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PRELIMINARY ASSESSMENT OF THERMAL MATURITY TRENDS OF SOURCE ROCKS IN THE INTERNAL IONIAN ZONE AT EPIRUS AREA, WESTERN GREECE, BY APPLYING ROUTINE AND ADVANCED GEOCHEMICAL METHODS

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ΧΡΥΣΗ-ΣΤΥΛΙΑΝΗ ΤΣΟΠΟΥΛΟΥ

Πτυχιούχος Γεωλόγος

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Abstract

The Ionian basin is located in western Greece and composes part of the external Hellenides. In the Mesozoic carbonate succession, intervals capable for hydrocarbon generation are detected. Stratigraphically, the source rocks layers are observed at the top of the Triassic evaporites, at the base of Jurassic carbonates (Pantokrator shales), at the top of Jurassic carbonates (Posidonia or Ammonitico Rosso) and at the top of lower Cretaceous carbonates (Vigla). The paleogeographic conditions were controlled by various factors which favored water stagnation, development of local euxinic conditions in the bottom waters, formation and preservation of the organic matter. The laboratorial results of routine source rock analyses (Rock Eval pyrolysis) and advanced geochemistry (petroleum biomarkers) of the critical source rock intervals are discussed in this study, in order to address maturity variation subjects from east to west part of the Ionian basin. The samples were analyzed by the Rock Eval II instrument and the Gas Chromatograph- Mass Spectrometer (GCMS). The diagrams that plotted for the Jurassic and Cretaceous source rocks with the Rock Eval method, are combined with the vitrinite reflectance (Ro %), the carbon preference index (CPI), the methylphenanthrene index (MPI) and a variety of biomarker classes. The results suggest source rocks dominated with kerogen type I, II, and mixed I-II deposited in a marine to terrestrial environment respectively. The maturation of source rocks tends to decrease from the internal towards the central-external zone, according the data. The Ionian zone in western Greece is also compared with the Southern Adriatic region, indicating a similar carbonate-evaporitic environment paleographically, in which hydrocarbons were generated.

Περίληψη

Η Ιόνια λεκάνη βρίσκεται στη δυτική Ελλάδα και αποτελεί τμήμα των εξωτερικών Ελληνίδων ζωνών. Στη Μεσοζωϊκή ανθρακική σειρά παρατηρούνται στρώματα ικανά για τη γένεση υδρογονανθράκων. Στρωματογραφικά, τα μητρικά πετρώματα παρατηρούνται στο ανώτερο τμήμα των Τριαδικών εβαποριτών, στο κατώτερο τμήμα των Ιουρασικών ασβεστολίθων (σχιστόλιθοι Παντοκράτορα), στο ανώτερο τμήμα των Ιουρασικών ασβεστολίθων (Ποσειδώνια ή Ammonitico rosso) και στο ανώτερο τμήμα των κατώτερων Κρητιδικών ασβεστολίθων (Βίγλα). Οι παλαιογεωγραφικές συνθήκες στην περιοχή ελέγχονταν από διάφορους παράγοντες, οι οποίοι ευνόησαν τη στασιμότητα των υδάτων, την ανάπτυξη οξειδοαναγωγικών συνθηκών στον πυθμένα, το σχηματισμό και την διατήρηση του οργανικού υλικού. Τα εργαστηριακά αποτελέσματα τόσο από την πυρόλυση Rock Eval όσο και από τις μεθόδους γεωχημείας (βιοδείκτες πετρελαίου) των μητρικών πετρωμάτων μελετώνται σε αυτή την εργασία, ώστε να προσδιοριστούν οι μεταβολές της ωριμότητας από τα ανατολικά προς τα δυτικά στην Ιόνια ζώνη. Τα δείγματα αναλύθηκαν με το όργανο Rock Eval II και με τη χρήση πλήρους σάρωσης αερίου χρωματογραφίας μάζας (GCMS). Τα διαγράμματα που έγιναν για τα Ιουρασικά και Κρητιδικά μητρικά πετρώματα με τη μέθοδο της Rock Eval πυρόλυσης, συνδυάστηκαν με την ανακλαστικότητα του βιτρινίτη (Ro%), το δείκτη προτίμησης άνθρακα (CPI), το δείκτη μεθυλοθεναμφρίνης (MPI) και ποικιλία τάξεων βιοδεικτών. Τα αποτελέσματα έδειξαν ότι στα μητρικά πετρώματα κυριαρχεί κηρογόνο τύπου I, II και αναμεμιγμένο I-II το οποίο αποτέθηκε σε θαλάσσιο ως χερσαίο περιβάλλον αντίστοιχα. Η ωριμότητα των μητρικών πετρωμάτων τείνει να μειώνεται από την εσωτερική προς την κεντρική-εξωτερική Ιόνια ζώνη, σύμφωνα με τα παραγόμενα αποτελέσματα. Επιπρόσθετα η Ιόνια ζώνη στη δυτική Ελλάδα συγκρινόμενη με την νοτιοανατολική Αδριατική περιοχή (Κροατία, Αλβανία, Ιταλία) δείχνει ένα παρόμοιο ανθρακικό-εβαποριτικό περιβάλλον παλαιογεωγραφικά, στο οποίο δημιουργήθηκαν υδρογονάνθρακες.

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Chapter 1

Introduction

1.1 Geological setting of the Ionian zone

The study area is located in Ionian zone in western Greece and constitutes part of the external zone of the Hellenides (Figure 1). The Ionian zone, together with the Paxos zone, represents the basin and the transitional zone of the Apulian platform respectively.

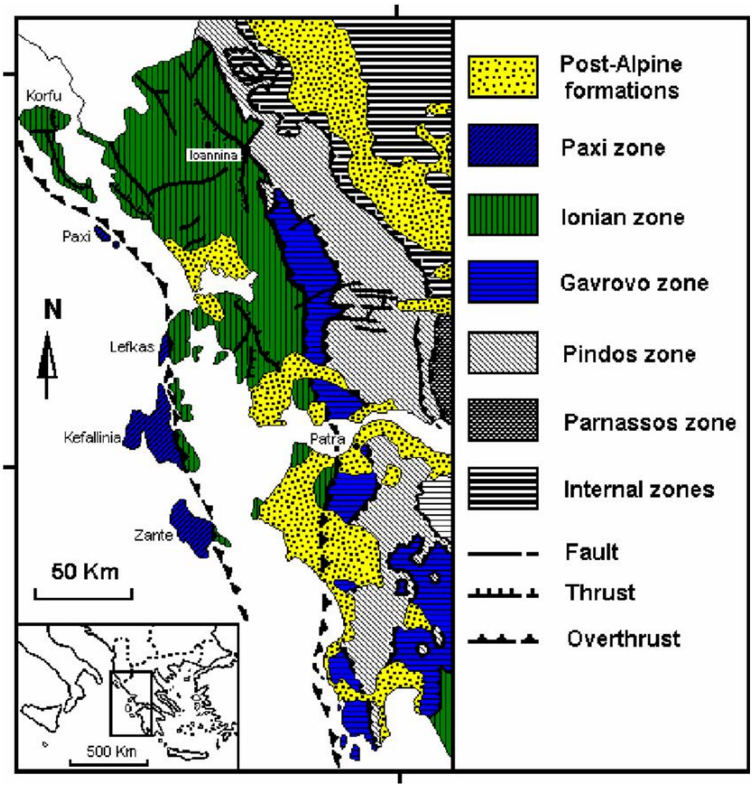

Figure 1: Geotectonic map of Western Greece (Karakitsios, Marnelis et al., 2013 [9])

More particular, during the Mesozoic (Pliensbachian) extensional tectonics related to the opening of the Tethys Ocean, activated the aperture of the Ionian basin. The halokinesis of evaporites mainly at the lower layers of the Ionian zone formation altered the region. Although the platform carbonates continued their formation during the whole Jurassic in the pre-Apulian zone, the faulting and the ensuing subsidence prevailed in the Ionian basin. In the Late Eocene the beginning of orogenic movements and flysch sedimentation was held, after the minor off and onlap movements in the basin margins which contributed to the paleogeographic configuration of the area. The compressional phase of orogenesis reactivated the structures which formed during the Jurassic extensional phase, expressed with westward and eastward displacements. Source rock horizons with capability to generate important quantities of hydrocarbons, were found in various Alpine horizons and potentially in shale sediments within the Triassic breccias, which have high amount of organic matter. The organic matter's deposition and preservation do not always happen under similar conditions, but often present considerable differences. "The organic rich shale fragments within the Triassic breccias were initially deposited as stratigraphic layers in subbasins of the evaporitic basin" (Rigakis, 1999). Initially, the eustatic sea level changes resulting in the preservation of the organic matter. Afterwards, the organic matter further preserved in the entire basin, due to the evaporitic sedimentation. The evaporite dissolution collapse breccias formed because of procedures which also favored the fragmentation of the organic rich layer, without any significant alteration of their organic matter. The source rocks contained in the syn-rift formations (Jurassic) and the Vigla shales were deposited in restricted subbasins, which formation was a result of the syn-rift period in the Ionian region and have preserved some of them, during the post-rift period. The water stagnation, the local anoxic conditions in the bottom water and the preservation of the organic matter associated with the geometry of these subbasins. The anoxic episodes of Toarcian and Cenomanian/Turonian age also favored the preservation of organic matter, as well as the high sedimentation rates in the eastern areas of the Ionian basin. Furthermore, the Ionian zone did not affect by the early orogenesis of Upper Jurassic – Late Cretaceous. Eventually, sedimentation was mostly continuous and uninterrupted from Triassic to Tertiary in the area. The rocks range from Triassic evaporates and associated breccias, to a mainly carbonate sequence until Upper Eocene, followed by Oligocene flysch (Figure 2). Palaeoclimatologically, "during arid conditions halite or gypsum/anhydrite was precipitated, dependent on the evaporation rate and during more humid conditions organic rich and carbonate rich layers were deposited" (Getsos et al., 2004).

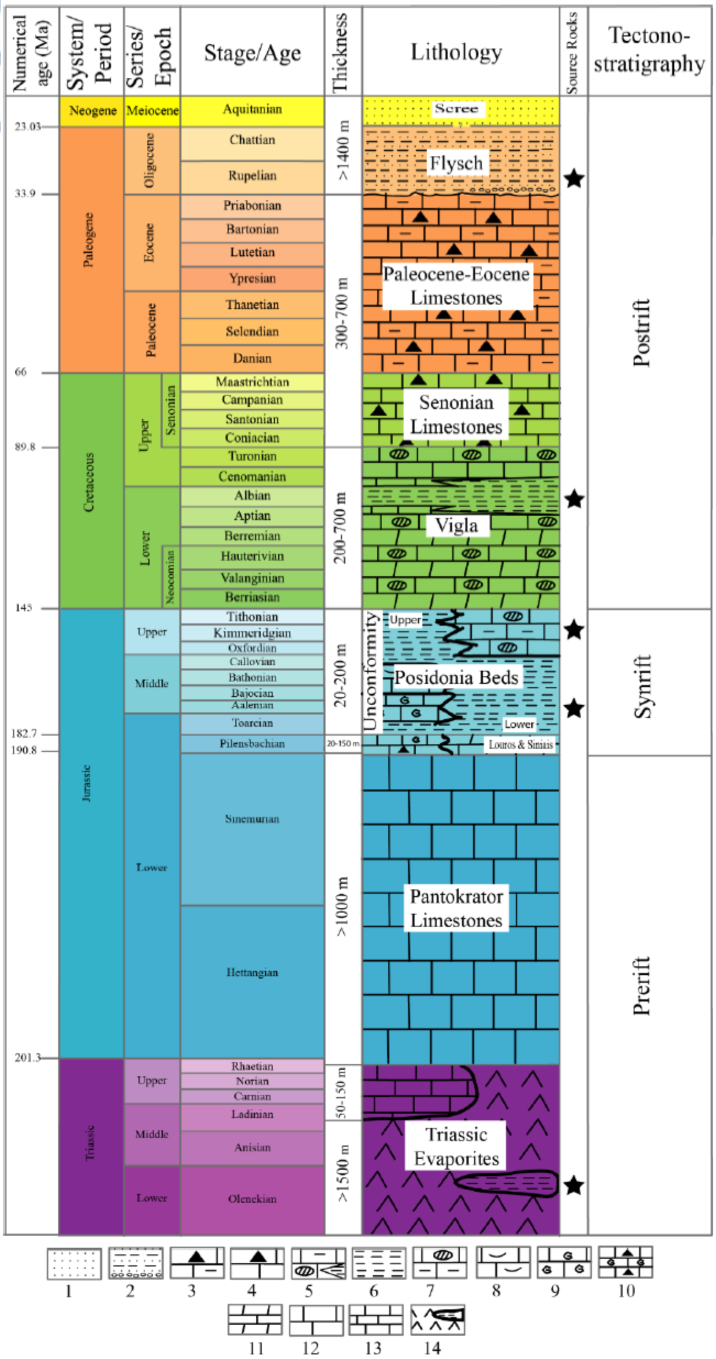

Figure 2: Synthetic lithostratigraphic column of the Ionian Zone:

1) Scree, 2) Pelites, sandstone and congomerates, 3) Limestone with rare cherty intercalations, brecciated, 4) Pelagic limestone with calciturbidite intercalation, 5) Pelagic limestone with cherts and shale intercalations, 6) Upper: Alternating cherty and shale beds, Lower: Marly limestone and laminated marls, 7) Pelagic limestone with cherty nodules and marls, 8) Pelagic limestone with lamellibranches, 9) Pelagic, nodular red limestone with ammonites, 10) External platform limestone with brachiopods and small ammonites, 11) Pelagic Limestone with rare cherty intercalations, 12) Platform limestone, 13) Thin-bedded black limestone, 14) Evaporites with shale horizons (Karakitsios 1995, Rigakis 1999).

Concerning the stratigraphy, the Ionian zone is divided to internal (eastern), central and external (west), based on the differential thickness of the formations. Furthermore, there are three distinct sequences (Figure 2): The pre-rift succession includes the Foustapidima limestones (Ladinian-Rhetian) which are found only in the external Ionian zone and the shallow water Pantokrator limestones (Liassic) overlying the Triassic evaporites. “The subevaporitic basement, of the Ionian zone in western Greece does not crop out, nor was penetrated by wells” (Karakitsios, 2013). The pelagic Siniais limestones and their laterally equivalent hemipelagic Louros limestones represent the syn-rift sequence. The general deepening of the Ionian domain is confirmed by these formations. The pelagic Vigla limestones deposited synchronously throughout the Ionian basin (Early Berriasian) and belong to the post-rift sequence. The existence of the breakup unconformity of post-rift sequence is represented by the base of the Vigla limestones in the Ionian basin. The Senonian limestones consist of calciturbidites comprising limestones with fragments of globotruncanids, rudists and microbrecciated intervals. The deposition of Paleocene and Eocene sediments was held without noteworthy facies changes. The Ionian basin supplied with brecciated rock fragments as a result of the erosion of Cretaceous carbonates on the Gavrovo zone and the Apulian platform (Paleocene). However, there was a significant reduction of clastic material especially in the central Ionian basin, during the Eocene. The platy wackstone and the mudstone with globigerinidae and siliceous nodules were the dominant depositional facies during this period, analogous to those of the Vigla limestones. In the main part of the Ionian zone the flysch sedimentation initiated at the Eocene-Oligocene age and a few marly limestone transitional beds deposited above the Upper Eocene limestones. The inversion of the Ionian sequence was accompanied by the major orogenic movements at the end of the Early Miocene (Burdigalian).

