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Organic Geochemical Signatures of the Upper Miocene (Tortonian—Messinian) Sedimentary Succession Onshore Crete Island, Greece: Implications for Hydrocarbon Prospectivity

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Abstract: The definition of pre-Messinian source rocks in the eastern Mediterranean is of paramount importance for hydrocarbon exploration because of the ability of salt to act as a high-quality seal rock. This research evaluates the organic geochemical features of the Upper Miocene (Tortonian—Messinian) sedimentary succession onshore Crete Island, Greece. The study employs original (Messinian, Agios Myron Fm) and published (Tortonian, Viannos Fm, Skinias Fm, Moulia Fm, and Messinian Ploutis section) results from organic geochemical analyses of mudstone samples. One hundred and one samples were examined using standard organic geochemistry methodology (Rock-Eval II and VI-TOC) to define the origin, type, and degree of organic matter maturity. The data indicate that the studied samples have poor to fair gas-prone source rock potential. These possible source rock units have not experienced great temperatures during burial, and, thus, their organic matter is thermally immature. The sub-salt (Tortonian—Messinian) source rock units are likely to be of higher thermal maturity in the western and eastern south Cretan trenches because of tectonic subsidence and a thicker sedimentary overburden. Several traps can grow in these regions, associated with normal faults, rotated blocks and unconformities (both below and above the unconformities). This research provides a basis for the further evaluation of the hydrocarbon potential in Crete Island. It is an area that shares geological similarities with the surrounding regions that contain proven reserves and is of crucial economic and strategic importance.

Keywords: Rock Eval analysis; pre-evaporitic source rocks; hydrocarbon potential; sedimentary basin dynamics; thermal maturity; kerogen type; hydrocarbon exploration; evaporites sealing quality; Messinian salinity crisis; eastern Mediterranean

1. Introduction

Technological advances (including modeling and 3D mapping) in geophysical research have been the driving force for hydrocarbon exploration in tectonically complicated settings, such as the eastern Mediterranean [1–3]. The petroleum industry has paid more attention to the eastern sector of the Mediterranean Sea because of recent discoveries of significant gas resources and the existence of promising frontier regions [3–5]. These promising results stimulated interest in further and more detailed exploration activities in the region. An important parameter that enhances the prospectivity of the eastern Mediterranean is the widespread accumulation of thick Messinian evaporitic successions. Such rock types are related to first-class seal rocks in numerous regions across the world, such as the Middle East, Russia, the Gulf of Mexico, and offshore Brazil [6–9]. Thus, the documentation of suitable source and reservoir rocks below the Messinian evaporites in the eastern Mediterranean could be very beneficial for future exploration activities.

There is active exploration in the region, such as in the Levantine Basin, Egypt, Israel, and, more recently, offshore Cyprus, while additional promising regions (e.g., Herodotus Basin and offshore Crete) have also been suggested [10–14]. The Levantine Basin contains significant conventional and unconventional resources, thus, there is a high likelihood for future significant discoveries offshore Cyprus [12]. Exploration in Egypt and Israel has proven very successful, resulting in a number of discoveries, which in turn has prompted extensive regional exploration [15]. The Hellenic part of the Herodotus Basin is largely unexplored, despite the active mud volcanoes that have been documented on seismic profiles in several locations along the Mediterranean Ridge [16–20]. The areas west of Crete Island exhibit comparable geotectonic histories to those of nearby regions, such as Cyprus, Egypt, and Israel, where major discoveries have been reported (e.g., Zohr, Calypso, Tamar, Leviathan, and Glafkos). This information is of paramount importance for Greece and has stimulated the petroleum industry to explore the potential for hydrocarbon resources located outside the already established petroleum province of western Greece [14,21–26]. As a result, exclusive right licenses were granted for west and south Crete. The potential for onshore Crete and nearby regions to contain Tortonian to Messinian (sub-salt) source and reservoir rocks has been suggested based on studies from Gavdos Island south of Crete [27], the Messara and Heraklion Basin in central Crete [28–31], and the Levantine Basin in the south-eastern Mediterranean [4,5,10–12].

