**Palynofacies and paleoenvironment of the Upper Jurassic mud-supported carbonates,
southern Croatia: preliminary evaluation of the hydrocarbon source rock potential**

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Abstract

Despite the vast research on various aspects of its stratigraphy, relatively little is known about the source-rock potential of the Upper Jurassic Adriatic platform, southern Croatia. Here a case palynological study has been provided to determine the kerogen type, quality, and thermal maturity, and assess its relative hydrocarbon generative potential. Palynofacies characteristics indicate a low-energy, shallow-marine oxygen-depleted setting. The deposited mud-supported carbonates contain organic matter that is almost entirely composed of a fluorescent amorphous organic matter of planktonic and bacterial origin. A high phycomata/dinocyst ratio suggests relative hydrographic stability in an environment favorable for motile-stage dinoflagellate community with reduced production of dinocysts. The lack of anaerobic degradation and very good preservation of lipid palynomorphs indicates dysoxic conditions; the latter also is suggested by a low proportion of algal-phytoplanktic carbohydrates. The lack of oxygen-deficient zone within the water column, coupled with well-preserved lipid sediment components, suggests that the boundary between the oxygen-rich and oxygen-poor levels was likely located at/near the sediment-water interface. The palyno-organic facies analysis suggests that the organic matter corresponds to the type II (possibly I/II) kerogen (VRo ~0.3-0.4%) that was protected from degradation before, during and after sedimentation. Well-preserved lipid components suggest a good hydrocarbon-generative potential, but the low TOC values (<0.1%) of studied outcropping Upper Jurassic carbonates prevent their designation as source rocks. Given the known source-rock potential of the Upper Jurassic succession in the wider region, further studies of subsurface samples are needed to exclude the Oligocene-recent subaerial weathering as a culprit for the low TOC values.

Keywords Palynofacies, palyno-organic facies, kerogen, source rocks, Adriatic carbonate platform, Croatia

1. Introduction

The Croatian Adriatic Basin has a number of organic-rich intervals with source-rock potential, including the Middle and Upper Carboniferous, Upper Permian, Lower and Middle Triassic, Lower and Upper Jurassic, Lower and Upper Cretaceous, Eocene, and Pliocene-Pleistocene (Velić et al., 2015). Few studies have focused on Upper Jurassic carbonates as potential source rocks within the Adriatic platform (Bulić and Trutin, 2006; Blažeković Smojić et al., 2009; Blažeković Smojić, 2011; Troskot-Čorbić, 2011). Based on these studies, coupled with the data recently collected during investigations for the geological map of Croatia (Prtoljan et al., 2015), we hypothesize that the Upper Jurassic carbonate strata of the southern Adriatic platform in Croatia could represent source rocks. Both biofacies and lithofacies characteristics of these predominantly mudstones and wackestones suggest a relatively shallow-marine, low-energy depositional environment with increased biomass production. The major biofacies characteristic of the Oxfordian portion of these deposits is the abundance of benthic foraminifer *Nubecularia* that flourished in the biologically diverse low-energy settings, where the accumulated biomass likely was protected from syngedimentary degradation and conditions were favorable for kerogen formation and its subsequent preservation.

The goals of this study, based on palynofacies analyses, are to (1) describe and interpret palynofacies, and depositional environment of the Upper Jurassic platform carbonates, Adriatic platform, and (2) determine the kerogen type, quality, and thermal maturity, and assess its relative hydrocarbon generative potential.

2. Geologic Setting

The Adriatic platform is part of the Alpine-Mediterranean orogenic system and its present structural and tectonic relations primarily are the result of the collision between Adria Microplate