Chapter 2

Source rocks

2.1 Geochemical methods

In petroleum geochemistry, there are many analytical procedures in order to determine characteristics of rocks and hydrocarbons. The Rock Eval method is considered routine analysis and the results are used as criteria to choose the appropriate samples for further lab investigation. It is about the only method that defines the quantity of the kerogen. Moreover, the Rock Eval provides data for the quality and the maturity of organic matter, and also confers conclusions about the migration of oil. The reported method relies on the controlled pyrolysis of the samples with helium attendance in pyrolysis oven. With the heating of the sample to an initial temperature of 350 ^{0}C, distilled out the free hydrocarbons already present in the rock. They are measured by the flame ionization detector (FID) and give S1 peak in diagram. Subsequently, when the sample temperature reaches the 550 ^{0}C, the thermal cracking of kerogen (S2 peak) causes the generation of an amount of hydrocarbons. At the top of the S2 peak, the temperature at maximum release of hydrocarbons (Tmax) is appeared. During the pyrolysis up to a temperature of 390 ^{O}C released the trapped CO2 and detected by thermal conductivity detector (TCD), constituting S3 peak (Figure 3) (Georgakopoulos [4]). Using the direct measurements of Rock Eval pyrolysis, some derived parameters can be calculated and conclusions about organic matter are deduced. Minutely, the hydrogen index (HI=S2/TOC) and the oxygen index (OI=S3/TOC) are evaluated and along with the S2/S3 ratio, indicate the type of organic matter in a pseudo van Krevelen diagram. The petroleum potential (PP mg/g), which is equal to the sum of S1 and S2 peaks and the total organic carbon (TOC %), are used as quantity parameters. Another variable, the production index (PI=S1/S2+S2) together with Tmax are used as maturity parameters.

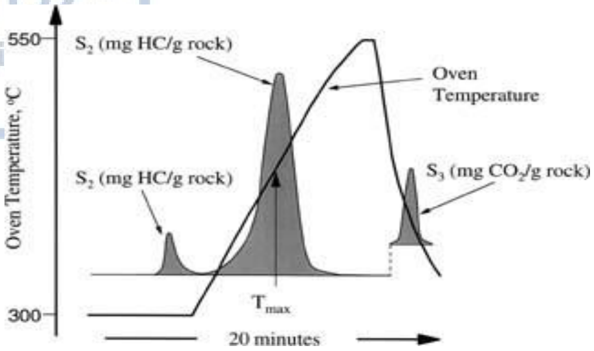

Figure 3: Schematic Rock-Eval pyrogram

(Source: https://link.springer.com/referenceworkentry/10.1007/1-4020-4496-8_276)

On the other hand, the samples are analyzed microscopically under fluorescent, transmitted or reflected light, after their selection from every horizon of interest. The identification of the principal maceral groups provides further information about the kerogen quality. In addition, the maturity can be calculated from the optical examination of the organic matter, with the vitrinite reflectance (Ro %) and the spore coloration, which is expressed by the thermal alteration index (TAI). The boundaries of oil window range from 0.6 to 1.35 %, whereas gas window from 0.8 to 3 %, regarding to vitrinite reflectance. In addition, the carbon preference index (CPI) is a ratio of alkanes equal to: 2× (nC_{23}+nC_{25}+nC_{27}+nC_{29}) / (nC_{22}+ 2× (nC_{24}+nC_{26}+nC_{28}) +nC_{30}), estimating the type of source material, the environment of deposition and the maturity of organic matter. The chemical analyses of bitumens obtain extra information on the organic matter characteristics of the potential source rocks. The combination, of gas chromatography (GC) and mass spectroscopy (MS) is applied for biomarkers designation. As maturity parameters are used biomarker classes, such as steranes, terpanes and aromatic steroids. The pristane and the phytane appertain to acyclic isoprenoids and define redox conditions in the depositional environments. Aromatic compounds, such as methylphenanthrene (MPI) are used widely as maturity indicators (Oikonomopoulos [10]).

2.2 Potential source rocks

The leading source rocks of the Ionian zone are the following: The Triassic shales in the subsurface evaporites. Their deposition took place in restricted subbasins, as stratigraphic layers in mainly shallow waters in the evaporite basin. The preservation of the organic matter was favored by the evaporitic sedimentation in the entire basin. The formation of the evaporite collapse breccias controlled by processes, via which also caused the fragmentation of the initial organic-rich layers, occurring today as organic-rich shale fragments within the Triassic breccias. The organic carbon content of these shale fragments indicates a very high total organic carbon of as much as 16.12 %, a very good petroleum potential (8.9-98.8 mg HC/g of rock) and type I oil-prone organic matter. Additionally, in the north Mavroudi outcrop there is type III gas-prone organic matter.

The lower Posidonia beds, which are comprised of well-bedded pelagic laminated marls, siliceous argillites, and marly limestones, show deviations in facies and thickness relying on their position in each half graben. The included ammonites and nannofossil assemblages indicating the Toarcian age of this formation. The TOC content of lower Posidonia beds varies from 1.05 % to 19.12 %, the organic matter is of types I to II (prone to oil generation) , their PP between 4 and 125.85 mg HC/g of rock and in most cases, are mature relatively the oil generation , having entered the oil window. The organic matter accumulated and preserved in the Ionian basin, affected by the geometry of the syn-rift period. The geometry of the restricted subbasins was beneficial for the water stagnation and consequently, the establishment of local euxinic conditions in the bottom waters.

The upper Posidonia beds of the Ionian zone include of jasper beds with cherty clays, usually bituminous. The cherty horizons have high percentage of Posidonia and radiolaria, Upper Callovian to Tithonian age. The TOC content ranges from 1.05 % and 3.34 % for the upper Posidonia beds and is mainly mature regarding to the oil generation. “In many places of the Ionian zone, the upper Posidonia beds are not clearly differentiated from the lower Posidonia beds, and the whole formation is examined as undifferentiated Posidonia beds” (Karakitsios et al., 2013). Based on possible differences in the geochemical analysis of the samples, it will be found if the Posidonia bed is undifferentiated or not in this area.

The Vigla shale horizons of the Vigla limestones formation, are marly limestone and cherty beds with shale interbedding. The age of Vigla shales is Aptian-Early Turonian based on radiolaria and globotruncanids. They have an average TOC of 3.29 % and a PP 16.21 mg HC/g of rock in wells, whereas the corresponding values in outcrops are 3 % and 19.04 mg HC/g accordingly. Their kerogen is of types I to II originating from marine organisms under reducing conditions and is able to generate mainly liquid hydrocarbons. "The Vigla shales, in the central and external Ionian zones, are in the early maturation stage, whereas, in the internal Ionian zone, they are mature in terms of oil generation" (Karakitsios, 2013). The accumulation and preservation of organic matter in the Vigla shale horizon is generally associated to preserved subbasins, due to the continuity of halokinetic movements during the post-rift period.

The marls underlying the Ammonitico Rosso limestones. They contain dark gray to blue-green foliated marls and marly wackestones. There are reduced quantities of organic matter (type II to III), to the majority of the horizons. In spite of that, two horizons were identified with high organic matter ranging between 3.46 to 4.07 %, petroleum potential up to 17.6 mg/g and type I highly oil prone kerogen.

The heat flow and therefore the geothermal gradient in the area, decreases towards the west, as well as the degree of maturation. Furthermore, the maturation takes place in greater depths, due to the low values of the geothermal gradient. The timing of maturation of the principal oil source rocks, as it is given from the maturity-versus-time model indicates that Triassic shales entered the oil window in the Late Jurassic, whereas the lower Posidonia beds in the Serravalian. The Vigla shale member in the internal Ionian zone entered the oil window after the Serravalian. "It is important that, in the two last cases, maturity occurred after the Ionian zone orogenesis (Burdigalian) and the subsequent formation of the trap structures" (Rigakis, 1999).

2.3 Source rocks presence in wells

2.3.1 Agios Georgios 3 well

Agios Georgios 3 well in the internal Ionian zone is located 30 km northwest of Arta and was held to the limits of Arta's syncline. Regarding the stratigraphy, at 210 to 1980 meters there is flysch, followed by Middle-Late Eocene limestones until 2100 m and Early Eocene-Senonian microbreccious limestones up to 2680 meters. The overlying Vigla sequence contains pelagic limestones and cherts alterations, whereas two shales horizons in the intervals 3120-3270 m (Vigla shale A) and 3375-3580 m (Vigla shale B) are found. From the depth of 3220 m till the total depth of drilling, the percentage of $MgCO_3$ is increased, indicating the dolomitization of the formation. The interval between 3960-4210 m is characterized by the Posidonia shales. Eventually, the last formation is Pantokrator's dolomites (Figure 4).

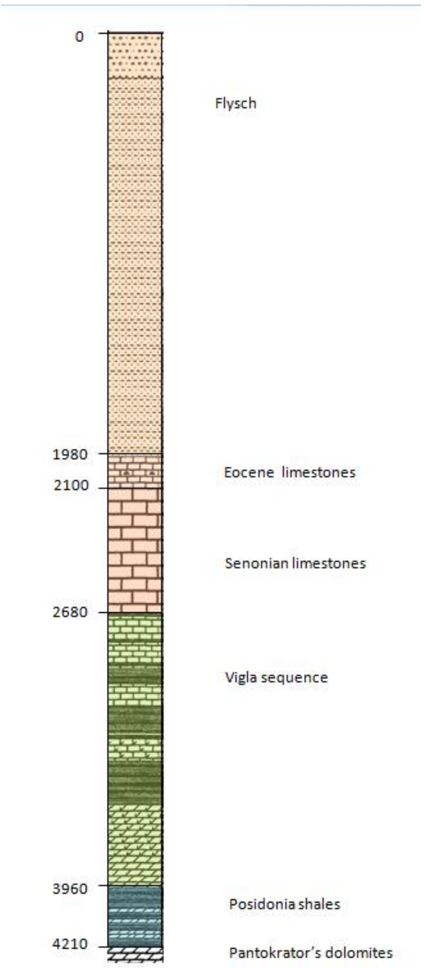

Figure 4: Cartoon of the actual Agios Georgios 3 well (data from Rigakis N., 1999 [11])

Using data of Hellenic Petroleum S.A. (Rigakis, 1999), abundance samples were analyzed with Rock Eval and other methods. The results reveal that, the main source rocks are the Vigla shales, which are rich to very rich in organic matter (Figure 5). The most promising horizons are the above ones, with total organic carbon (TOC) up to 11.7 % and petroleum potential (PP) up to 60.9 mg/g while TOC up to 4.8 % and PP up to 23.5 mg/g ,respectively (Figure 6).

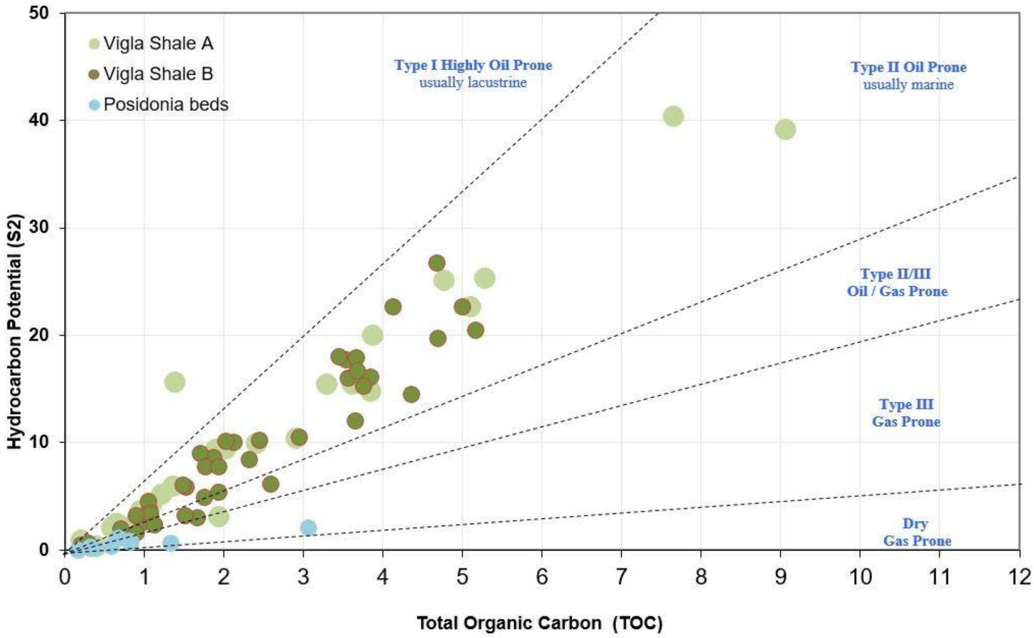

Figure 5: Total organic carbon versus hydrocarbon potential of source rocks of Agios Georgios 3 well (data from Rigakis N., 1999 [11])

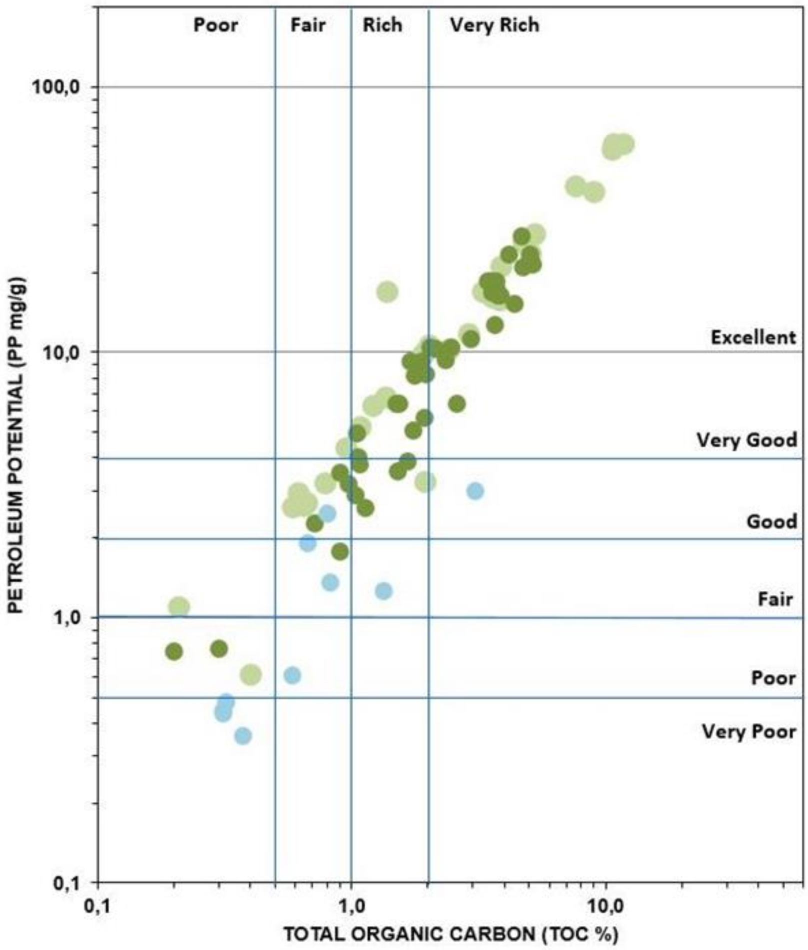

Figure 6: Determination of the quantity of the organic matter (Rigakis N., 1999 [11])

The very high hydrogen indexes in relation to the very low oxygen indexes and also their maceral content indicate a type I to II organic matter, capable for oil generation (Figure 7). Since total organic carbon and hydrogen index comprise high values, a deep sea environment with anoxic conditions can be assumed.

