI and TOC from Rock-Eval pyrolysis (Tab. 1), it is obvious that the higher amounts of liptinite (L, Bit, Lam) in samples result in higher values of HI, especially in those of Cretaceous age (up to 827 mg HC/g TOC), which are near the onset of oil generation and thus have full generative potential. Besides liptinite, the Triassic samples have significant amounts of vitrinite as well and also are at higher stages of maturity, so the HI varies between 333 and 535 mg HC/g TOC. All samples with scarce liptinite (Jurassic, Eocene, and Neogene) have low HI values (up to 156 mg HC/g TOC). TOC seems to be less dependent on maceral composition, as values both in vitrinite- and liptinite-dominated samples showed marked variability.
Data sets for vitrinite reflectance are given for all localities, where the sediments contained an adequate amount of phytoclasts, i.e., vitrinite and huminite (Tab. 4). Samples from five Cretaceous localities and one Jurassic locality did not contain any vitrinite particles, so measurements could not be done.

The results of thermal maturity determination of the Triassic sediments analysed show that they have a mean vitrinite reflectance between 0.66% Rr and 0.78% Rr (Klobuk), so both reflectance values support the oil window stage.

For the Jurassic sedimentary rocks, measurements of vitrinite reflectance were performed on the sample from Avtovac. The sample from the Necvijeće locality had no reliable phytoclasts for the measurement of reflectance. The results show that the Avtovac locality had a lower mean reflectance of 0.41% Rr (huminite), corresponding to the immature stage. It should be noted, however, that this locality belongs to a different tectonic unit (Pre-Karst), in the northern part of the area. Measurements were done on detrohuminite, which is known to have slightly lower values than telohuminite at the same maturity level (ICCP, 1998).

In the Cretaceous samples, vitrinite particles were observed only at two localities, Todorići (middle Turonian) and Bugovina (upper Turonian). At Todorići, there were 14 measurements on a representative vitrinite population. At Bugovina, there were many more (61) measurements, but all of them in rather fine-grained particles.

The Eocene coaly marl from Kljen has plenty of huminite particles (456 measurements), which frequently are large, and therefore very reliable results could be obtained. The mean huminite reflectance was 0.38% Rr, which corresponds to an immature stage of thermal maturity.

The Miocene coal sample analysed (Fig. 7) from the Gacko coal mine, with huminite as the major maceral group, provided the most reliable data. More than 450 measurements were made, and the mean reflectance was 0.34% Rr (lignite coal rank). These are also the first results on vitrinite/huminite reflectance of the Gacko coal, as no such data have been published to date.

**DISCUSSION**

The first results on organic matter composition indicate that Mesozoic sedimentary rocks in the southern part of East Herzegovina (the Lastva Anticline) have some good, possible source rock (Triassic and Cretaceous) that are in the oil window stage (>0.50% Rr).

A cross-plot for values of vitrinite reflectance and Tmax is shown in Figure 8. According to vitrinite reflectance, a more reliable maturity indicator, the Triassic rocks are well within the oil window and the Cretaceous rocks are at its onset. It is important to note that both Triassic and Cretaceous (oil-prone) samples have a characteristic petroleum odour, indicating petroleum generation, which also is supported by the presence of bitumen, observed in the petrographic study. The Jurassic sedimentary rocks, lying between the Triassic and Cretaceous successions in the southern area (the Lastva Anticline), lack representative vitrinite particles, but it is almost certain that they are in the oil window as well. The Cenozoic sedimentary rocks are immature in the entire area.

Triassic samples 1 and 2 (Klobuk) also show a Tmax of 437–439 °C, which corresponds to the oil window stage. The Jurassic sample from the nearby Necvijeće locality shows marginal maturation with a Tmax of 434 °C. However, Tmax of all Cretaceous samples is anomalously low (up to 422 °C) for the observed maturity level, indicated by vitrinite reflectance (0.53–0.54% Rr).

As already noticed and discussed in the literature (Wilhelms et al., 1991; Snowdan, 1995; Yang and Horsfield, 2020), the Tmax parameter may be suppressed as a result of either a bitumen contribution to the S2 peak (a “carry-over” and/or asphaltenes effect) or the presence of hydrogen-rich or sulphur-rich (and hence thermally labile) kerogen.

The results of Rock-Eval pyrolysis on the East Herzegovina samples indicate a significant impact of heavy hydrocarbons (bitumen) on some parameters. It could be concluded that at the surface, there was degradation of free hydrocarbons by bacteria and by weathering, resulting in the escape of the lightest hydrocarbons. Apart from the expected decrease in the original S1 (hence PI and to a lesser extent TOC), it was presumed that there was also a relative increase of S2 and HI, due to the presence of solid bitumen and heavy/asphaltic oil.