Rock Eval (RE) pyrolysis is viewed as an economic and reliable methodology to evaluate the hydrocarbon generative potential and maturation level of potential source rocks in sedimentary basins [32–34]. This study integrates both original and already published data derived from outcrop-based organic geochemical studies to assess the hydrocarbon generative potential of the Upper Miocene sub-salt formations in onshore Crete. This research examines available data from the Tortonian deposits that belong to Viannos Fm, Skinias Fm, and Moulia Fm (at Faneromeni) and from the Messinian Ploutis section (central Crete). Additionally, it presents new numerical constraints to the organic geochemical signatures of the Messinian Agios Myron Fm (new data), providing information about the type, quantity, quality, and maturation level of the organic material. Our results offer a comprehensive insight into the existence and nature of Late Miocene source rocks in the region. The results obtained from an inland frontier basin could enhance current exploration activities in the region and stimulate future exploration activity, such as the drilling of new exploration wells and the acquisition of new seismic data.

2. Geological Setting

The Aegean Sea has attracted both scientific and economic attention. The Aegean region is positioned on continental crust that comprises several stacked upper crustal nappes [35,36] (Figure 1). These nappes were stacked because of the northward dipping subduction of the African plate under the European plate that has occurred since the Cretaceous [35–37]. These plate tectonics were responsible for: (1) the orogenic processes, (2) the disruption of the marine junctions to the Indo-Pacific and Paratethys, and (3) the progressive restriction of the marine passage to the Atlantic Ocean [38]. The southeast Hellenides form part of a synorogenic orocline that illustrates modifications regarding the internal deformational pattern and the nature of the margin, as evidenced by geotectonic analysis [39]. Although orthogonal collision prevails in the western edge of the orocline, the central and eastern part is developed because of oblique subduction that is influenced by strike-slip tectonics (NE-directed transpressional faults). These strike-slip faults developed transverse zones that split apart some of the structural elements, such as salients, recesses and linear segments [40,41]. Structural and stratigraphic analyses have documented that the style of the compressional tectonic activity and the total thickness of Mesozoic sedimentary successions [41–43] are highly variable across strike, suggesting that these transverse zones had an impact on the Mesozoic sedimentary basins. From the Late Miocene to more recently, the regional post-orogenic extension occurred along these transverse zones that are oriented parallel to the thrust belt in eastern Crete [39,44,45].