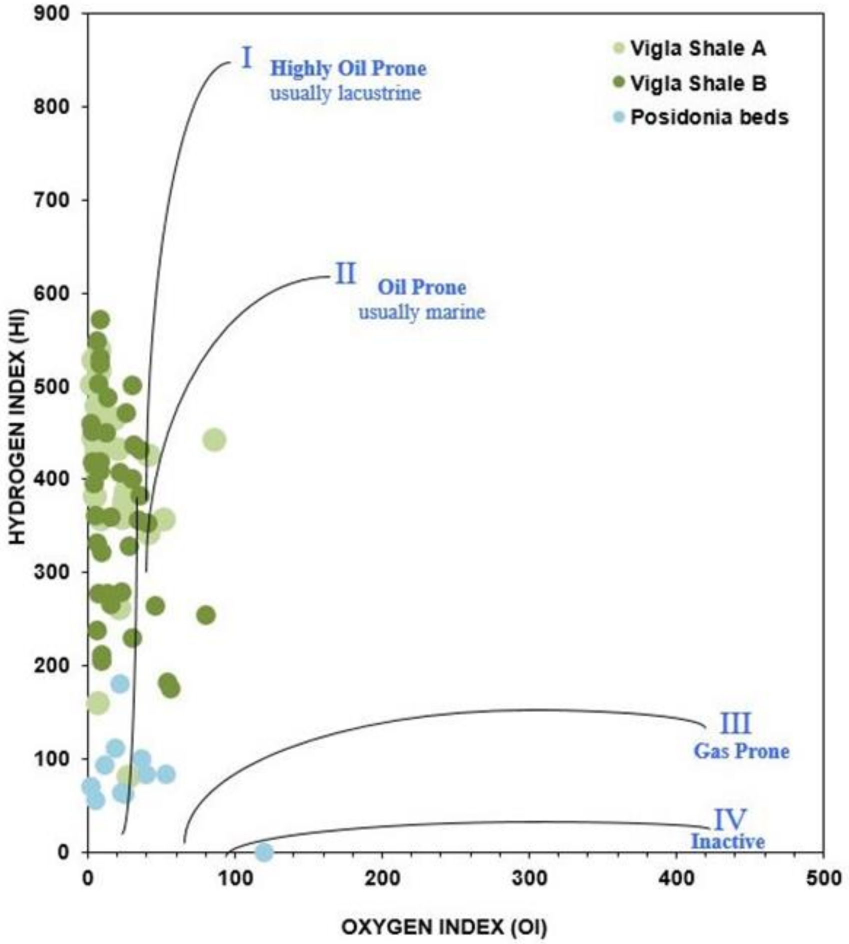

Figure 7: Hydrocarbon index versus Oxygen index showing the hydrocarbon generation types (Rigakis N., 1999 [11])

The Vigla source rocks are mature, since the onset of oil generation is identified at 2950m depth, as concluded from vitrinite reflectance (Ro %) measurements and confirmed by biomarker maturity ratios and Rock Eval data (Tmax and PI) (Figure 8).

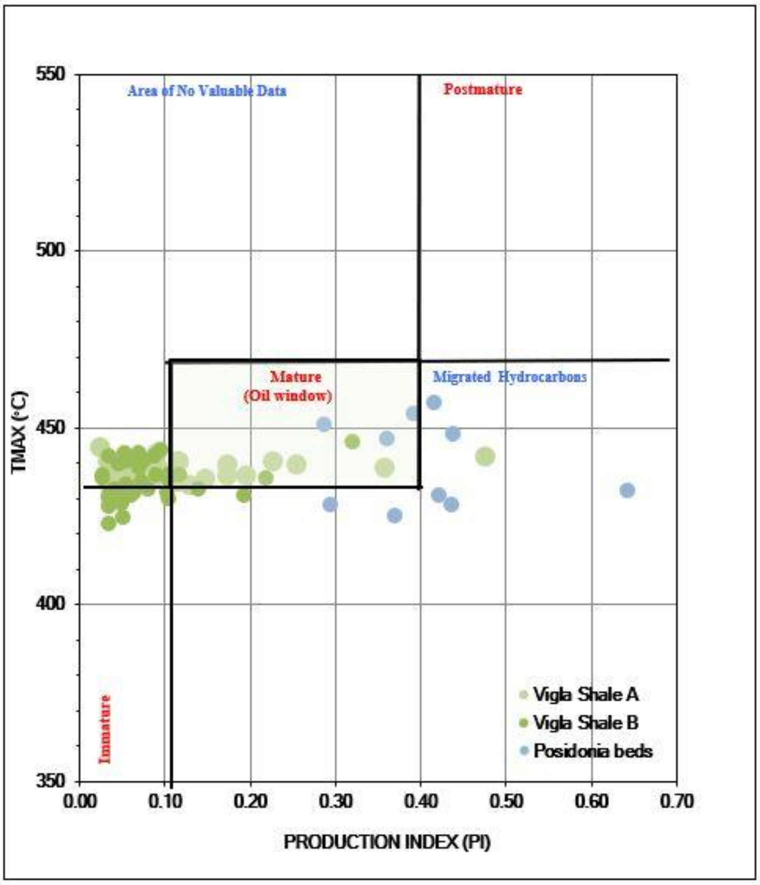

Figure 8: Determination of the maturity of the organic matter using PI and Tmax (data from Rigakis N., 1999 [11])

In Agios Georgios 3 well, almost all samples from carbonate sequence have a Tmax greater than 430 ^{0}C, leaking out they have entered the oil window. The highest rate reaches 460 ^{0}C (Figure 9).

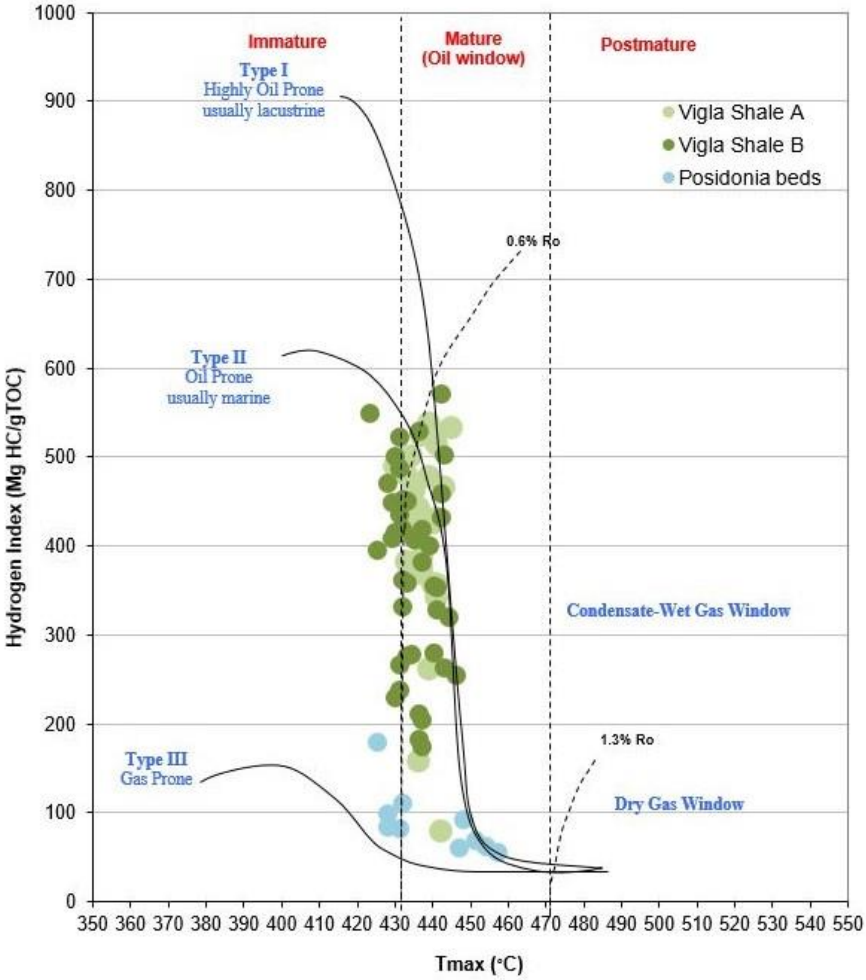

Figure 9: Determination of the maturity of the organic matter using HI and Tmax (Rigakis N., 1999 [11])

Additionally, seven samples have been examined with the following biomarker parameters: C_{29} steranes 20S/20R +20S, Ts/Tm+Ts terpanes, C_{32} homohopanes 22S/22R + 22S, triaromatic steroids $C_{20}/C_{20}+C_{28}$ and the triaromatic to triaromatic plus monoaromatic steroids ratio (T/T+M), where T represents C_{20}, C_{28} compounds and M is C_{29} compound. The information concludes about organic matter maturity from biomarkers, is not always compatible to other methods. The homohopanes ratio has value 0.64 which remains stable in almost all samples. The balance of this chemical reaction succeeding in mature degree 0.6 % Ro. Consequently, the outset of oil generation depending on homohopanes, has been made at a depth lesser than 2300 meters. Commensurate results have the aromatic steroids. On the contrary, the beginning of oil generation is done at 2900 m depth, based on steranes diagram. This depth is well correlated to vitrinite reflectance method one. From the Ts/Tm+Ts ratio, oil generation starts at a depth of 2300 to 3200 meters. Ultimately, another important inference from this well is that, clastic sediments dispose organic matter type III which may produce gas hydrocarbons, while carbonate sediments contain organic matter type I or II available for oil generation (Rigakis, 1999).

2.3.2 Dragopsa 1 well

The lower Posidonia beds are the most promising hydrocarbon source rocks in the central and external Ionian zone, containing high quantities of organic matter in several outcrops and drilled wells. In this well, the undiffererentiated Posidonia beds were penetrated in the depth interval of 1477.5 to 1601 m. According to the lithological characteristics there are siliceous marly limestones in alterations with very thin-bedded marls and thin layers of chert. The real formation thickness is evaluated to be less than 80 m, as the dip differs from 36-50 ^{o} in the core samples at 1450-1485 m depth respectively. The horizons of the siliceous marly limestones have high rates of organic carbon (TOC=1.10-5.88 %) and also great petroleum potential (PP =5.91-39.46 mg/g). The parallelism of the high HI and the low OI, as well as the high quantities of algal matter concentrated in the kerogen, indicating that the organic matter is type I to II. Even remarkable amounts of organic matter are detected within the thin-bedded marls, with TOC between 6.85-19.12 % and petroleum potential between 46-125.85 mg/g. “These horizons are the best known source rocks in western Greece” (Karakitsios and Rigakis, 1998). Additionally, the PI values in the well samples are too low and the Tmax is less than 435 ^{0}C in all the formations, indicating first immaturity and second lack of any migrated hydrocarbons. Immaturity of organic matter is also corroborated by high HI values. Regarding the biomarkers, the values of different compounds designate immaturity of the samples. More specifically, the 20S/20R +20S ratio of C_{29} steranes are increasing with well depth and in correlation with the vitrinite method, the ratio value of 0.40 was defined as the upper limit for oil generation. The Ts/Tm+Ts ratio of terpanes has values which increase from the youngest to the oldest formations, indicating the gradual maturation of the organic matter. Combining the above ratio with the vitrinite reflection method, the inception of oil generation is carried out at the value of 0.48. What’s more, the equilibrium value of 22S/22R + 22S ratio of C_{32} homohopanes is 0.60, estimating to be the onset of oil generation. This value is reached at 1880 m depth. From the aromatic steroids, measurements of (T/T+M) ratio give similar results to those of the other methods.

2.3.3 Ioannina 1 well

In this well, which is located north of Ioannina city, the Vigla formation is the first Alpine formation underlying the Quaternary and Neogene sediments. It is found between 300 to 610 meters depth. Some shaly horizons were found from 460 to 480 m depth. The interval from 610 to 990 m depth is covered by the undifferentiated Posidonia beds. They consist of alternations of marly limestones, black shales and cherts. Continuing the stratigraphic sequence, Siniais limestones enclose 990 to 1.150 meters, whereas Pantokrator limestones represent the interval from 1.150 to 1.240 m depth. Last but not least, there are Triassic breccias from 1.240 to 1.530 meters. In addition, several horizons of possible source rocks have been identified. The shales of the Vigla formation can potentially generate hydrocarbons as TOC ranges from 1.44 to 2.24 % and petroleum potential from 7.3 to 13.6 mg HC/g of rock. The HI values are greater than 475, indicating good quality of the organic matter. Moreover, the kerogen is of type I to II originated from marine organisms, with the ability to generate mainly liquid hydrocarbons. This outcome is enhanced by the kerogen concentrates, as the percentage of algal and amorphous material reaches 57 to almost 100 %. The undifferentiated Posidonia beds have a high potential of oil generation. More detail, the TOC ranges from 1.05 to 4.50 %, with two excessive values of 5.87 and 9.82 % at 910 m and 940 m respectively. Petroleum potential ranges from 4 to 21.54 mg HC/g of rock, with three extremely high values at 945, 910 and 940 m depth of 28.90, 33.88 and 64.09 mg HC/g of rock in the order given. The HI values vary from 460 to 565, expressing the good quality of the organic matter. Correlating the mentioned index with the low OI values in the pseudo van Krevelen diagram, the type of organic matter is defined as I-II, prone to oil generation. In the Ioannina 1 well, very high amounts of organic matter detected after the analysis of few shale fragments from the Triassic breccias. Initially the processing of a pure shale fragment from a core at 1250 m depth, indicating a very high TOC up to 11.15 %. The analogous petroleum potential value was too high, reaching 74.02 mg HC/g of rock. This sample has a very good quality (type I) organic matter (Karakitsios and Rigakis, 1996). Furthermore, a few shale fragments in the interval of 1.250-1.270 m were analyzed and gave very high TOC (1.62-16.12 %), very good petroleum potential (8.9 -98.8 mg HC/g of rock) and type I oil-prone organic matter. The Tmax values are less than 435 ^{0}C,indicating the immaturity of the organic matter and only the sample at 1.250 m depth has a Tmax value of 436 ^{0}C, referring to the top of the oil window. Depending on the diagram between Tmax and depth, the upper limit of the oil window measured at about 1400 m depth. Relating to the biomarker maturity parameters, the equilibrium value of 22S/22R + 22S ratio of C_{32} homohopanes is 0.60 reached at 1100 m depth. By using the 20S/20R +20S ratio of C_{29} steranes, the oil window will be at 1250 m depth, corresponding to calculated depth from different methods. From the aromatic steroids, the beginning of oil generation is at 1100 m depth. According to the above methods for the maturity determination in western Greece, using the biomarkers, is indicated to examine the data initially with C_{32} homohopanes and C_{29} steranes, which values are very sensitive to low maturity ranges. Provided that the equilibrium of these compounds has occurred, specifically in increased maturity stages of the organic matter, the maturity degree can be defined by aromatic steroids methods (Rigakis, 1999).