and European Plate (McKenzie, 1972; Dewey et al., 1973; Ricou et al., 1986; Dercourt et al., 1993; Prtoljan et al., 2007; Fig. 1). The intraoceanic, Mesozoic Adriatic platform was relatively large (several 100s km long, ~200 km wide) and developed a ~5-7 km thick succession of predominantly shallow-marine carbonates (Tišljarić et al., 2002; Vlahović et al., 2005; Husinec and Jelaska, 2006). Well-exposed Mesozoic sections of the platform along the southern Croatian coast nicely reveal the platform-interior carbonate succession. This succession is underlain by Upper Carboniferous-Lower Triassic mixed carbonate-siliciclastic epeiric sea deposits that formed along the northern Gondwana margin (Pamić et al., 1998). Following the regional Middle Triassic volcanism and rifting, the Adria Microplate separated from Gondwana. Subsequently, during the Middle to Late Jurassic, the Adria Microplate was characterized by regional extension and underwent further disintegration that resulted in the establishment of several isolated carbonate platforms (Adriatic, Apenninic, and Apulian) separated by deep basins (Stampfli and Mosar, 1999; Vlahović et al., 2005). In deeper water settings of the Adriatic platform, the late Early Jurassic Toarcian Oceanic Event (OAE) is recorded in burrowed spotty limestone (Sabatino et al., 2013). The overlying Middle and Upper Jurassic deposits are represented by predominantly shallow-marine carbonates; the Late Kimmeridgian initiation of compressional tectonics resulted in local formation of relatively shallow troughs (Vlahović et al., 2005), with deposition of dark, thin-bedded, Lemeš limestone with TOC >3% (Blažeković Smojić et al., 2009). Lower and mid-Cretaceous carbonates indicate subtidal to peritidal depositional environments with periodic and locally prolonged subaerial exposure (Husinec and Jelaska, 2006). The platform equivalent of basinal black shales associated with Aptian OAE1a is locally found within an up to ~10 m thick succession of unfossiliferous platy lime mudstone beds (Husinec et al., 2012). The end-Cenomanian to Early Turonian platform flooding was accompanied by the OAE2 (Jenkyns, 1991). Following this flooding event, the shallow-marine environments were reestablished, while

deeper-water settings became subordinate. Parts of the platform became exposed, while elsewhere, deposition continued into the Maastrichtian, and was followed by a regional end-Cretaceous emergence that characterized the end of the Adriatic platform deposition (Vlahović et al., 2005).

Numerous studies from southern Croatia have described in detail the Upper Jurassic biostratigraphy (e.g., Velić, 1977; Velić and Sokač, 1978; Velić, 2007) and sedimentology (e.g., Tišljarić et al., 2002; Velić et al., 2002b; Vlahović et al., 2005; Husinec and Read, 2006, 2007; Prtoljan et al., 2015; Read et al., 2016). The uppermost Callovian rocks under investigation (Šilješci Unit, thickness ~300 m; Fig. 2) are made up of bioturbated bioclastic packstone and grainstone with vertical burrow infills. The abundance of bioclasts, coupled with rare findings of stromatoporoids (*Cladocoropsis*), suggests a high-energy subtidal setting. The conformably overlying pale brown to gray Oxfordian limestones (Jasenice Unit, thickness ~300 m; Fig. 2) are medium- to thick-bedded (40 to 150 cm), or rarely massive. The basal Oxfordian is characterized by the predominance of locally dolomitized grainy, intraclast-skeletal wackepackstone. Up section, the abundance of mud-supported limestone increases, with mudstone and peloidal packstone predominating. Skeletal grains include benthic foraminifera (including nubecularids), micritized fragments of echinoderms, bivalves, and gastropods. Non-skeletal grains are predominated by intraclasts; ooids and oncoids are subordinate. Occasional findings of calcified radiolarians and/or calcispheres in the middle-upper Oxfordian suggest recurring pelagic influences. This overall deepening trend was characterized by the establishment of a low-energy subtidal setting throughout the mid-Oxfordian Adriatic Platform; the warm, shallow-subtidal waters supported a rich association of green algae and benthic foraminifera. The predominantly shallow subtidal environment continued into Early Kimmeridgian, with deposition of foraminifera-algal wackestone with chert nodules (Brotnice Unit, thickness 150-200 m; Fig. 2). A

major environmental change followed in the mid-Kimmeridgian, with overall shallowing and establishment of more diversified subtidal settings. Subsequently, the topmost Kimmeridgian and basal Tithonian are predominated by bioclast-intraclast-peloid packstone and grainstone that formed in shallow, high-energy settings of the platform interior (Stravča Unit, thickness 150-200 m; Fig. 2). The total organic carbon (TOC) values of the subaerially exposed Upper Jurassic limestones in the study area are very low (average <0.1 %; Troškot-Čorbić, 2012). However, such low values from uplifted and exhumed outcrops could be the result of surface weathering processes that could have dramatically altered rock properties (e.g., Jonk et al., 2014, Haeri-Ardekani, 2015). No TOC data is currently available from the subsurface equivalents in southern Adriatic.