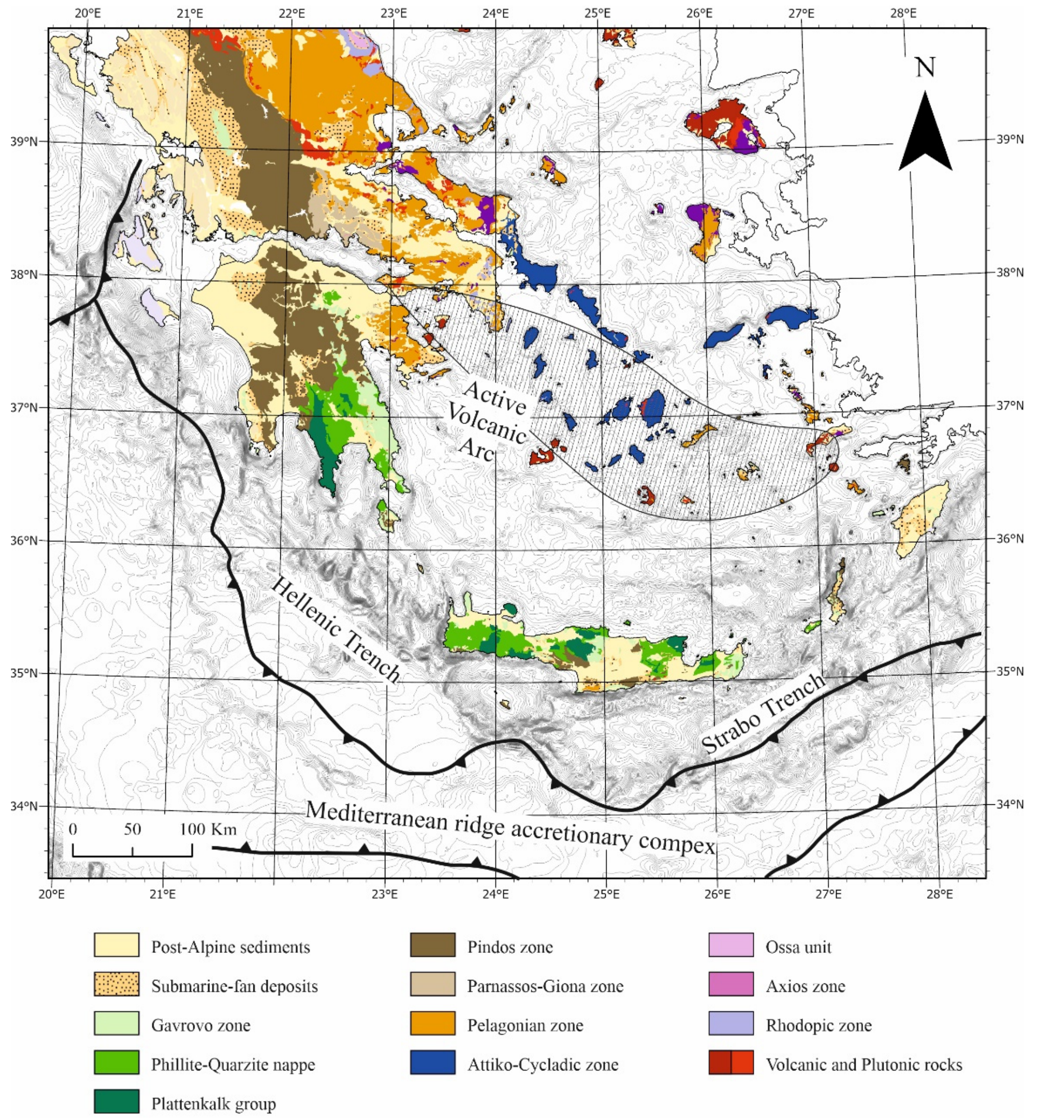

Figure 1. Scheme illustrating the tectonic zonation of Greece based on the main tectonostratigraphic zones (modified after [14]).

The Island of Crete includes several nappes of Triassic to Quaternary rock units that belong to different geotectonic zones (Figure 2). The nappes are subdivided into a lower member that contains high pressure and low temperature (HP-LT) metamorphic rocks and an upper member with no metamorphic rocks [46–48]. These nappes are thought to have been placed together through south-directed subduction and/or collision and accretion to the northern Gondwanan edge [49,50]. The pre-Miocene basement rocks were tectonically fragmented into numerous parts because of uplift and exhumation of the nappe pile and were responsible for the development of Lower to Middle Miocene sedimentary basins. Several mechanisms have been proposed to explain this uplift and exhumation and involve both extensional [51–53] and contractional tectonics [50,54,55]. Younger (Late Miocene to Early Pleistocene) thrust-associated depocenters are ascribed to the migration of thrust activity to the southwest [56,57]. Comprehensive studies in central Crete have revealed two phases of compression [54]: An early phase of ductile exhumation of high-pressure metamorphic rocks that is related to NNW–SSE compression, responsible for the formation of low-angle reverse faults (thrusts) that contributed to nappe emplacement. A subsequent phase of brittle exhumation ascribed to NNE–SSW compression and dominated by large fault-associated folds and tectonic imbrication. The older, underlying nappes are commonly intersected by younger, large-scale thrust faults [54].

Figure 2. Scheme illustrating the tectonic zonation and main structural elements and depocenters of Crete Island and surrounding regions. Red cycles correspond to the sampling locations.

3. Stratigraphic and Environmental Constraints

Updating former lithostratigraphic models [58], the Tortonian-upper Messinian stratigraphic succession of central Crete has been divided into five formations, namely Viannos, Skinias, Kasteliana, Moulia, and Agios Myron formations that are overlain by the Marine Upper Messinian (MUM) and Lago Mare deposits [48] (Figure 3).