Chapter 3

Biomarkers analysis of potential source rocks

The petroleum biomarkers are defined as complex organic compounds, which provide important information about the depositional environment and preservation conditions of the organic matter of a source rock. Using the available data of biomarkers for source rocks of the Ionian zone, the depositional paleoenvironment and the maturity trend of these source rocks can be assessed. The Pr/Ph ratios in combination with CPI index and the MPI versus Vitrinite reflectance are used in this study (diagrams below). The results together with those of Rock Eval method indicate parameters beneficial for further research and modeling of the region. The table below (Table 1) summaries the biomarker data derived from a Triassic source rock interval (well) and an oil seep (surface exposure of hydrocarbons) at central Ionian basin.

Table 1: Biomarkers data results of the Triassic source rock

Depth (m)	Area/Well	Formation	Pr/Ph	Pr/nC17	Ph/nC18	CPI
922	Well C - Delvinaki	Triassic shales	1,02	0,46	0,44	1,11
5075	Delvinaki	Triassic	0,64	0,98	1,43	3,79

The derivative diagrams are:

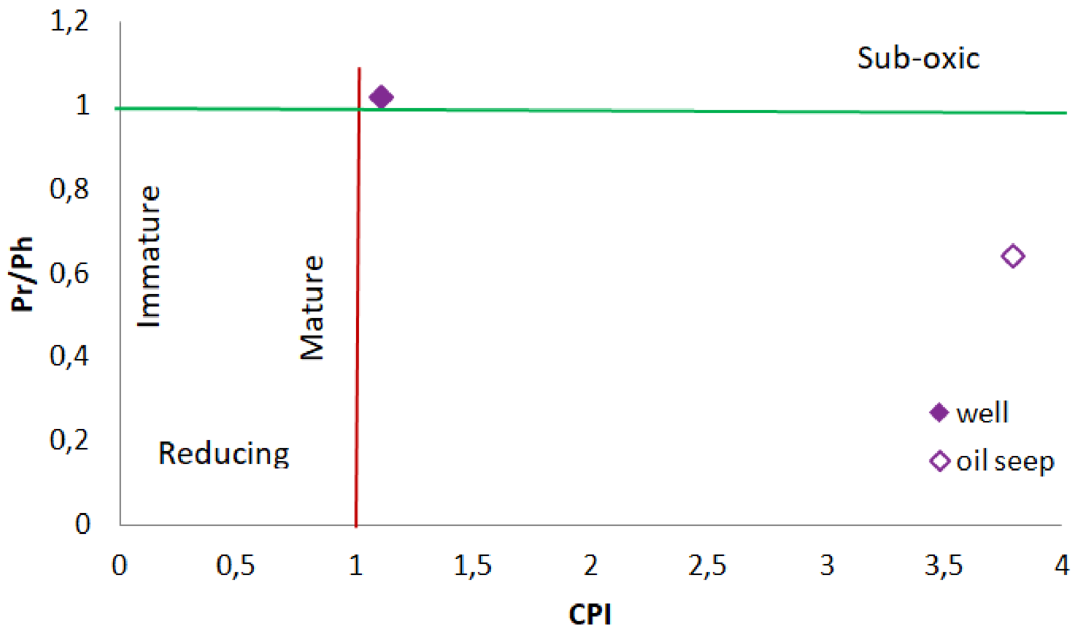

Figure 10: Pr/Ph versus CPI plot for the Triassic source rock

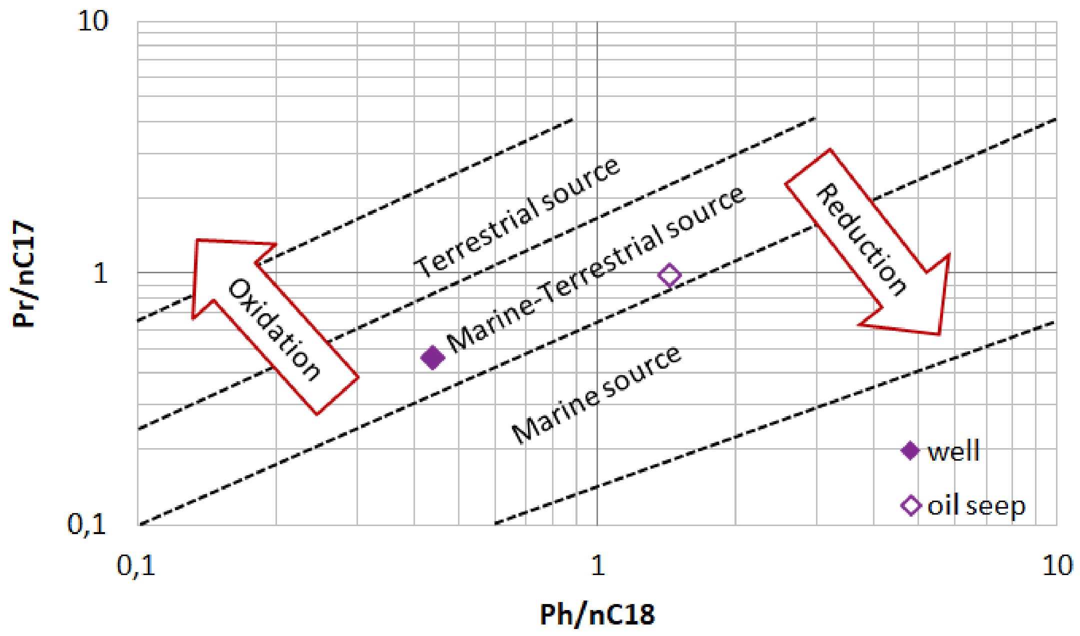

Figure 11: Pr/nC17 versus Ph/nC18 plot for the Triassic source rock

The Pr/nC17 versus Ph/nC18 plot (Figure 11) of the Triassic source rock sample shows a mixed marine-terrestrial source of organic matter (kerogen type II and III), whereas the Pr/Ph ratio is > 1 (Figure 10) suggesting sub-oxic conditions during the deposition and preservation of organic matter. The CPI value of the Triassic source rock sample is 1.1 (Figure 10) indicating that the organic matter is at the onset of the oil window and thus at the early maturity stage. On the other hand, the Pr/Ph ratio of the oil sample is < 1 indicating that the oil is related with the type II kerogen of the above described Triassic source rock. Correlation with marine organic matter is also suggested by the Pr/nC17 versus Ph/nC18 plot (Figure 11). The CPI of the oil sample is much higher than 1.2 (Figure 10) pointing to immature oil, which is in accordance with the early mature Triassic source rock.

The Jurassic Posidonia source rocks are studied in the internal, the central and the external Ionian zone (westwards). The samples from the internal Ionian and their following results are presented below.

Table 2: Biomarkers data results of the Posidonia source rocks in the internal zone

Depth (m)	Area/Well	Formation	Pr/Ph	Pr/nC17	Ph/nC18	CPI
4004	Well B - Agios Georgios	lower Posidonia beds	0,61	0,39	0,64	0,95
4204	Well B - Agios Georgios	lower Posidonia beds	1,03	0,23	0,26	0,98

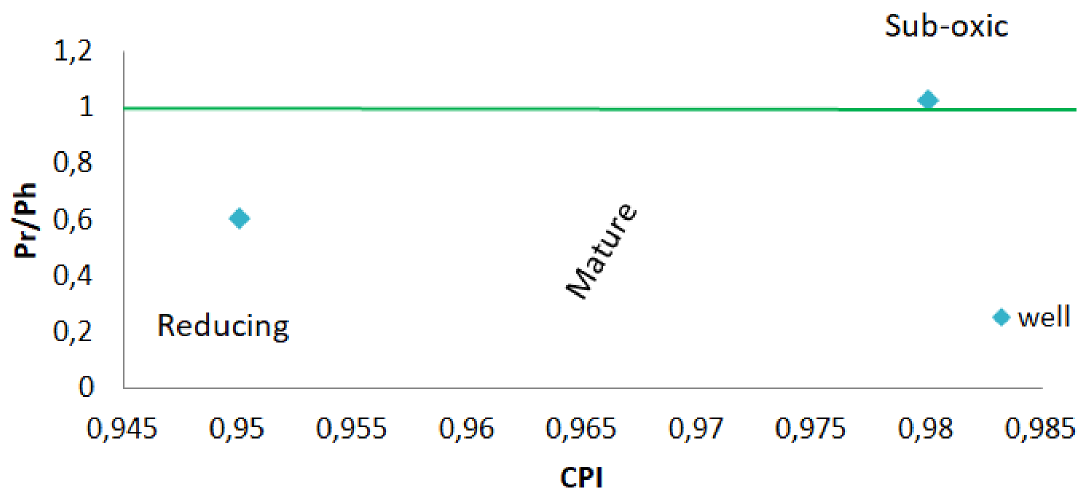

Figure 12: Pr/Ph versus CPI plot for the Jurassic Posidonia source rocks in the internal zone

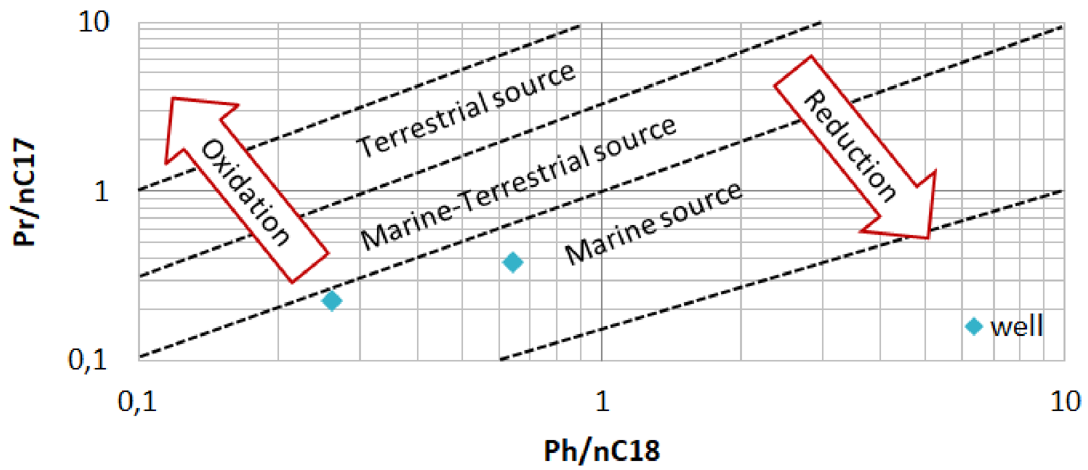

Figure 13: Pr/nC17 versus Ph/nC18 plot for the Jurassic Posidonia source rocks in the internal zone

The Pr/nC17 / Ph/nC18 ratio is < 1, indicating marine origin of the organic matter (kerogen type II) for the Posidonia source rocks in the internal zone (Figure 13). The Pr/Ph ratio ranges till the unity (Figure 12), showing mainly reducing conditions during the deposition and preservation of organic matter. The CPI values of the samples are < 1 pointing out that the organic matter is mature (Figure 12).

The data and the diagrams for the Jurassic Posidonia source rocks in the central Ionian zone are:

Table 3: Biomarkers data results of the Posidonia source rocks in the central zone

Depth (m)	Area/Well	Formation	Pr/Ph	Pr/nC17	Ph/nC18	CPI
690	Well A-GEMEE	upper Posidonia beds	1,74	1,01	0,7	0,83
945	Well A-GEMEE	lower Posidonia beds	0,65	0,15	0,73	1
2078	Paliogribiani	Posidonia beds	1,06	1,16	2,23	1,06
57	Sistrouni	Posidonia beds	1	3,3	1,8	1
60	Sistrouni	Posidonia beds	1,1	4,3	3,6	1
61	Sistrouni	Posidonia beds	1,2	1,02	0,63	ND
65	Sistrouni	Posidonia beds	1,9	1,5	0,5	1,07
67	Sistrouni	Posidonia beds	2	1,4	0,3	1
1485	Dragopsa 1	Posidonia beds	1,4	0,6	0,6	1,14
1486	Dragopsa 1	Posidonia beds	1,22	0,97	0,94	0,98
928	Elataria	Posidonia beds	1,79	1,25	1,4	1,09
938	Elataria	Posidonia beds	1,28	1,65	1,63	1,23
947	Elataria	Posidonia beds	1,19	0,94	0,63	1,06
5010	Petousi	Posidonia beds	1,25	0,93	1,28	1,18
5023	Petousi	Posidonia beds	1,11	0,63	0,79	1
5030	Petousi	Posidonia beds	0,99	1,04	3,14	0,95
4054	Petousi	Posidonia beds	0,92	1,21	2,96	1,23

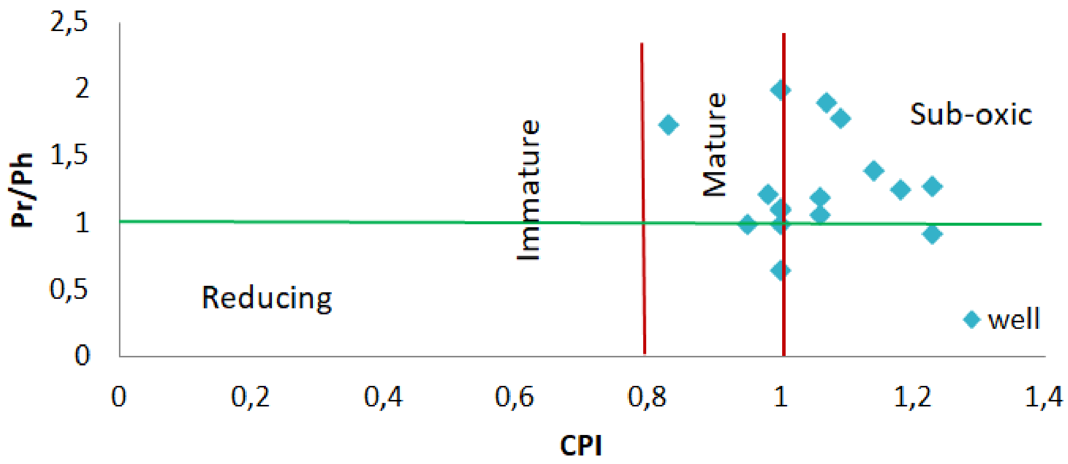

Figure 14: Pr/Ph versus CPI plot for the Jurassic Posidonia source rocks in the central zone

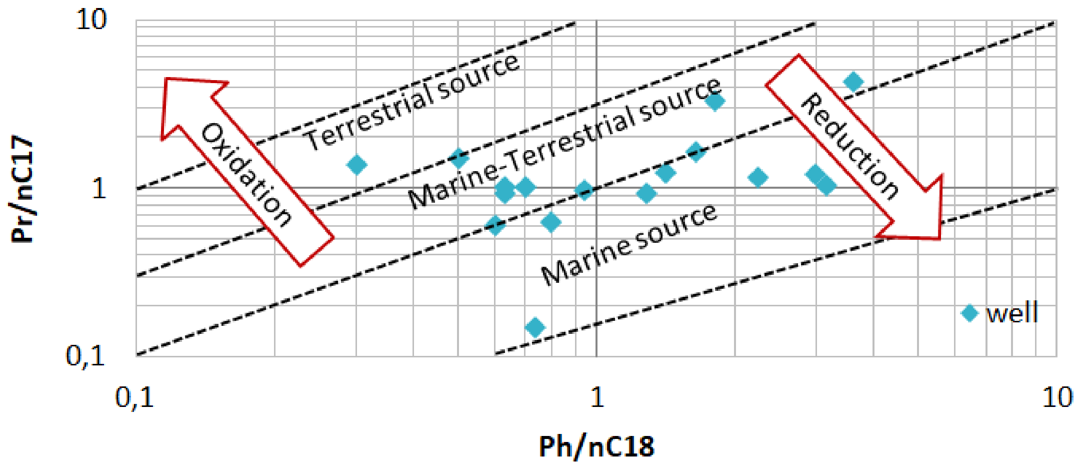

Figure 15: Pr/nC17 versus Ph/nC18 plot for the Jurassic Posidonia source rocks in the central zone

The Pr/nC17 versus Ph/nC18 plot of the Jurassic Posidonia source rocks samples in the central zone (Figure 15) shows a mixed marine-terrestrial to marine source of organic matter (kerogen type II and III). The majority of the samples have a Pr/Ph > 1 recommending sub-oxic conditions during the deposition and preservation of organic matter (Figure 14). The CPI values vary < 1-1.2 (Figure 14), indicating that the organic matter is within mid mature stage.