3. Methods

3.1 Palynological processing

Fifty grams of organic matter was prepared for palynological analysis from each sample (n=27; Fig. 2) following carbonate dissolution in dilute (10%) HCl. The remaining inorganic fraction was then removed by flotation of the residue in zinc chloride (ZnCl₂) with a specific gravity of 2.1 kg/l. In order to preserve the structures and avoid change or loss of the organic component, the residues were not subjected to further maceration treatment. The organic residues were mounted onto palynofacies slides using a glycerine jelly as a mounting medium, and analyzed under an Olympus SZX 10 optical microscope, with magnifications of 200×–1000×. The inorganic residues remaining after floatation treatment were used to optically check on pyrite content.

3.2 Microscopic analysis of palynological organic matter

Microscopic analysis of palynological organic matter was performed using bright transmitted light and incident blue/ultraviolet fluorescent light. Given that the organic matter of analyzed samples was composed almost exclusively of moderately to well preserved fluorescent clasts, the analysis under the blue/ultraviolet fluorescent light enabled qualitative determination of biological origin, type, preservation and thermal alteration of organic matter.

3.2.1 Palynofacies

Palynofacies analysis was based on the qualitative determination of the biological origin of the palynological organic matter and classification of palynological groups and categories according to their primary facies distribution. In order to better understand the depositional environment, the palynofacies analysis also was accompanied by an assessment of organic matter quantitative distribution and relationship between different categories. Due to the low concentration of palynomorphs with respect to the total organic matter (most samples <1%; rarely ~ 1%), quantitative analysis was based on counts from three palynofacies slides per sample.

3.2.2 Kerogen type and relative hydrocarbon-generative potential

Microscopic analysis of non-covered palynofacies slides under incident blue/ultraviolet fluorescent light was undertaken in order to determine kerogen type and its relative hydrocarbon generative potential. Almost all samples were composed entirely of lipid-rich amorphous organic matter - AOM (amorphous liptinite), whereas wood tissue (inertinite, vitrinite) is subordinate. From the palynological standpoint, the fluorescent AOM and other lipid components present in the studied samples represent well-preserved primary organic matter, which in turn enables correlation with organic chemical parameters, identification of the kerogen type and relative hydrocarbon generative potential (Tissot and Welte, 1984; Robert, 1988; Tyson, 1995).

3.2.3 Kerogen maturity assessment

Changes in liptinite fluorescence (intensity, color) are affected by thermal diagenesis, i.e., at the same thermal rank different types of liptinites show diverse fluorescence features, and thus need to be calibrated against vitrinite reflectance (VRo) (Teichmüller, 1987). Similarly, calibration needs to be done for changes in coloration of organic components in transmitted light (Fig. 3).

All of the analyzed samples contain organic matter composed almost entirely of different marine lipid components, predominantly fluorescent AOM, which enabled us to use fluorescence light as an indicator of the relative thermal maturity of organic matter with respect to vitrinite reflectance (% VRo; Fig 3). In addition, the relative thermal maturity also is defined by pollen, prasynophycean phycmata, dinoflagellate (dinosporin) cyst and AOM analyses in transmitted light. The maturity of lipid-rich organic matter was assessed under the incident blue/ultraviolet fluorescent light based on changes in fluorescence intensity and color, with liptinites exhibiting characteristic alterations with increase in thermal maturity (Teichmüller and Ottenjann, 1977; Teichmüller, 1982, 1987; Ottenjann, 1985; see also references in Fig. 3). The color of re-emitted light progressively changes from green and yellow (immature) to orange and red (mature); the fluorescence intensity of liptinite types generally decreases towards the end of the oil generation; however, the fluorescence intensity of different liptinite types ceases at different higher ranks (see Fig. 3). Under the incident blue/ultraviolet fluorescent light, immature liptinite exhibits an increase in fluorescence intensity with a shift towards shorter wavelengths (green), i.e., it shows negative spectral alteration. Mature liptinites show a decrease in fluorescence intensity and a shift towards longer wavelengths (red), i.e., positive spectral alteration. Different liptinite types are differently resistant to thermal breakdown, marking the color/fluorescence intensity changes at different ranks. For example, sporomorphs have a

turnover rank at ~ VRo 0.5%, prasinophycean phycomata at 0.7%, and AOM between 0.45% and 0.5% (depending on sulfur content), respectively. Given that the bulk of oil is generated from AOM within a thermal range between VRo 0.5%-1.0%, once in the oil window, the prasinophycean phycomata are still immature (VRo <0.7%). Overmature, non-fluorescent organic matter is also marked by slightly different VRo values dependent on the type of organic matter (Fig. 3). In addition to the above, our assessment of relative thermal maturity was accompanied by a comparative analysis of the same types of organic matter in fluorescent light, as different types of degradation before, during or after sedimentation can cause changes similar to thermal maturation (Tyson, 1995; Yeloff and Hunt, 2005; Hartkopf-Fröder et al., 2015).