The pre-Neogene basement underlies Viannos Fm, and its boundary contains abundant coarse, angular debris [48]. Viannos Fm is approximately 400 m thick and includes sandstone and mudstone alternations, with some rare conglomeratic beds. Additionally, mud-rich (silty) limestone occurs, whereas fine-grained material (mud) with an increased level of coalification is rarely present. Viannos Fm includes a broad array of depositional elements and environments that include channel-belts, overbanks, and lakes. The clasts within the conglomeratic deposits are mainly sub-angular, pointing to an alluvial fan with sheet-flood deposition as the most suitable depositional environment [48]. Paleocurrent directions suggest a westward transport direction within this formation. The contact between

Viannos Fm and the overlying Skinias Fm is conformable. Skinias Fm is 150–250 m thick and is represented by marine fine-grained (muddy) deposits that are intercalated with sandstone beds. Coarser-grained deposits are represented by scarce pebbly beds [48]. The depositional environments for Skinias Fm are regarded as shallow to deep marine (from the bottom to the middle of the formation) and display an upward trend towards shallower environments [48]. Paleocurrent measurements in this area suggest an east to southeast transport direction. The overlying Kasteliana Fm is 300–350 m thick and consists of both fine- and coarse-grained deposits (mudstone, siltstone, sandstone, and conglomerate). Deposits, such as travertine and lignite, along with oyster beds and coral bioherms, are scarcely present. Kasteliana Fm is interpreted to include several depositional environments, including fluvial-lacustrine, lagoonal, and inner neritic. The contact between Kasteliana Fm and the underlying Skinias Fm is unconformable [48]. Moulia Fm overlies Kasteliana Fm and is 70–80 m thick. It is represented by both siliciclastic and carbonate deposits and is divided into two members. The lower part contains sediments that have been deposited in an inner neritic environment, and the upper part illustrates an upward increase in water depth towards deeper marine environments [48]. In most of the cases, Moulia Fm conformably overlies Kasteliana Fm.

The samples from Moulia Fm have been collected from the Faneromeni section that comprises a sedimentary succession (up to 37-m-thick) and can be subdivided into two members. Coarse-grained deposits (conglomerate) separate these members, with the lower one containing thick-bedded sandstone and mudstone couplets (12 m thick) and the upper one including thin-bedded sandstone and mudstone alterations [59,60]. Sapropels occur in the upper parts of the succession. Agios Myron Fm is approximately 120 m thick and consists of bioturbated and fossiliferous sandstone, along with calcarenite and calcrete palaeosols. The upper parts, Messinian in age, designated here by the analyzed samples from the eponymous section (7.2–6.5 Ma) contain cyclically-bedded alternations of deep marine bluish-grey homogeneous and laminated brownish marls (sapropels) along with three distinct ash beds [48,61]. Paleobathymetric calculations of the samples from this location have shown that this sedimentary succession was deposited under upper bathyal conditions of 350–650 m [62]. Overall, Agios Myron Fm displays an upward increase in water depth, similar to the trend observed in Moulia Fm, and unconformably overlies Viannos Fm [48]. The overlying formation consists of Upper Messinian alternations of turbidites, sapropels and marls (up to 40 m thick, MUM, Marine Upper Messinian in Zachariasse et al. [63]) that are overlain by evaporites, where exposed (e.g., Ploutis section) [30], and Lago Mare deposits (generally up to 60 m thick) [63,64] or Lower Pliocene gravity failure deposits (mass wasting deposits of Zachariasse et al. [63]).