The Table 4 presents the biomarkers data for the Jurassic Posidonia source rocks in the external Ionian zone:

Table 4: Biomarkers data results of the Posidonia source rocks in the external zone

Depth (m)	Area/Well	Formation	Pr/Ph	Pr/nC17	Ph/nC18	CPI
2203	Fanеromeni	lower Posidonia beds	1,2	0,39	0,75	1,12
2218	Faneromeni	lower Posidonia beds	2,67	2,18	1,37	1,01
2250	Skandalo	lower Posidonia beds	0,64	0,6	0,98	1,07

The diagrams for the above samples are:

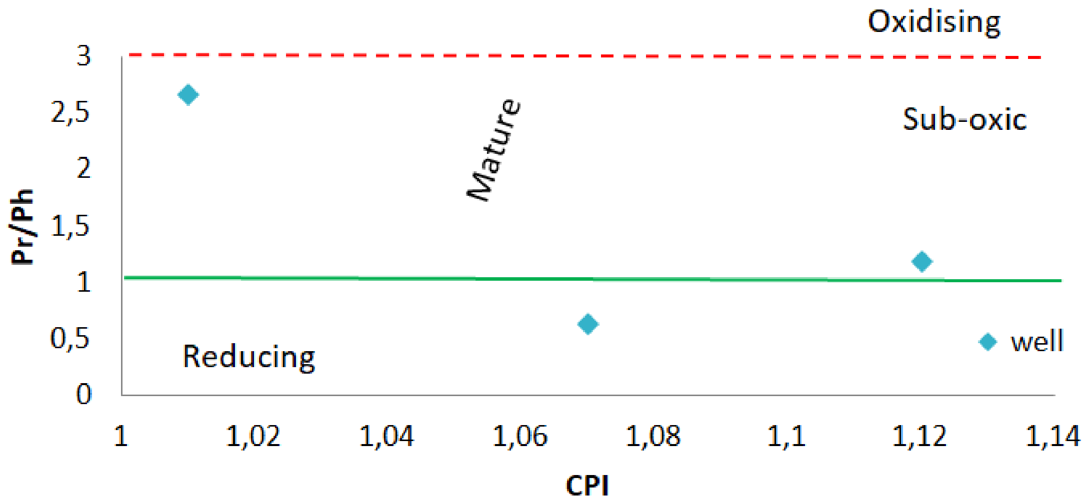

Figure 16: Pr/Ph versus CPI plot for the Jurassic Posidonia source rocks in the external zone

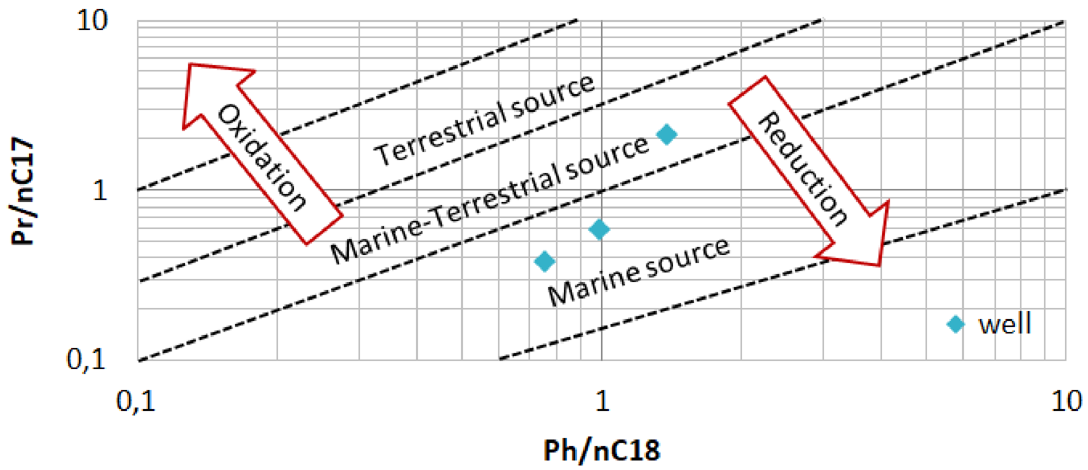

Figure 17: Pr/nC17 versus Ph/nC18 plot for the Jurassic Posidonia source rocks in the external zone

The Pr/nC17 versus Ph/nC18 plot (Figure 17) of the Posidonia source rocks samples in the external zone shows a mixed marine-terrestrial to mainly marine source organic matter. The Pr/Ph ratio is > 1 representing sub-oxic conditions, except the Scandalo sample of which ratio is < 1 representing reducing conditions during the deposition and preservation of organic matter (Figure 16). The CPI values are between 1-1.1 indicating an early mature stage of the organic matter (Figure 16).

The Tissot equation ((Tmax × 0.018)–7.16 = VRoeq) is used together with the MPI biomarker, in order to determine the maturity of the Posidonia source rocks. The available data and the plot for the internal zone are:

Table 5: Biomarker and Rock eval data results of the Posidonia source rocks in the internal zone

Depth (m)	Area/Well	MPI	VRoeq (Tissot)	Tmax (Rock eval)
4204	Well B – Agios Georgios	0,96	0,96	451

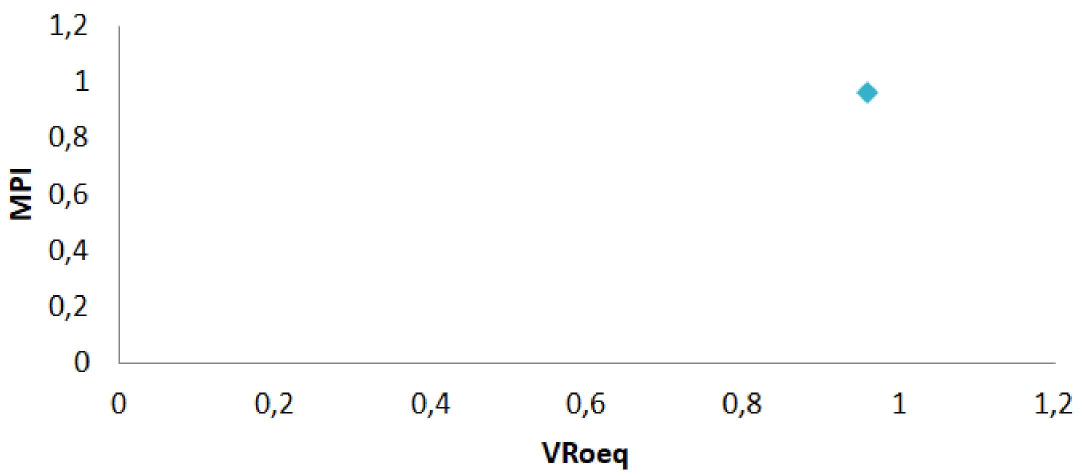

Figure 18: MPI versus Vitrinite reflectance for the Posidonia source rocks in the internal zone

The sample is mature and probably in peak oil window area based on the above data (Figure 18).

The data and the plot for the Posidonia source rocks in the central Ionian zone are:

Table 6: Biomarker and Rock eval data results of the Posidonia source rocks in the central zone

Depth (m)	Area/Well	MPI	VRoeq (Tissot)	Tmax (Rock eval)
690	Well A - GEMEE	0,58	0,42	421
945	Well A - GEMEE	0,51	0,6	431

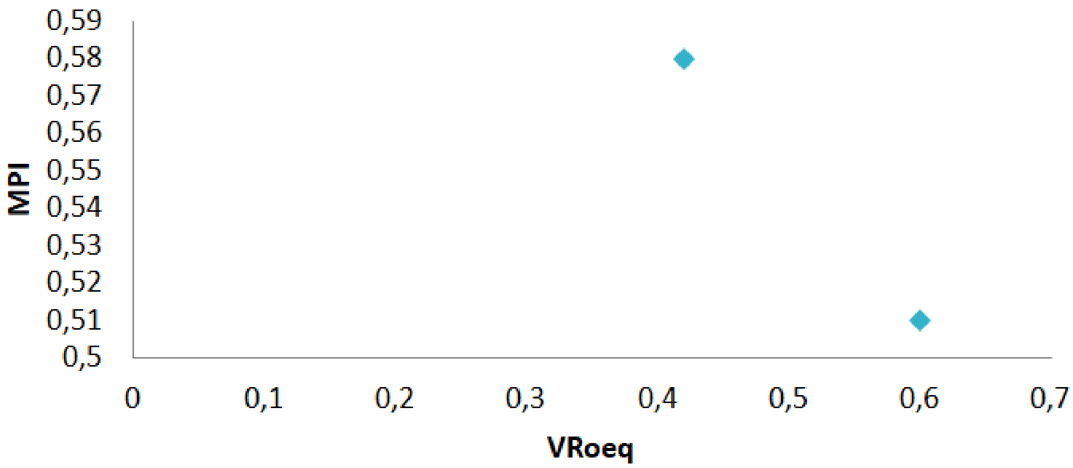

Figure 19: MPI versus Vitrinite reflectance for the Posidonia source rocks in the central zone

In accordance to the MPI and the VRo values, the samples are possibly found in the early oil window (Figure 19).

The examined sample and the plot of the Posidonia source rock in the external Ionian zone is:

Table 7: Biomarker and Rock eval data results of the Posidonia source rock in the external zone

Depth (m)	Area/Well	MPI	VRoeq (Tissot)	Tmax (Rock eval)
2218	Faneromeni	0,46	0,47	424

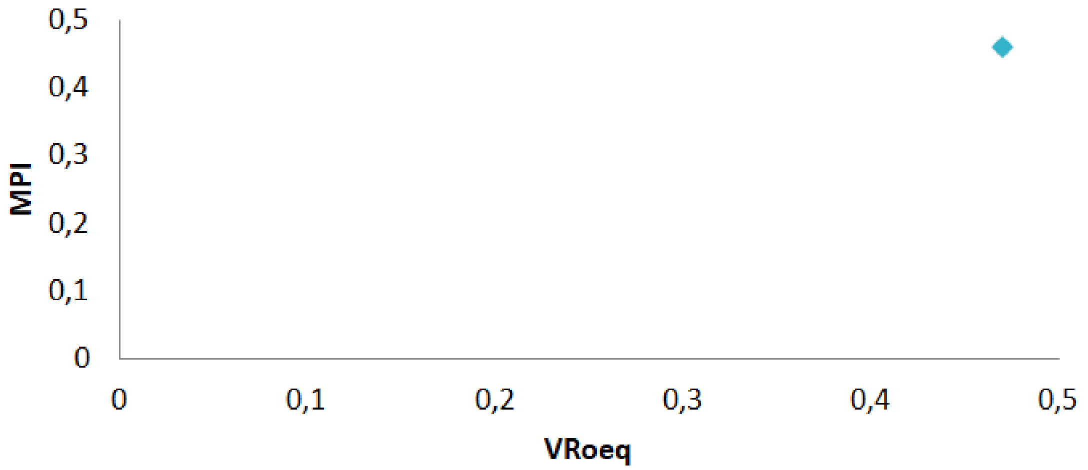

Figure 20: MPI versus Vitrinite reflectance for the Posidonia source rock in the external zone

The sample from the Posidonia source rock in this zone is immature relying on the given data (Figure 20).