4. Results and Discussion

4.1 Palynofacies

4.1.1 Classification and distribution of palynological organic matter

Based on its primary distribution, the palynological organic matter (Figs. 4, 5) is classified below into (I) terrestrial and (II) marine organic matter (Table 1).

Palynofacies analysis shows that almost all of the analyzed samples contain ~100 % category II organic matter (marine organic matter), with variable proportions of fluorescent categories IIA-C,E,F. Category IIE (AOM) is very abundant (~70-99%), with variable proportions of subcategories IIEa (~30-50%), IIEb (~10-30%) and IIEc (~30-40%). Category IIC (marine macrophytes) comprises only ~1% in structured, and up to ~15% as a structureless organic matter that was added to category IIF (liptodetrinite), making together up to ~30% of the organic matter in some of the analyzed samples. Most of the samples contain <1% terrestrial organic matter of predominantly category IA (inertinite, relatively well rounded and sorted clasts mostly <5 µm); categories IB (vitrinite) and IC (bisaccate pollen) are subordinate (<<1%). Two

of the analyzed samples (J-9 and J-12; Fig. 2) contain ~95% marine and ~5% terrestrial organic matter composed of predominantly category IA (inertinite, relatively subrounded and poorly sorted clasts <20 µm) and less commonly category IC (bisaccate pollen). Within the total palynological organic matter, categories IC and IIA,B,D (palynomorphs) comprise only ~1%, although in most samples they are <1%. Categories IIA,B,D (marine palynomorphs) are ubiquitously present (~100%), whereas category IC (terrestrial palynomorphs) is very rare (<<1%). Among the marine palynomorphs, the most abundant is category IIA (prasynophycean phycomata; 90-99%), followed by ~1-10 % of categories IIB (dinospore cysts) and IID (chitinous foraminifera); IIB is typically more common than IID.

4.1.2 Depositional environment and preservation of organic matter

The majority of the analyzed samples are characterized by a very low I/II (terrestrial/marine) ratio, an even lower IC/IIA,B,D ratio, as well as by a very low concentration of relatively well-sorted and moderately rounded equidimensional inertinite (category IA) clasts. An absolute domination of marine organic matter, coupled with a complete absence of spores and cuticles, as well as rare presence of organic matter categories IA,B (inertinite more abundant than vitrinite) and IC (airborne bisaccate pollen), implies that the depositional environment was isolated from possible terrestrial influences (cf., Steffen and Gorin, 1993; Tyson, 1995). That parts of the Upper Jurassic Adriatic platform could have locally been periodically subaerially exposed and associated with oxidation of plant fragments is suggested by the two analyzed samples (J-9 and J-12; Fig. 2) that contain small amounts of inertinite and bisaccate pollen. Given the good preservation of all primary fluorescent lipid components, sedimentary oxidation is highly unlikely as such degradation would have also altered the total organic matter and converted amorphous components to a non-fluorescent huminitic amorphous matter (Tyson, 1995). Thus,

locally present inertinite and bisaccate pollen suggest periodical input of clasts derived from distant emergent areas of the platform, either by wind or ocean currents.

Prasynophycean phycomata of green algae are the most abundant component of marine palynological organic matter. This is typical for open-marine facies where they are commonly found in organic matter-enriched, fine-grained sediments deposited in low-energy, oxygen-depleted settings (Tyson, 1995; Batten, 1996). High IIA/IIB (phycomata/dinocyst) ratio indicates relative hydrographic stability and conditions favorable for the development of motile-stage dinoflagellate association with reduced cyst production (Tyler et al., 1982; Tyson, 1995). Slight variations in the above ratio likely are due to periodical changes in water column stratification that control the inhibition degree of dinoflagellate cyst production. These variations could also have been driven by high-frequency sea-level oscillations documented on the Upper Jurassic Adriatic platform (Husinec and Read, 2006, 2007).