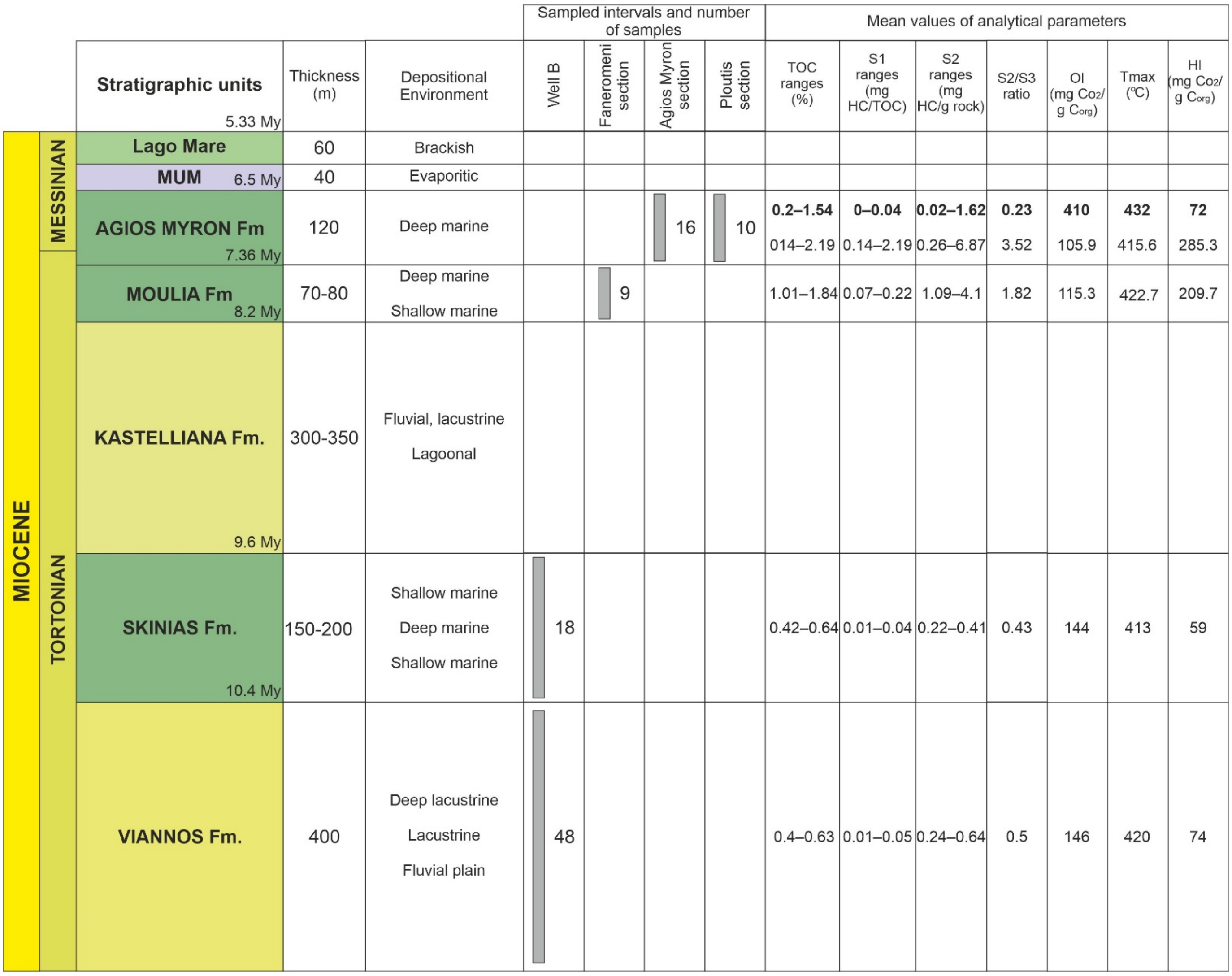

Figure 3. Stratigraphic column of the study region that illustrates the evolution of the Upper Miocene (Tortonian—Messinian) depositional environments. The age constraints of the study formations come from Zachariasse et al. [48]. To the left upper corner, the stratigraphic interval that the study sections and formations cover is displayed. Abbreviation, MUM: Marine Upper Messinian.

4. Material and Methods

One hundred and one (101) samples in total were selected for organic geochemical analysis. Forty-eight (48) samples from Vianos Fm, eighteen (18) samples from Skinias Fm, nine (9) samples from Moulia Fm (at Faneromeni), sixteen (16) samples from Agios Myron Fm, and ten (10) samples from Ploutis section, respectively. The samples from Agios Myron are new data (16 samples) and the data from the other formations come from previous studies (85 samples). Most of the samples that belong to Vianos and Skinias Fms come from an exploration well (well D, Figure 2). The samples that belong to the other Fms were collected from outcrops. The outer surface of the sections was removed prior to sampling in order to avoid contamination from weathering. The fresh samples were immediately placed, and protected from oxidization, in plastic sample bags.