The Table 8 summaries the biomarker data derived from Cretaceous Vigla source rocks (wells) and an oil seep (named Xirovouni) at internal Ionian basin:

Table 8: Biomarkers data results of the Cretaceous Vigla source rocks in the internal zone

Depth (m)	Area/Well	Formation	Pr/Ph	Pr/nC17	Ph/nC18	CPI
2016	Abelochori	Vigla	0,29	0,62	2,49	0,68
3224	Agios Georgios 3	Vigla	2,04	1,04	0,57	1,24
3235	Agios Georgios 3	Vigla	2,64	1,59	0,64	0,92
3236	Agios Georgios 3	Vigla	2,89	1,14	0,47	1,01
3378	Agios Georgios 3	Vigla	2,29	2,33	1,15	1,38
	Xirovouni	Vigla	0,5	0,33	0,36	1,27

The plots for the above data are:

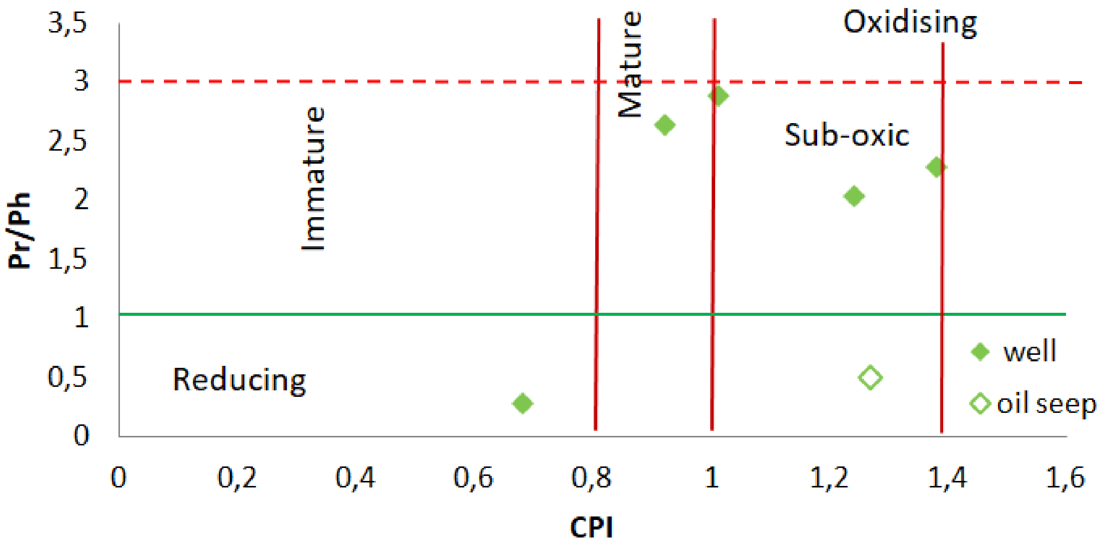

Figure 21: Pr/Ph versus CPI plot for the Cretaceous Vigla source rocks in the internal zone

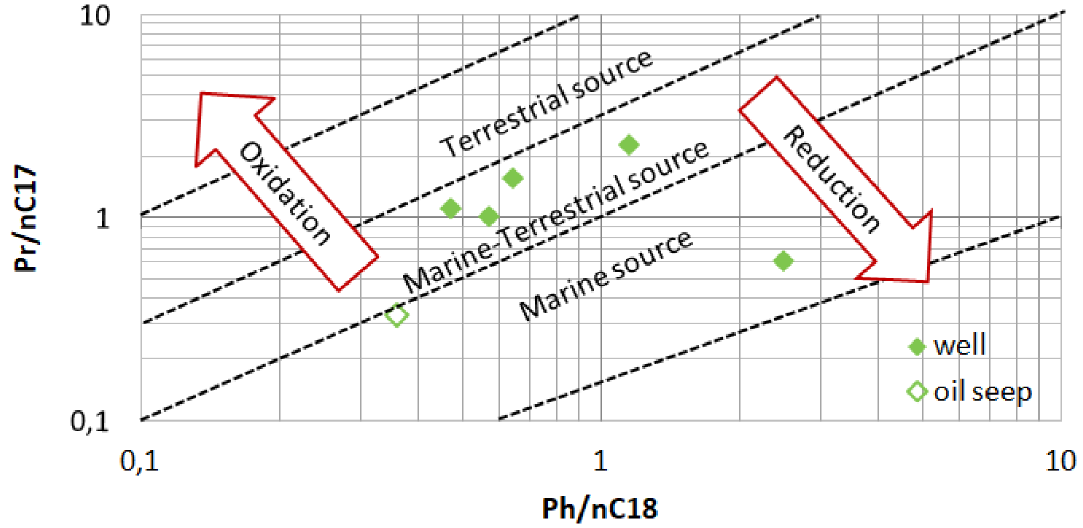

Figure 22: Pr/nC17 versus Ph/nC18 plot for Cretaceous Vigla source rocks in the internal zone

The Pr/nC17 versus Ph/nC18 plot (Figure 22) of the Cretaceous Vigla source rocks samples in the internal zone shows mainly a mixed marine-terrestrial source of organic matter (kerogen type II and III), whereas the Pr/Ph ratio is > 1 (except the Abelochori sample) suggesting sub-oxic conditions during the deposition and preservation of organic matter (Figure 21). The CPI values of the Vigla source rocks samples are < 1-1.3 (Figure 21) indicating that the organic matter is immature to medium mature. On the other hand, the Pr/Ph ratio of the oil sample is < 1 indicating that the oil is related with the type II kerogen of the above described Vigla source rocks. Correlation with marine organic matter is also suggested by the Pr/nC17 versus Ph/nC18 plot (Figure 22). The CPI of the oil sample is almost 1.3 (Figure 21) pointing to immature oil, which is in accordance with the immature-medium mature Vigla source rocks.

Moreover, there is a sample from Abelochori examined with the MPI and the VRo as shown:

Table 9: Biomarker and Rock eval data results of the Vigla source rock in the internal zone

Depth (m)	Area/Well	MPI	VRoeq (Tissot)	Tmax (Rock eval)
2016	Abelochori	0,41	0,49	425

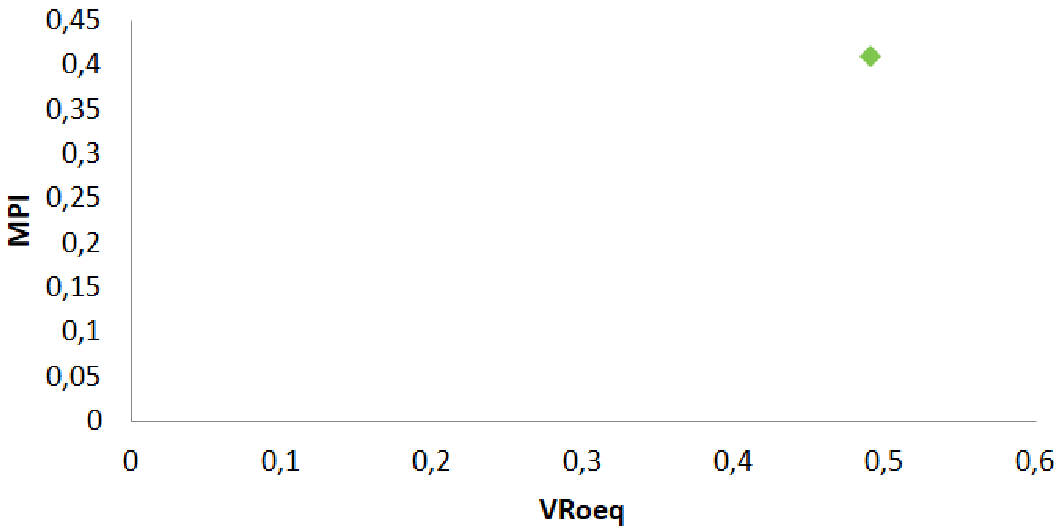

Figure 23: MPI versus Vitrinite reflectance for the Vigla source rock in the internal zone

The specific sample is probably found in the early oil window based on data (Figure 23).

The biomarkers measurements for Cretaceous Vigla source rocks and an oil seep (Giourganista) in the central Ionian zone together with their plots are:

Table 10: Biomarkers data results of the Cretaceous Vigla source rocks in the central zone

Depth (m)	Area/Well	Formation	Pr/Ph	Pr/nC17	Ph/nC18	CPI
480	Well A - GEMEE	Vigla	1,44	1,27	1,2	0,93
2275	Koukliou	Vigla	0,12	0,9	6,04	0,91
290	Gotzikas	Vigla	1,11	2,84	3,37	ND
296	Gotzikas	Vigla	2,05	3,93	2,04	0,95
1403	Gotzikas	Vigla	1,81	1,21	0,78	0,86
1413	Gotzikas	Vigla	2,07	1,79	1,15	1,05
2098	Giourganista	Vigla	0,13	0,18	0,93	5,19

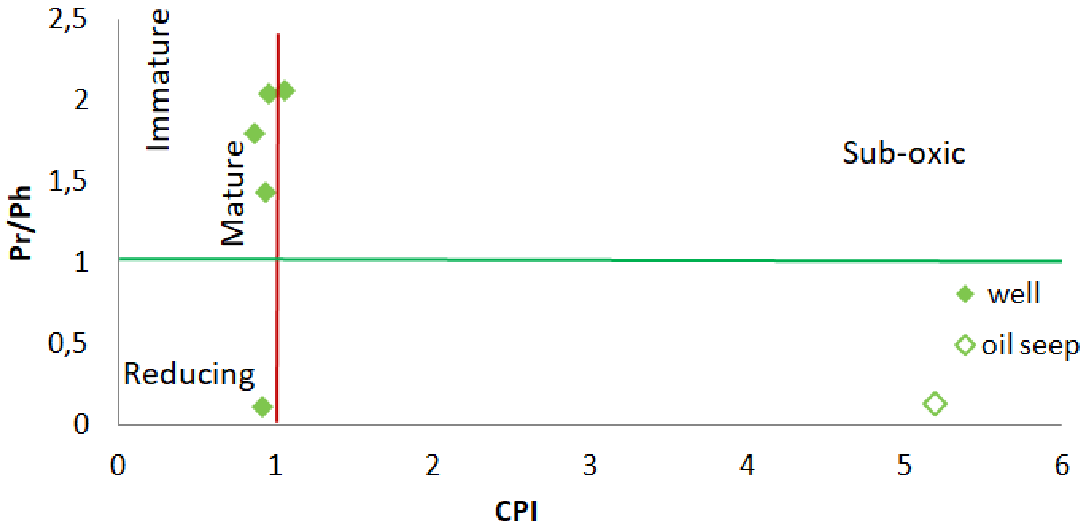

Figure 24: Pr/Ph versus CPI plot for the Cretaceous Vigla source rocks in the central zone

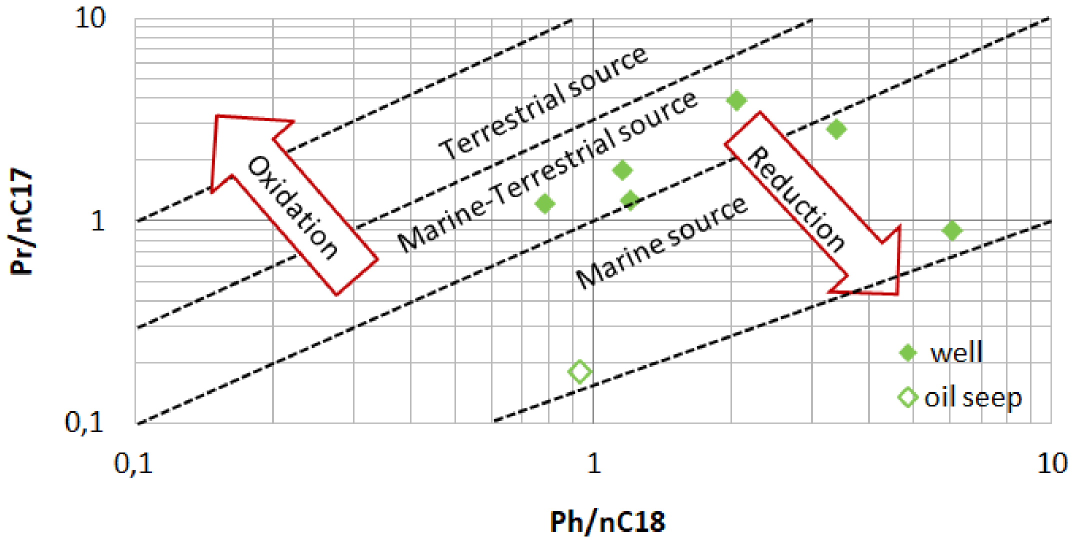

Figure 25: Pr/nC17 versus Ph/nC18 plot for Cretaceous Vigla source rocks in the central zone

The Pr/nC17 versus Ph/nC18 plot (Figure 25) of the Vigla source rocks samples in the central zone shows a mixed marine-terrestrial to marine source of organic matter (kerogen type II and III), whereas the Pr/Ph ratio is > 1 (except the Koukliou sample) suggesting sub-oxic conditions during the deposition and preservation of organic matter (Figure 24). The CPI values of the Vigla source rocks samples are ≤ 1 (Figure 24) indicating that the organic matter is at the onset of the oil window and thus at the early maturity stage. On the other hand, the Pr/Ph ratio of the oil sample is < 1 indicating that the oil is related with the type II kerogen of the above described Vigla source rocks. Correlation with marine organic matter is also suggested by the Pr/nC17 versus Ph/nC18 plot (Figure 25). The CPI of the oil sample is high (5.19) pointing to immature oil, which is in accordance with the early mature Vigla source rocks.

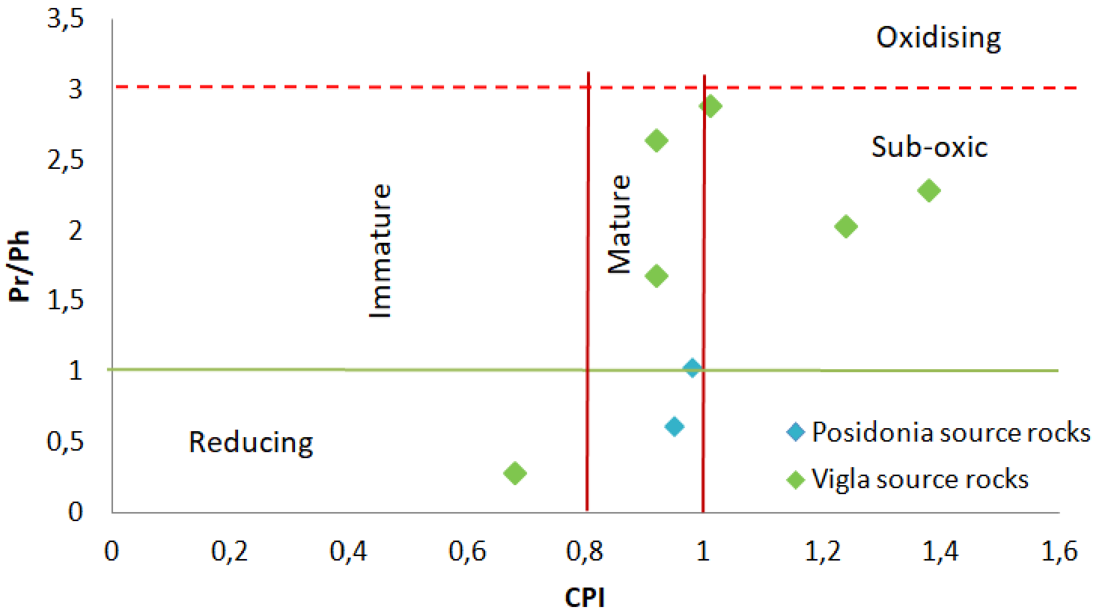

Figure 26: Pr/Ph versus CPI plot for the source rocks in the internal Ionian zone

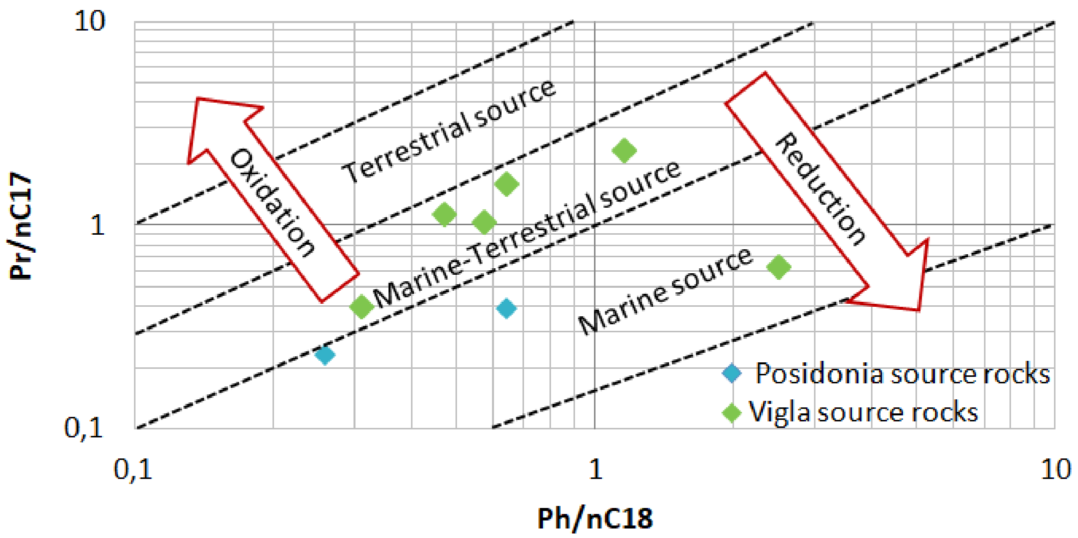

Figure 27: Pr/nC17 versus Ph/nC18 plot for the source rocks in the internal Ionian zone

Comparing the Cretaceous Vigla shales with the Jurassic Posidonia beds at the internal Ionian zone it seems that the organic matter has mixed terrestrial-marine and marine origin respectively (Figure 27). The organic matter was deposited under similar but not the same conditions. The Figure 26 suggest sub-oxic conditions for the Vigla shales (one sample only at the anoxic area), whereas the Jurassic Posidonia source rock was deposited and preserved under anoxic conditions (Pr/Ph about 1 or less). Based on CPI and VRo measured values, the organic matter is immature to medium mature for the Vigla source rock and within the middle oil window for the Posidonia source rock.