The organic matter of the Oxfordian nubecularid facies can be identified as the prasynophycean palynofacies, locally transitioning into dinocyst palynofacies. Several samples (J-16, J-26, and J-27; Fig. 2) are characterized by a lower phycomata/dinocyst ratio. They also contain large prasynophycean phycomata of *Pterospermella* sp. (Figs. 11, 2g); these are subordinate to other prasynophyceans and are absent from organic residue of other samples. At present, the above is poorly understood due to lack of comparative correlatives on the Adriatic platform. However, the lower phycomata/dinocyst ratio may reflect variations in the water column stratification that control the inhibition degree of dinoflagellate cyst production and/or sea-level oscillations. On the other hand, the presence of *Pterospermella* suggests a slight and/or short regressive phase accompanied by a minor decrease in salinity (Kustatscher et al., 2014, and references therein). The organic matter content of all analyzed samples is composed of predominantly fluorescent amorphous components, which suggests that the primary organic

matter was not affected by either pre-, syn- or post-sedimentary oxidation (Tyson, 1995). All lipid palynomorphs fluoresce and are morphologically well-preserved, which indicates their deposition in a low-energy setting where aerobic and anaerobic processes were either of short duration or low intensity, both during sedimentation and later during diagenesis (Orr and Gaines, 1973; Hart, 1986). Such conditions include dysoxic environments and settings where deposited sediments contain preserved autochthonous planktonic and benthic organic matter of bacterial origin. Very low IIA,B/IIC,E,F (structured/amorphous) ratio of marine lipid categories indicates that the majority of the fluorescent amorphous component is made up of lipid aggregates of blooming phytoplankton, as well as algal and zooplankton extracellular fluids and other marine lipid components. Within the organic residue, algal/phytoplanktonic carbohydrates content is low due to the dysoxic depositional environment (cf., Van Kaam-Peters et al., 1998; Kok et al., 2000). Given that the processes of anaerobic biodegradation are weak under dysoxic conditions, the preserved organic matter within the analyzed samples contains only low quantities of anaerobic bacteria-derived biomass. The above discussed high phycomata/dinocyst ratio does not accurately reflect phytoplankton dynamics due to inhibited dinocyst production, which suggests that within the palynofacies, the portion of dinoflagellate biomass is much greater as compared to the quantities of dinocysts in the palynological record. A part of the fine fraction of the AOM characterized by non-uniform fluorescence (classified within category II/F: liptodetrinite) suggests that it was derived from fecal pellets of zooplankton origin within an oxygen-depleted setting (Robbins et al., 1996). The studied Oxfordian part of the succession is characterized by an abundance of nubecularid foraminifera (*Nubecularia*) that commonly are permanently fixed on seagrasses in shallow and warm seas (phytal assemblages *sensu* Murray, 2006). Relatively common cyanobacteria likely reflect dysoxic conditions where organic components with lower preservation potential were reduced. The variations in cyanobacterial content are in positive

correlation with the phycomata/dinocyst ratio variations, i.e., an increase in phycomata/dinocyst ratio is associated with an increase in cyanobacterial abundance and *vice versa*.

Palynofacies analysis indicates that the organic matter component of analyzed samples is almost exclusively composed of fluorescent organic matter of predominantly marine origin (Table 1). Biological origin of the organic matter suggests that the carbonate depositional environment was characterized by high organic production under conditions favorable for preservation of deposited organic matter. Research on phytoplankton dynamics in modern shallow-marine depositional environments along the Croatian Adriatic Coast, deposits somewhat similar in character to the studied Upper Jurassic carbonates, show that most ecosystems are moderately eutrophic (Viličić, 1989; Viličić et al., 1998), although with associated sediments rich in preserved organic matter and with up to 5 wt. % of organic carbon. (Koch et al., 2002; Bačani et al., 2004; Šparica et al., 2005a,b). This further implies that, in formation of sediments enriched in preserved organic matter, the processes leading to organic matter preservation are much more important than high primary production. In addition, despite benthic activity within recent shallow-marine ecosystems along the Croatian Adriatic Coast, oxidation-related processes have left no to very little footprint on the condition of the preserved organic matter. Given the high proportion of preserved fluorescent AOM that is typical for the oxygen-depleted environment, the oxycline between normal oxygen and oxygen-depleted water is located at the sediment/water interface. Such oxygen distribution is assisted by the development of cyanobacterial meadows that reduce the vertical permeability of sediment, which in turn contributes to retention of hypersaline, oxygen-depleted pore waters and prevents lateral mixing of pore waters and the introduction of aerobic bacteria. Given the relatively high proportion of cyanobacterial material in this study, a similar mechanism for the preservation of the Upper Jurassic organic matter is possible.