The organic geochemical features of the sedimentary rocks studied were assessed using RE analysis. After overnight drying, the rock samples were crushed and sieved using a 60 mesh (250 µm) sieve. The analysis was performed using RE II and VI (Delsi Inc., Edison, NJ, USA) analyzers under standard conditions utilizing ~100 mg of pulverized rock. The samples were then heated in a helium atmosphere using a suitable oven [65–67].

The RE analysis was performed at the Technical University of Crete, Greece (Hydrocarbons Chemistry and Technology Research Unit). Analytical descriptions of the RE VI methodology and interpretations of the obtained results have been offered by several authors [66–73]. Principal parameters, including total organic carbon content (TOC, wt%), free (S1, mg HC/g rock) and pyrolysable (S2, mg HC/g rock) hydrocarbons, total hydrocarbon generative potential (SP, S1 + S2, mg HC/g rock), hydrogen index (HI, mg HC/g Corg), oxygen index (OI, mg CO_2/g Corg), Tmax (°C), and production index (PI, S1/S1 + S2) were documented. The data assessment was based on the works of Tissot and Welte [74], Peters [70], Burwood et al. [75] and Dymann et al. [76].

5. Results

The experimental data of the RE VI-TOC analysis for the 101 samples are illustrated in Supplementary Materials, Table S1.

The TOC contents fluctuated within the examined samples, from 0.4% (D304–307) to 0.63% (D415–420) in Viannos Fm, 0.42% (D128–132) to 0.64% (D14–17) in Skinias Fm, 1.01% (DT15) to 1.84% (DT16) in Moulia Fm (at Faneromeni), 0.14% (PL04) to 2.19% (PL07) in Ploutis section and 0.2% (AM18C) to 1.54% (AM14) in Agios Myron Fm. Based on the TOC values and the criteria established by Peters [70] and Dembicki [77], the studied samples could possess poor to excellent hydrocarbon generation potential. The studied sections included samples that could serve as source rocks (0.5% > TOC > 1%, Table S1) and samples that deserve a more thorough evaluation (TOC >1%, Table S1). Nevertheless, TOC values alone are not sufficient to characterize the samples as potential source rocks. The determination of the hydrocarbon generative potential is a function of the TOC and the hydrogen that is related to the organic material (Dembicki, 2009). Therefore, additional parameters (e.g., S2 values) need to be taken into consideration. The samples exhibited S2 values that fluctuated between 0.24 (D234–238 and D254–260) to 0.64 mg HC/g rock (D420–424) in Viannos Fm, 0.22 (D128–132) to 0.41 mg HC/g rock (D14–17) in Skinias Fm, 1.09 (DT15) to 4.1 mg HC/g rock (DT18) in Moulia Fm (at Faneromeni), 0.26 (PL04) to 6.87 mg HC/g rock (PL02) in Ploutis section, and 0.02 (AM4) to 2.62 mg HC/g rock (AM14) in Agios Myron Fm.