The plots of the biomarkers for the source rocks in the central Ionian zone in total are:

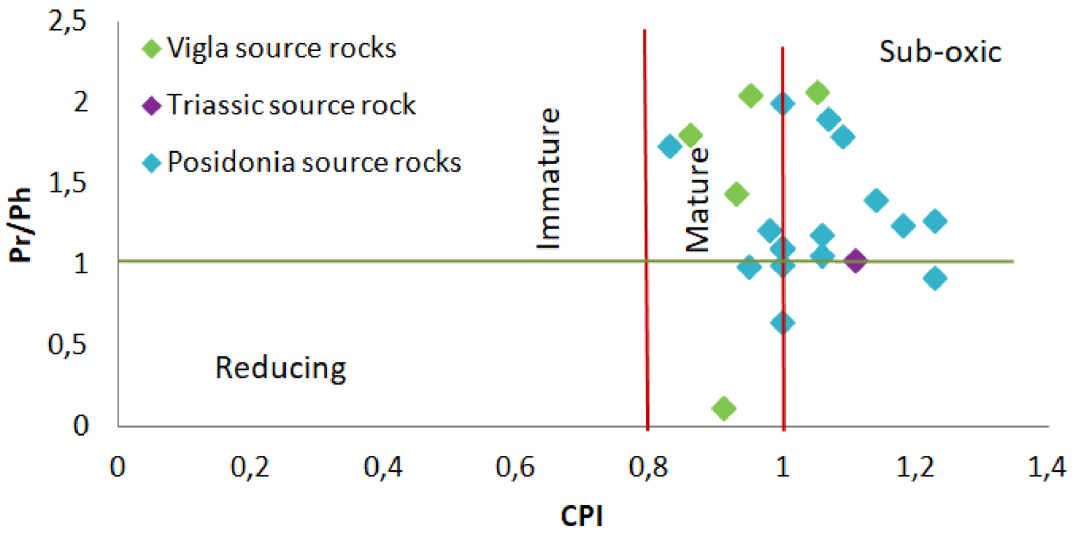

Figure 28: Pr/Ph versus CPI plot for the source rocks in the central Ionian zone

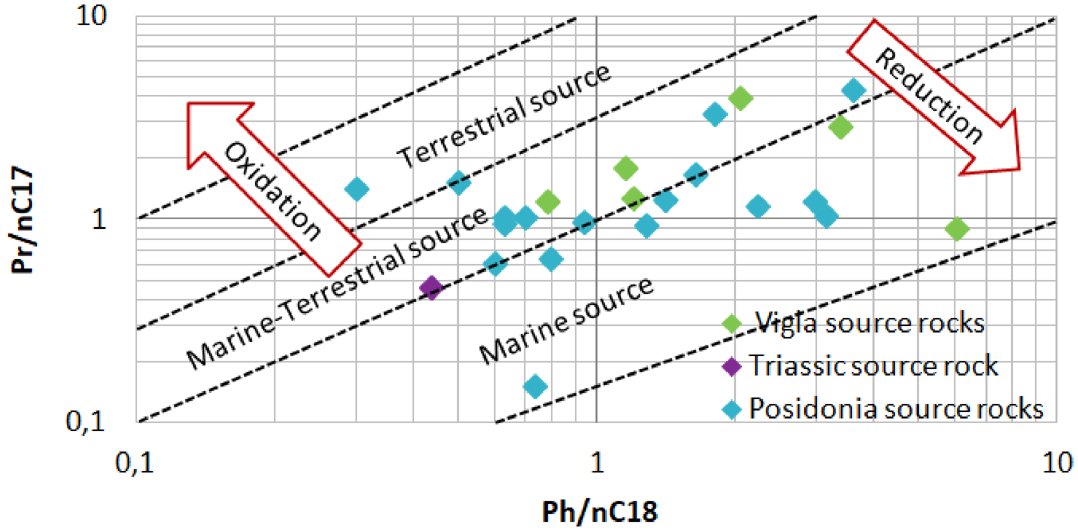

Figure 29: Pr/nC17 versus Ph/nC18 plot for the source rocks in the central Ionian zone

The organic matter of both Vigla source rocks and Posidonia source rocks at the central Ionian zone has mixed terrestrial-marine and marine origin (Figure 29). The sample from the Triassic source rock interval has also mixed terrestrial-marine origin. The organic matter was deposited under similar conditions. The Figure 28 suggest sub-oxic conditions for the Vigla shales (one sample only at the anoxic area), whereas the Jurassic Posidonia source rock was deposited and preserved under sub-oxic conditions too with four samples being under anoxic conditions (Pr/Ph about 1 or less). The Pr/Ph ratio is a little bit higher than the unity for the Triassic source rock sample, indicating that sub-oxic conditions were prevailed during the deposition and preservation of organic matter. Based on CPI values, the organic matter is at early maturity stage for the Vigla source rocks and within the middle maturity stage for the Posidonia source rocks. The CPI value of the Triassic source rock sample is 1.1 (Figure 28) indicating that the organic matter is at the early maturity stage.

There are available data of biomarkers only for the Posidonia source rocks in the external Ionian zone (Figure 16, Figure 17). As it is was mentioned, the Pr/nC17 versus Ph/nC18 plot (Figure 17) shows a mixed marine-terrestrial to mainly marine source organic matter. The Pr/Ph ratio is > 1 representing mainly sub-oxic conditions during the deposition and preservation of organic matter and the CPI values are between 1-1.1 indicating an early mature stage of the organic matter (Figure 16).

In summary, the biomarkers of a sample from a Triassic source rock interval at the central Ionian zone indicates a mixed marine-terrestrial source of organic matter, which was deposited and preserved under sub-oxic conditions. The organic matter is at the onset of the oil window and thus at the early maturity stage, according the CPI value.

The Posidonia source rocks in the entire Ionian zone have a mixed marine-terrestrial as well as a marine origin of organic matter (kerogen type II and III), which deposited and preserved under redox conditions based on biomarkers. The CPI values are increased from the internal to the central-external Ionian zone suggesting a decrease of the maturity level from east to west. This is also confirmed by the decrease of the Vitrinite reflectance and the MPI biomarker towards the same direction.

The Vigla source rocks in the Ionian zone have a mixed marine-terrestrial and marine origin of organic matter as specified by the Pr/nC17 and Ph/nC18 biomarkers. There were both anoxic and sub-oxic conditions during the deposition and preservation of organic matter. The available data are not enough for reliable conclusions on the maturity trend of the Vigla shales using the CPI values.

Chapter 4

4 Comparison between Ionian zone and Southern Adriatic area

The eastern part of the Greek Ionian Sea belongs to the pre-Apulian zone, whereas the western part, to the Apulian platform (Figure 30). For many decades, the area has been explored and accumulations of oils have been identified. The organic-rich sediments into the Triassic Burano evaporites are the principal hydrocarbon source rocks of the Apulian platform. In the peri-Adriatic area, the majority of hydrocarbon concentrations originate from source rocks appearing in Triassic formations (commonly associated with evaporites) which the deposition was held in intracontinental basins. In addition, much of the petroleum of Albania originates from Triassic limestones (Karakitsios, 2013). Afterwards, the source rocks which generate the oils of south eastern Adriatic are examined in terms of common features. Specifically areas in Croatia, Albania and Italy are mentioned.

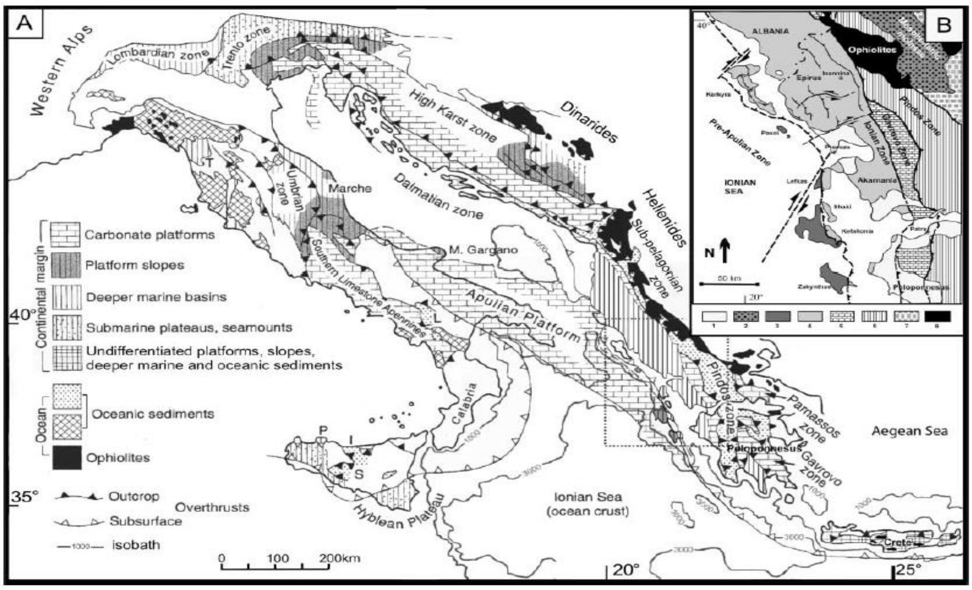

Figure 30: Tectonic units and paleography of the peri-Adriatic area, Late Jurassic (Karakitsios V., 2013 [8])

4.1 Source rock to oil correlation in central western Greece and Croatia

Comparing Ioannina 1 well and Vlasta 1 well, there is plethora of similarities. Initially, in the Ioannina 1 well there are evaporites and very rich source beds indentified in the shales of Triassic breccias in the interval 1250 to 1270 m (this thickness is not representative as the area is highly deformed), whereas in the Vlasta 1 well carbonate and evaporite facies are developing through Upper Triassic at 5403 to 5640 m depth. In the first case, the organic matter is of type I-II, oil prone, while in Vlasta 1 well kerogen is of type II, indicating a marine origin (algal-bacterial) with minor input of terrigenous components , an also oil prone kerogen. Samples analyzed by Rock Eval method, intimate an average TOC of 3.38 % and 1.2 % respectively, and a Tmax value of 436 ^{0}C showing a common burial depth, as well as an immaturity of the organic matter. Relating to biomarker compounds, C_{29} steranes are ascendant and have similar values in both wells.

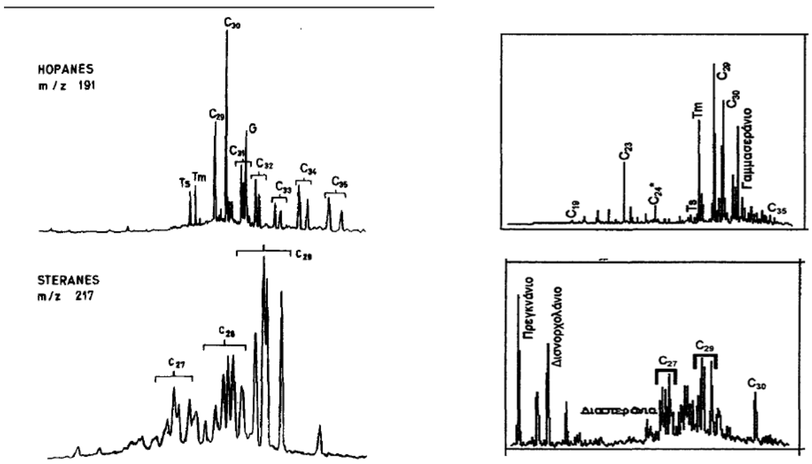

Figure 31: Chromatograms of the Triassic oil, Vlasta 1 well and the Triassic shale, Ioannina 1 well (Cota L. and Baric G., 1998 [2], Rigakis N., 1999 [11])

As much in Ioannina 1 drilling, as well in Vlasta 1 drilling, gammacerane is high defining an evaporitic environment (Figure 31). Furthermore, the pristane / phytane ratio is less than unity, indicating an anoxic environment in these areas of research.

Comparing Delvinaki oil seep with Ioannina 1 and Vlasta 1 wells, many resemblances are noticed. The chromatograms of source rocks detected in samples of Triassic shale of Ioannina 1 well, in contrast with oil shows of Delvinaki, give the following results. Regard to steranes and terpanes, is observed the same pattern in chromatograms. Also in both cases, C_{29} terpanes dominate C_{30} ones and increasing content to characteristic elements gammacerane, C_{30} sterane and pregnane is discerned (Figure 32).

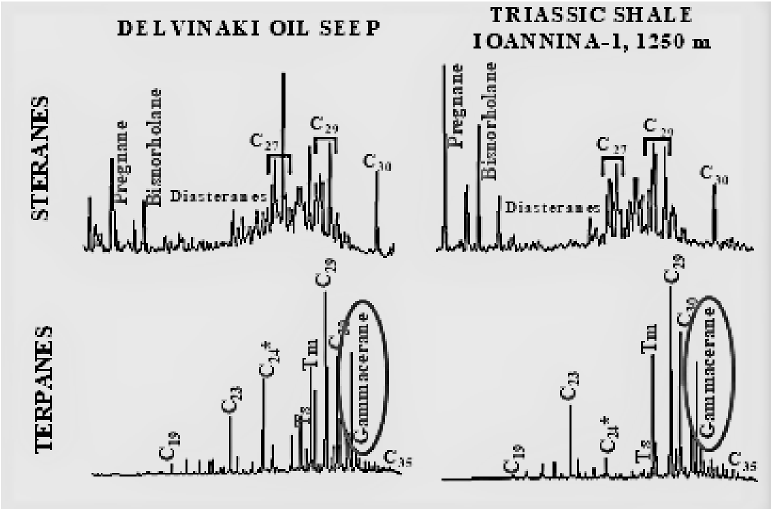

Figure 32: Typical biomarkers indicating direct correlation (Rigakis N., 1999 [11])

Consequently, typical biomarkers indicate direct correlation of Delvinaki oil and Triassic source rocks of Ioannina 1 well, as well as possible, same depositional conditions despite the different location of basins. Furthermore, considerable oil quantities origin from these source rocks, excepting to be underneath the Triassic evaporates.