None of the analyzed samples has pyrite inclusions within the organic matter (even within the inorganic residue). Pyrite is common in anoxic clastic sediments and is mostly associated with AOM (Tissot and Welte, 1984; Tyson, 1995). If a carbonate facies is oxygen-depleted and isolated from the terrigenous iron input, biogenous sulfur, produced by bacterial sulfur reduction, can be incorporated in organic molecules. Under dysoxic conditions, the degree of anaerobic activity is low which hinders crystallization of pyrite even if there is an input of iron ions. However, the ions of iron can be brought into carbonate platform sediments from distant volcanic sources, as evident by tufa within palynologically similar Upper Jurassic Adriatic platform deposits of Lemeš and Velika Kapela in Croatia (Velić et. al., 2002a,b; Blažeković Smojić et al., 2009; Blažeković Smojić, 2011; Troskot-Čorbić, 2011). Organic-rich protected shallow subtidal carbonate platform facies, lithologically and palynologically similar to the one in the study area, also is found in the Cenomanian deposits of western Croatia (Istria Peninsula), NW Adriatic platform (Matičec, pers. comm., 2010; Blažeković Smojić, 2011). This suggests that even minor platform flooding episodes could have resulted in the formation of a well-stratified water column leading to anoxia, and, if associated with moderate primary bioproduction, lead to accumulation and preservation of the complete biomass, and subsequently formation of source rocks.

4.2 Palynological kerogen classification and relative generative potential

The major characteristic of the analyzed samples is that they predominantly contain marine organic matter that is almost entirely composed of moderately to well preserved fluorescent AOM of varied biological origin. Based on palynological analysis of biological origin, as well as assessment of lipoid components, the analyzed organic matter corresponds to kerogen type II, possibly I/II if protected from secondary degradation processes (e.g., surficial weathering, tectonics), and contains small amounts of sulfur given the dysoxic environmental conditions of

kerogen generation. From the palynological standpoint, the analyzed Upper Jurassic kerogen has a good hydrocarbon generative potential.

4.3 Kerogen thermal maturity assessment

Fluorescent AOM and other fluorescent organic matter components of analyzed samples are well preserved. Generally, different types of degradation of organic matter, including syn- and post-diagenetic processes as well as surficial weathering and tectonics that are reflected in heterogeneous fluorescence, are known to cause changes similar to thermal maturation (Tyson, 1995; Yeloff and Hunt, 2005). Fluorescence heterogeneity can be a consequence of primary variable lipid content, i.e., hydrogen-rich organic clasts, and thus can be most pronounced within AOM containing components of diverse biological origin. Certain regularity can be distinguished within the IIEa-IIEb-IIEc sequence that shows an increase in fluorescence intensity, which correlates with the amount of lipid component within the above categories, i.e., associated primary organic matter. However, almost every sample exhibits at least partial heterogeneity in fluorescence intensity within all types of category IIE, locally even the reverse of the trend described above, which likely is a consequence of subaerial exposure, not syngenetic degradation or later thermal degradation. Given their resistivity to thermal and other types of degradation, marine palynomorphs, especially prasynophycean phycomata, show minimal fluorescence heterogeneity.

Based on optical characteristics under transmitted and incident blue/ultraviolet fluorescent light, kerogen of analyzed samples shows the thermal maturity of ~0.3-0.6% VRo (see Fig. 3). Given the known irreversibility of kerogen alterations due to thermal and syn- and/or post-diagenetic degradation, a portion of kerogen that is best preserved (high fluorescence intensity, negative spectral alternation; see Table 1) has a thermal maturity rank of ~0.3-0.4% (immature).