Several parameters from RE analysis were utilized to define the type of organic matter in the sedimentary rocks, including S1, HI and OI values, and the S2/S3 ratio [73]. The examined samples exhibited S1 values that ranged between 0.01 (D402–406 and D406–409) and 0.05 mg HC/g TOC (D415–420) in Viannos Fm, 0.01 (D210–214) and 0.04 mg HC/g TOC (D6–14) in Skinias Fm, 0.07 (DT5) and 0.22 mg HC/g TOC (DT16) in Moulia Fm (at Faneromeni), 0 (PL04) and 0.7 mg HC/g TOC (PL02) in Ploutis section and 0 and 0.04 mg HC/g TOC (AM14) in Agios Myron Fm (Table S1). The mean HI values in the studied succession were 74 mg HC/g Corg (Viannos Fm), 59 mg HC/g Corg (Skinias Fm), 209.7 mg HC/g Corg (Moulia Fm at Faneromeni), 285.3 mg HC/g Corg (Ploutis section) and 72 mg HC/g Corg (Agios Myron Fm). The average S2/S3 ratios were 0.5 (Viannos Fm), 0.43 (Skinias Fm), 1.82 (Moulia Fm at Faneromeni), 3.52 (Ploutis section) and 0.23 (Agios Myron Fm). The average OI values were 146 mg CO_2/g Corg (Viannos Fm), 144 mg CO_2/g Corg (Skinias Fm), 115.3 mg CO_2/g Corg (Moulia Fm at Faneromeni), 105.9 mg CO_2/g Corg (Ploutis section) and 410 mg CO_2/g Corg (Agios Myron Fm). The level of thermal maturity of the examined samples can be assessed using Tmax values. The mean Tmax values were 420 °C (Viannos Fm), 413 °C (Skinias Formation), 422.7 °C (Moulia Fm at Faneromeni), 415.6 °C (Ploutis section), and 432 °C (Agios Myron Fm). Most of the samples exhibited values of S2 > 0.2 mg HC/g rock, and, therefore, the obtained Tmax values were thought trustworthy [70]. Seven samples from the Agios Myron Fm exhibited S2 values that were below 0.2 mg HC/g rock and were not included in the interpretations relating to thermal maturity [73].

6. Discussion

6.1. Amount, Type and Maturation Level of the Organic Material

The diagrams of S2 vs. TOC [77] (Figure 4A) and SP vs. TOC plot [74,76] (Figure 4B) indicate the potential of the sedimentary rocks to generate hydrocarbons. The examined samples exhibited poor to good hydrocarbon generative potential. The most promising samples came from Moulia Fm (at Faneromeni) and the Ploutis section, whereas the Viannos, Skinias and Agios Myron samples exhibited little hydrocarbon generative potential. Analogous information was obtained from the HI vs. TOC [78] (Figure 4C), where, additionally, the samples clustered in the fields of both oil and gas generative potential. However, the determination of oil prone source rocks requires the integration of additional information (i.e., gas chromatography–mass spectrometry data; GC-MS). Except for Moulia Fm (at Faneromeni), such data were not available for the other formations and sections. The GC-MS data in Moulia Fm illustrate the prevalence of type III kerogen and a gas-prone source rock [59]. It needs to be borne in mind that processes such as surface weathering and oxidization need to be taken into consideration when evaluating organic geochemical data because it is possible to reduce the S1, S2 and TOC values obtained by the RE analysis [66,70,79]. Although the sampling was performed with the purpose of reducing the impact of weathering and oxidization in the samples (see methodology section), it is highly possible that the studied samples may exhibit more promising organic geochemical signatures.

The integration of S2/S3 ratios and HI values suggest that the organic matter contained is of kerogen types II, III and IV. A similar interpretation of the kerogen type is provided by the HI vs OI, S2 vs. TOC and the S2/S3 vs. TOC plots that illustrate a well-oxygenated environment of deposition and a terrestrial origin for the contained organic matter (Figure 5A–C). The samples that contain type IV kerogen organic material suggest severe alteration and/or oxidation of organic material in the depositional site [74]. The diagrams suggest that Moulia Fm (at Faneromeni) and Ploutis section could represent source rocks with the potential to generate gas. In contrast, Viannos Fm, Skinias Fm and Agios Myron Fm principally contain kerogen IV organic matter, with no or little hydrocarbon generative potential. The distinction between migrated and autochthonous hydrocarbons, as well as evaluation of sample contamination and kerogen mixing are important when defining the organic geochemical features of sedimentary rocks [80]. The application of S1 vs. TOC cross-plot [81] can shed light on the determination of hydrocarbons and suggests that autochthonous hydrocarbons predominate in all the studied samples and have the potential to generate gas (Figure 5D). The kerogen mixture can obscure the nature of the generated hydrocarbons [77,82]. However, the studied samples contain kerogen of type III and IV only and provide a correct representation of the source rocks.