Comparing Vlasta 1 oil to Delvinaki oil, it is recognized explicit correlation in biomarkers. More particular, C_{29} steranes dominate C_{27}, C_{28} and C_{30} in both cases.

The oils which generated in this area have low API gravities and remarkable sulphur concentrations. The presence of gammacerane in high concentration, implying that organic matter deposited in anoxic, carbonate-evaporitic environment, which was existed from Epirus until Croatia paleographically.

4.2 Source rocks in Albania

Exploration interest has been mainly focused on the external Albanides, where the tectonic zones are: the Ionian zone, the Kruja zone and the Krasta-Cukali zone. Oil occurrences in the Ionian basin are controlled by extensional tectonics (Jurassic-Early Cretaceous) and compressional tectonics (Cretaceous-Quaternary). The external Albanides characterized as a carbonate-evaporite platform during Late Triassic. The Ionian zone constituted an evaporitic anoxic lagoon which generated favorable conditions for the sedimentation of source rocks (Late Triassic). The Ionian basin altered periodically into an euxinic basin with specific boundaries, causing the sedimentation of source rocks (Toarcian, Dogger, Malm, and Lower Cretaceous age). The onset of oil generation from the source rocks is related to Miocene and Pliocene burial. The Ionian zone also, consists of anticline belts: the Berati referring to its eastern margin, the Kurveleshi in the central part and the Cika representing the western margin of the Ionian (Figure 33).

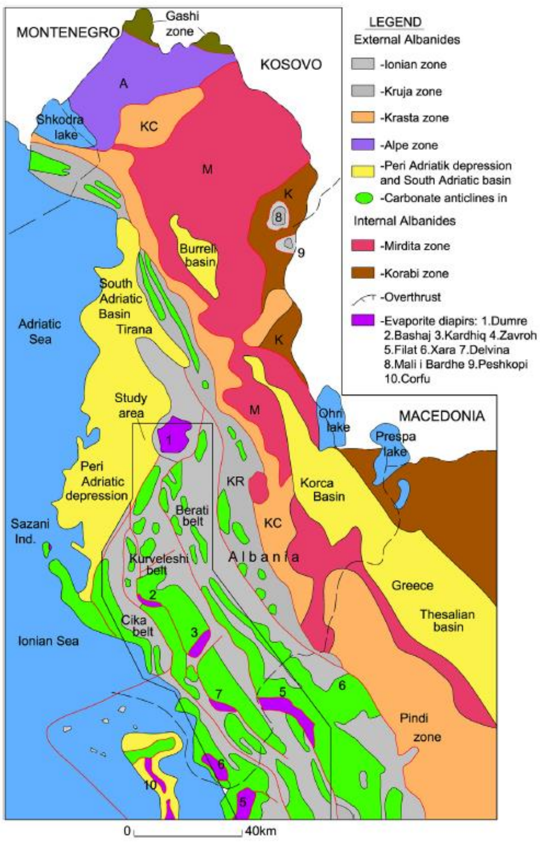

Figure 33: Albanian tectonic zones (Telo Velaj, 2015 [13])

Most commercial oil fields occur in Kurveleshi belt, where numerous source rocks have been noticed in outcrops and deep wells. The majority of source rocks presents a high content of oil prone organic matter (type I-type II) and is associated with Upper Triassic, Lower Jurassic and Lower Cretaceous. Furthermore, they have high contents of total organic carbon (2 to 44 %), high hydrogen index (400-700) and high contents of amorphous organic matter. "In fact, in the Upper Triassic-Lower Jurassic, there are black shales with a TOC of up to 5.5 %, comparable to those of the Burano formation (Lower Triassic) in Southern Italy" (Velaj, 2015). It is remarkable that, the Upper Triassic evaporites are accompanied by Triassic breccias. There is good to excellent potential for the generation of liquid hydrocarbons from all the carbonate source rocks. A plethora of the Ionian zone oils have high sulphur content, low API and pristane/phytane ratios < 1 indicating that their origin is from rich source rocks within carbonate and evaporitic environments. Concerning the biomarkers, several oil samples give the following values from the terpane m/z 191 and the sterane m/z 217 chromatograms: a 29 norhopane/C_{30} hopane ratio > 1, abundant C_{31} to C_{35} extended hopane, abundant C_{24} tricyclic terpane, low contents of diasteranes, predominance of C_{29} sterane, abundant sterane with low molecular weight and high hopane/sterane ratios (Curi, 1993). The oils are derived from algal/bacterial marine source rocks, depending on the above results.

4.3 Source rocks in Italy

The Adriatic Basin consists of two petroleum systems: a Plio-Pleistocene biogenic gas system and an Upper Triassic-Lower Jurassic oil system. The deposition of the carbonate succession took place during Permian-Mesozoic extension, whereas the following Cenozoic succession deposited during regional compression and thrust belt activity. More particular, the composition of the Cenozoic succession is mostly of sandstones and shales. There are five potential source rocks varying from Middle Triassic to Pleistocene age, found in Italy (Figure 34).

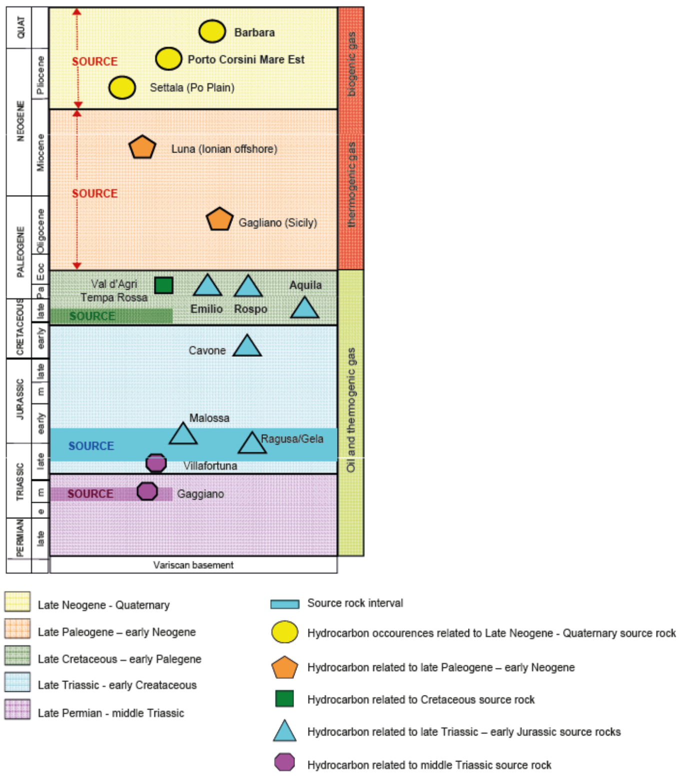

Figure 34: Stratigraphic distribution of source rocks and hydrocarbon occurrences in the Apennine-Adriatic area (Cazzini F. et al, 2015 [1])

Specifically oil and thermogenic gas are originated from Middle Triassic, Upper Triassic-Lower Jurassic and Upper Cretaceous source rocks. The onshore western Po Plain and southern Apennine foldbelt contain Middle Triassic and Upper Cretaceous source rocks respectively, whereas the source rocks of Upper Triassic-Lower Jurassic age appear in central and southern Adriatic. There are intervals within the Upper Triassic-Lower Jurassic sequence which have remarkable source rock potential. “The

Toarcian 'Marne di Monte Serrone' Formation at Sparviero 1bis well could be equivalent to the Toarcian Lower Posidonia beds found in the Ionian zone of Greece" (Cazzini, 2015). Also, the 'Calcari Anossici' unit drilled in this well has low thermal maturity, but kerogen quality is very good with HI often 700-800 mg HC/g TOC and type II oil prone. The Sparviero 1bis and the Grifone 1 wells consist of Liassic organic-rich shaly limestones, indicating the development of a pelagic basin leastwise throughout the Upper Triassic in the southern Adriatic. The carbonate reservoir rocks trapped the produced hydrocarbons during Late Triassic to Late Cretaceous. Another noticeable element is the presence of Triassic slope breccias within Emma 1 and Grifone 1 wells, suggesting pelagic conditions and hence the source rocks intervals can be possibly found in the basinal depocentres. The deposition of the source rocks generating Adriatic oils, probably occurred under anoxic conditions in intraplatform basins, based on geochemical data. These oils have high sulphur contents and low API gravity (except for the Aquila and Rovestri oils). There is a lack of diasteranes, C_{29}/C_{30} hopanes are > 1, Pr/Ph < 1 and gammacerane is also present. The existence of potential source rocks can also confirm with the continental deposits of Permian-Lower Triassic age, particularly in the deep water of the Adriatic basin.

In sundry sectors of the Adriatic, a considerable part of the Mesozoic sedimentary sequence involves of evaporites, basically Triassic. The Triassic evaporites are broadly categorized from Middle-Upper Triassic (Croatian offshore) to the Upper Triassic (Italian Adriatic and Apennines) age. The deepest part of the central and southern Adriatic basin includes the salt tectonics, as well as the evaporites. "The Triassic platform carbonates associated with evaporites have been of significant interest for petroleum exploration in the Mediterranean region, due to their interaction during any tectonic activity, controlling this way characteristics of reservoirs and seals" (Scisciani, 2017). The early salt movement may generate early structures with the presence of evaporites, probably from the Mesozoic, with higher odds of early trapping and source rock existence. The hydrocarbon source rocks from Triassic are connected with the anoxic conditions dominated either in local intraplatform basins as mentioned, or with diachronic evaporitic episodes in the region, which are in control of syn-rift structures.

Chapter 5

Conclusions

The Ionian basin contains source rocks layers capable for hydrocarbon generation. Specifically, samples from the Mesozoic carbonate sequence are studied using Rock Eval pyrolysis data and petroleum biomarkers.

In the internal Ionian zone the studied source rocks interval is mainly the Vigla shales which are available from the Agios Georgios 3 well. Very limited source rock intervals from deeper parts of the Mesozoic section are available from the internal Ionian zone. The Vigla shales show Tmax values higher than 430 ^{0}C and PI values about 0.4, having entered the oil window according to the vitrinite reflectance values from the Agios Georgios 3 well data. The organic matter type is I-II and III (mainly a mixed marine-terrestrial source) and is mature to generate hydrocarbons as suggested by the Vitrinite reflectance (> 0.6 %), the steranes, the homohopanes, the aromatic steroids and the Pr/nC17 and Ph/nC18 biomarkers. The Pr/Ph ratio is > 1 suggesting sub-oxic conditions during the deposition and preservation of the organic matter. The CPI values of the Vigla source rocks samples are < 1-1.3 indicating that the organic matter is immature to medium mature. The sample that plotted according the MPI biomarker and VRoeq values is in the early oil window. The Posidonia source rocks in the same geological domain (internal Ionian zone) have a Pr/nC17 / Ph/nC18 ratio < 1, indicating a marine origin of the organic matter and mainly reducing conditions during the deposition and preservation of organic matter (Pr/Ph ratio < 1).The CPI values of the samples are < 1 pointing out that the organic matter is mature (middle oil window). Based on MPI biomarker and VRoeq, the only sample examined, for Posidonian beds is mature and in peak oil window area.

In the central Ionian zone the main source rocks are the Posidonia beds which have Tmax values below 435 ^{0}C and low PI values according the Dragopsa 1 and Ioannina 1 wells, indicating immature to marginally mature in cases organic matter. This is also confirmed by Vitrinite reflectance (0.4 %) and steranes, homohopanes and aromatic steroids diagrams. The Pr/nC17 and Ph/nC18 biomarkers show a mixed marine-terrestrial to marine source of organic matter (kerogen type II and III). The majority of the samples have a Pr/Ph > 1 suggesting sub-oxic conditions during the deposition and preservation of organic matter. The CPI values vary < 1-1.2 indicating that the organic matter is within the middle oil window. Using the MPI and the VRoeq values, the samples are found in the early oil window. The Pr/nC17 and Ph/nC18 biomarkers of the Vigla source rocks samples in the central zone shows a mixed marine-terrestrial to marine source of organic matter (kerogen type II and III), whereas the Pr/Ph ratio is > 1 suggesting sub-oxic conditions during the deposition and preservation of organic matter. The CPI values are ≤ 1 indicating that the organic matter is at the onset of the oil window and thus at the early maturity level. In this central part of the Ionian zone there is a few information about the Triassic source rocks. According to only one sample derived from a Triassic source rock interval, the Pr/nC17 and Ph/nC18 show a mixed marine-terrestrial source of organic matter (kerogen type II and III), whereas the Pr/Ph ratio is > 1 suggesting sub-oxic conditions during the deposition and preservation of organic matter. The CPI value of the sample is 1.1, indicating that the organic matter is at the onset of the oil window and thus at the early maturity level.

In the external Ionian zone the Pr/nC17 and Ph/nC18 biomarkers of the Posidonia source rocks samples shows a mixed marine-terrestrial to mainly marine source organic matter. The Pr/Ph ratio is > 1 representing sub-oxic conditions during the deposition and preservation of organic matter. The CPI values are between 1-1.1 indicating an early mature stage of the organic matter. The sample from the Posidonia source rock in this zone is immature based on MPI and VRoeq values.

The results suggest source rocks dominated mainly with kerogen type I, II, and mixed I-II deposited in a marine to terrestrial environment respectively in the Ionian basin. The maturation of source rocks tends to decrease from the internal towards the central-external zone, according the data. Especially for the Posidonia source rock levels (undivided) the CPI values are increased from the internal to the central-external Ionian zone suggesting a decrease of the maturity level from east to west. This is also confirmed by the decrease of the Vitrinite reflectance and the MPI biomarker towards the same direction. The results for the source rocks in the Ionian zone (except from the Triassic source rocks due to the lack of samples) are summarized in the following quantitative Table:

Ionian Zone				
Source rocks	Maturity parameters	Internal	Central	External
Jurassic Posidonia beds	Tmax		←...............	
	PI		←...............	
	Vro		←...............	
	CPI		...............→	
	MPI		←...............	
Cretaceous Vigla shales	Tmax		←...............	
	PI		←...............	
	Vro		←...............	
	CPI		lack of data	
	MPI		←...............	

The source rocks of Ionian zone in western Greece compared with those of Croatia, Albania and Italy present many common features, indicating that there were similar conditions during the deposition and preservation of organic matter paleographically in the area. Regarding the biomarkers, C_{29} steranes are ascendant, Pr/Ph ratio is < 1 and gammacerane is also present. Some oils of this area have high sulphur content. All these elements show that the source rocks of Middle-Upper Triassic and Jurassic-Cretaceous sequences generated hydrocarbons from marine (type I,II) to mixed marine-terrestrial (mixed I-II and III) organic matter under anoxic conditions, in an evaporitic-carbonate environment which dominate in different located intraplatform basins of southern Adriatic region.

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