5 Conclusions

The studied Upper Jurassic deposits enriched in organic matter were formed within low-energy, shallow-marine and oxygen-depleted settings of the southern Adriatic platform. Palynofacies and kerogen analyses indicate the presence of well-preserved, lipid-rich organic matter. Given the dysoxic environmental conditions, kerogen is depleted in sulfur and is almost exclusively composed of fluorescent AOM of algal-planktonic-cyanobacterial origin that can be classified as type II (I/II) kerogen with good generative potential. In general, the entry into the oil window of kerogen type II without sulfur is at $V_{ro} \sim 0.5\%$, while kerogen type II with sulfur (II-S) at 0.45% , respectively. Lower thermal breakdown rank for kerogen type II-S is due to sulfur ions being directly incorporated into the complex kerogen structure, which weakens the bonds allowing earlier hydrocarbon expulsion (Tissot and Welte, 1984; Robert, 1988; Tyson, 1995).

Finally, the samples used in this study were obtained from outcrops only. Given that the TOC can be significantly reduced by outcrop weathering, further studies of subsurface and outcrop samples accompanied with organic geochemical analyses are needed to exclude the Oligocene-recent subaerial weathering as a driver of low TOC values of Upper Jurassic Adriatic Carbonate Platform deposits.

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Figure Captions

Fig. 1 Location map of the study area in southernmost Croatia; yellow stars indicate the sampled area. Inset map shows general tectonic setting of SE Europe; black rectangle indicates study area. Modified from Prtoljan et al. (2012).

Fig. 2 Generalized stratigraphic column of the study area showing age, lithostratigraphic units, sample positions, lithology and stratigraphic range of major benthic foraminifera and calcareous green algae. Modified from Govoni et al. (2012) and Prtoljan et al. (2015).

Fig. 3 Correlation of thermal maturity parameters used in this study and vitrinite reflectance (% VRo). Modified after: 1- Staplin (1969), 2 - Pearson (1984); Mao et al. (1994); Pross et al. (2007), 3 - Legall et al. (1981), 4 - Staplin (1969), Van Gijzel (1990), 5 - Ottenjann et al. (1974), Collins (1990), Mao et al. (1994); (6) Robert (1988), Obermajer et al. (1999); (7) Van Gijzel (1979), Collins (1990).

Fig. 4 Paired transmitted light (left) and fluorescent light (right; UV light cut with 570 nm filter) photomicrographs of the Croatian Upper Jurassic types of amorphous organic matter (AOM): **a,b,d,h-k** category IIc; **c** fragment of a marine macrophyta partly covered by IIc; **e,g** IIc; **f** IIc; **l** *Pterospermella* sp.; **m** *Barbatacysta* sp. Note small prasynophycean phycmata (18-20 µm) in photomicrograph **a**. Scale bar is 20 µm. See Table 1 for description of palynological organic matter categories.

Fig. 5 Paired transmitted light (left) and fluorescent light (right; UV light cut with 570 nm filter) photomicrographs of the Croatian Upper Jurassic types of amorphous organic matter (AOM): **a-c,e,f,j,k** category IIc. Note *Leiosphaeridia* sp. in photomicrograph **j**; **d** IIc; **h** IIc; **g** *Pterospermella* sp.; **i** fragment of marine macrophyta. Scale bar is 20 µm. See Table 1 for description of palynological organic matter categories.

LEGEND

- mudstone and mudstone-wackestone
- wackestone
- wackestone-packstone
- packstone and grainstone
- limestone with chert nodules
- dolomite
- green algae
- large benthic foraminifera
- nubecularid foraminifera

TRANSMITTED LIGHT				FLUORESCENCE LIGHT (UV, BLUE)		
				INTENSITY: ▲ INCREASING ▼ DECREASING		
VITRINITE REFLEC- TANCE % VR _o 1	SPORO- MORPH THERMAL ALTERATION INDEX TAI 2	PRASINO- PHYCEAN PHYCOMATA 3	AMORPHOUS ORGANIC MATTER AOM 4	SPORO- MORPHS 5	PRASINO- PHYCEAN PHYCOMATA 6	AMORPHOUS ORGANIC MATTER AOM 7
0.20	Pale yellow	Translucent	Light yellow	Green ▲	▲	▲
0.30	1+ Yellow (1.3)	Light yellow	Light yellow	Green yellow		Yellow
0.38	2- Sunny yellow (1.7)	Light yellow	Medium brown	Yellow	Green	
0.40	2 Yellow orange	Pale yellow		Yellow-orange		Orange
0.45	2	Pale yellow				
0.50		Pale yellow	Dark yellow	Light orange	Yellow	
0.60	2+ Bright orange (2.3)	Orange	Light brown	Medium orange		Red
0.65		Orange		Dark orange	Orange	
0.70	3- Orange (2.7)	Orange				
0.85			Medium brown	Orange red	Red	Brown
0.90	3 Yellowish brown	Dark brown		Red ▼	▼	
1.00	0.98 3		Dark brown	Dark red-brown		
1.15	1.16 3+ yellowish brown (3.3)		Dark brown			
1.30	1.35 Very dark		Very dark brown	none	none	none
1.50	1.71 4- dark (3.7) grayish brown	Black				
1.75	4 Very dark gray		Black			
2.00	2.58 4					
2.50	5.30 5 Black (opaque)					
4.00						
6.00