By analysing the Rock-Eval pyrolytic curves of the Mesozoic samples and their “shoulder” shape between S1 and S2 peaks (at 300 °C), it was suspected that the remaining free hydrocarbons were degraded and are much more thermally resistive and hence do not distill at 300 °C. This implies that bitumen has artificially increased and widened the S2 peak in its lower temperature range (300–400 °C), as illustrated in Figure 9. The higher temperatures needed for bitumen cracking probably resulted in partial merging of the S1 peak into the S2 one, so it was assumed that such an anomalous S2 also decreased the Tmax to some extent. The remaining generative potential (S2) in most samples is thus a result not only of the cracking of kerogen, but also of bitumen.

As first noticed by Clementz (1979), solid bitumen and the heavy fraction of oil produce a measurable S2 response in the 350–450 °C range, so large quantities of bitumen or migrated petroleum in rocks can affect the values of S2 and Tmax. This could even cause non-source rocks to be misidentifed as source rocks.
COMPOSITION OF ORGANIC MATTER AND THERMAL MATURITY

Besides the observed increase of $T_{\text{max}}$ after solvent extraction (Tab. 2), an additional conclusion from the Rock-Eval extraction tests is that the standard, procedural temperature of 300 °C is obviously not sufficient for obtaining accurate $S_1$ (and hence $S_2$) values from the surface samples, containing heavy hydrocarbons. Furthermore, the artificial increase in $S_2$ due to bitumen cracking turned out to be as much as 25%–30% and in one of the samples was even more than doubled (M. Gruda, sample 16). The chemical extraction of the samples from Pridvorci and Todorići left a substantial fraction that distilled at 300 °C ($S_1'$), indicating that part of the bitumen is not extractable by standard solvents or is embedded in the mineral matter/kerogen. Those observations are similar to the conclusions of Wilhelms et al. (1991).

Since the initial decrease of $T_{\text{max}}$ could not be attributed solely to bitumen cracking, it is proposed that besides the impact of the significant presence of bitumen in almost all Cretaceous and some Jurassic (6, 7; Avtovac) and Triassic (3, 4; Župa) samples, Cretaceous kerogen represented by lamalginit and bituminite generates petroleum at lower values of $T_{\text{max}}$. It is well known that bituminite can generate petroleum when the huminite reflectance is close to 0.4% Rr (Cook, 1982; Pickel et al., 2017), so such kerogen could have a lower $T_{\text{max}}$ range during pyrolysis. This could also be the case for the highly oil-prone kerogen of algal origin, especially when it is also sulphur-rich.

Since $T_{\text{max}}$ data were ambiguous for most of the Cretaceous rocks, more detailed microscopic study of the different bitumen generations and microsolubility experiments with a stronger solvent mixture would help to bridge the gap between %Rr and $T_{\text{max}}$ measurements.

The Cenozoic sediments (Eocene coaly marl and Miocene coal) are immature, i.e., at an early stage of diagenesis. The maturity level is confirmed by both Rock-Eval pyrolysis and huminite reflectance. The Eocene sample 19 (Kljen) has a mean huminite reflectance of 0.38 % Rr, which correlates well with the $T_{\text{max}}$ value of 433 °C (for kerogen type III), and the Miocene lignite sample 20 (Gacko) has a $T_{\text{max}}$ value of 411 °C and a mean vitrinite reflectance of 0.34% Rr.

CONCLUSION

The results of the organic matter study show that the outcropping Mesozoic rocks in the southern part of East Herzegovina (the Lastva Anticline) have some good, possible source rocks (Carnian and Turonian) and are in the oil window, while the Cenozoic rocks are immature throughout the area. Vitrinite reflectance measurements showed sufficient thermal maturity of the Mesozoic rocks – with mean values between 0.53% (Cretaceous) and 0.78% Rr (Triassic). The finding that the Triassic to Cretaceous sedimentary rocks are mature enough at ground level implies significant erosion in an area with such a low geothermal gradient (due to the uplift of the orogen and high thermal conductivity), but could also indicate a higher heat flow in the past, i.e., processes related to the evolution of the oceanic crust of the Tethys.

Considering the results of the methods applied in the determination of thermal maturity, it is concluded that Rock-Eval is less reliable than vitrinite reflectance for the outcrop-ping sedimentary rocks. Many Mesozoic samples showed anomalously low $T_{\text{max}}$ values obtained by Rock-Eval pyrolysis, especially those of the Cretaceous rocks. Low $T_{\text{max}}$ values are partly due to the presence of bitumen, but probably more related to the specific kerogen that generates petroleum at a lower maturation level, hence at lower $T_{\text{max}}$ values.

The Cenozoic samples show good correlation between mean huminite reflectance and $T_{\text{max}}$. Their maturity level corresponds to a diagenetic stage, characterized by mean reflectance from 0.34% Rr for the Miocene coal (the Gacko lignite) to 0.38% Rr for the Eocene coaly marl.

Further study of organic matter in East Herzegovina should include more detailed microscopic studies and microsolubility experiments, but also analyses of biomarkers and kerogen transformation kinetics.

Acknowledgements

The study was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Projects TR-33001 and OI-176006). The article greatly benefitted from critical remarks by the reviewers George Siavalas and Boško Vuković.
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