Table 1 Classification of Upper Jurassic palynological organic matter, southern Adriatic platform, Croatia

	Category	Description	Illustration in text
I. Terrestrial (allochthonous) organic matter	IA. Black clasts (oxydized woody tissue – inertinite)	Mostly rounded and well-sorted, non-fluorescent clasts	
	IB. Brown to dark brown clasts (skeletal and vascular tissue of higher plants – vitrinite)	Moderately rounded, structure poorly preserved, non-fluorescent, no pyrite inclusions	
	IC. Bisaccate conifer pollen	Well preserved, yellow, yellow-orange to light orange fluorescence, negative to positive spectral alteration, translucent to light yellow to yellow in transmitted light, no pyrite inclusions	
II. Marine (autochthonous) organic matter	IIA. Prasynophycean phycomata (planktonic algae)	Well preserved, bright green, green-yellow and yellow-green fluorescence, negative spectral alteration, translucent to light yellow to yellow in transmitted light, no pyrite inclusions	Figs. 1a, 1f: small phycomata; 2j: <i>Leiosphaeridia</i> sp.; Figs. 1l, 2g: <i>Pterospermella</i> sp.
	IIB. Dynoflagellate (dinospirin) cysts, phytoplankton	Well preserved, yellow-green, yellow to light yellow-orange fluorescence (less bright compared to prasynophycean phycomata), negative to positive spectral alteration, translucent to light yellow in transmitted light, no pyrite inclusions	Fig. 1m: <i>Barbatocysta</i> sp.
	IIIC. Marine macrophytes (sea grasses)	predominantly pseudoamorphous clasts <10 µm, subordinate membranous, wispy, structured (polygonal thickenings) and homogenous (faintly structured) clasts 10-100 µm, moderate yellow, light yellow-brown to light yellow fluorescence, negative to positive spectral alteration, in transmitted light thin clasts are translucent, thick clasts show light yellow, orange to light brown color, no pyrite inclusions	Figs. 1c, 2i
	IIID. Chitinous foraminiferal test linings	Non-fluorescent, no pyrite inclusions	
	IIIE. Amorphous organic matter (AOM) originating from lipid components of different organisms, including algae, phytoplankton, zooplankton, various bacteria, marine macrophytes and fecal pellets	Three types are identified based on their morphology and fluorescence features: a. heterogenous liptodetrinite type: matrix composed of lumps of algal-planktonic-fecal-bacterial origin and non-uniform fluorescence, liptinite clasts and fine globular algal phycomata fluoresce brighter (pale to moderate yellow-orange, orange to orange-brown) than the matrix, negative to positive spectral alteration (depending on the type of organic clasts present), in transmitted light color varies with clast thickness from translucent to light yellow, yellow, orange, red-brown to dark brown, no pyrite inclusions; b. spongy liptinite type of algal-bacterial origin: AOM without matrix, irregular relief with sporadic molds of minerals, well preserved, compared to heterogenous liptodetrinite type exhibits more uniform and slightly brighter yellow-orange to orange fluorescence, negative to positive spectral alteration, in transmitted light color varies with clast thickness from yellow, light brown, brown to dark brown, no pyrite inclusions; c. homogenous liptinite type of cyanobacterial origin: clasts compact, homogenous, commonly with distinct contours, well preserved, uniform intense golden-yellow, golden yellow-light orange to less commonly orange-yellow and orange fluorescence, negative (dominant) to positive (subordinate) spectral alteration, in transmitted light color varies with clast thickness from yellow, orange, brown to dark brown, no pyrite inclusions	Figs 1c, 1f, 2c, 2d Figs. 1e, 1g, 2h Figs. 1a, 1b, 1d, 1h-k, 1m, 2a-c, 2e, 2f, 2j, 2k