A low maturation status resulting from low temperatures during burial is suggested for the studied succession by the HI vs. Tmax diagram [73,74] (Figure 6). The PI index is also considered as a parameter to evaluate thermal maturity, with mature rocks displaying values above 0.1 and post-mature rocks displaying values over 0.4 [83]. PI values below 0.1 point to low levels of thermal maturity. The studied succession has PI values that fall below the bottom threshold of 0.1, supporting the interpretation of a thermally immature succession.

In sum, the studied sections exhibit a similar degree of thermal maturity, but a different quantity and quality of organic material. This could be partly related to the nature of the depositional environments and sub-environments that encompass the different sections, and partly to the shoreline trajectories that are associated with their accumulation. The stratigraphic framework proposed by Zachariasse et al. [48] implies that, in contrast to Vianos and Skinias Fms, Moulia Fm (at Faneromeni) and the Ploutis section exhibit a deepening upward trend and associated transgression during their deposition. Relative sea level rise increases the available accommodation space, favoring the accumulation of organic material [2]. Furthermore, shoreline transgression decreases the sediment supply in the deep parts of the sedimentary basins because the terrigenous clastic material is accumulated in the nearshore environments. This depositional trend develops condensed sections that are often rich in organic matter [84]. Additionally, enriched organic productivity, eutrophication, and water stratification often lead to anoxia [85]. The difference in the quantity and quality of organic material between the different Fms and sections could also be associated with the nature of the depositional environments, with the continental-in-origin Vianos Fm being less favorable for accumulation and preservation of organic material. Furthermore, even though shallow marine settings contain sufficient sources that can deliver organic material, their high oxygenation levels can prevent the formation of suitable source rocks and can explain the unpromising geochemical signatures of the marine Skinias and Agios Myron Fms.

6.2. Exploration Opportunities

With worldwide energy demand rising and stricter environmental regulations being introduced, natural gas has become an increasingly important substitute for fuel oil. In this context, prospective regions that deserve further investigation have been the focus of the petroleum industry, despite existing technical challenges (stemming from the complex geology and deep water depths). The eastern Mediterranean is a region with proven hydrocarbon reserves and is the subject of extensive exploration and exploitation activity [4,10–12]. Despite the promising exploration results in western Greece [14,21–26,86] and the Thrace Basin [87], several regions in the Hellenic Domain are still underexplored. In Crete, this study enriches existing knowledge about the potential regional source rocks by including new organic geochemical results on the pre-evaporitic (Tortonian–Messinian) sedimentary succession. This study defines the organic geochemical signatures of the Agios Myron Fm (Messinian, weak source-rock potential and low maturation levels) and builds on the hydrocarbon generative potential of the pre-evaporitic deposits that contain units with fair to good source-rock attributes (Tortonian Moulia Fm at Faneromeni [59], and Mesinian Ploutis [30] section). A common feature of all existing onshore rock units, with merit for further exploration, is their low maturity levels that indicate low thermal evolution. Nevertheless, the offshore counterparts of these units may have experienced higher burial temperatures because of a thicker sedimentary overburden. Indeed, the sedimentary succession that crops out in Gavdos Island reflects the deepest parts of the Crete Basin and contains units with more promising organic geochemical signatures. The organic material in these units (Tortonian—Messinian, Metochia Fm) is of kerogen types II, III and IV, with fair to very good potential for hydrocarbon generation [27]. Despite the promising results, the organic material in Metochia Fm is thermally immature. The regional structural framework suggests tectonic subsidence and the accumulation of thick Pliocene—Pleistocene deposits in the offshore central parts of the region (western and eastern south Cretan trenches) that cover the Tortonian—Messinian potential source rocks [14,88]. This thicker sedimentary cover could likely facilitate the maturation of organic material and the development of source rocks that have reached the oil and/or gas window [29,31,59]. Pre-Messinian mature source rocks have been reported in the eastern Mediterranean. In the adjacent Levantine Basin, the occurrence of asphalt in the Upper Cretaceous sedimentary succession onshore Lebanon suggests the existence of a thermogenic petroleum system (Nader [89]). As in the region covered by the present study, the source rocks in the Levantine Basin are likely pre-Messinian in age (Jurassic—Cretaceous and Cretaceous—Miocene) and occur at the margins and deeper parts of the basin, where they have probably reached the oil/gas window [3,90].

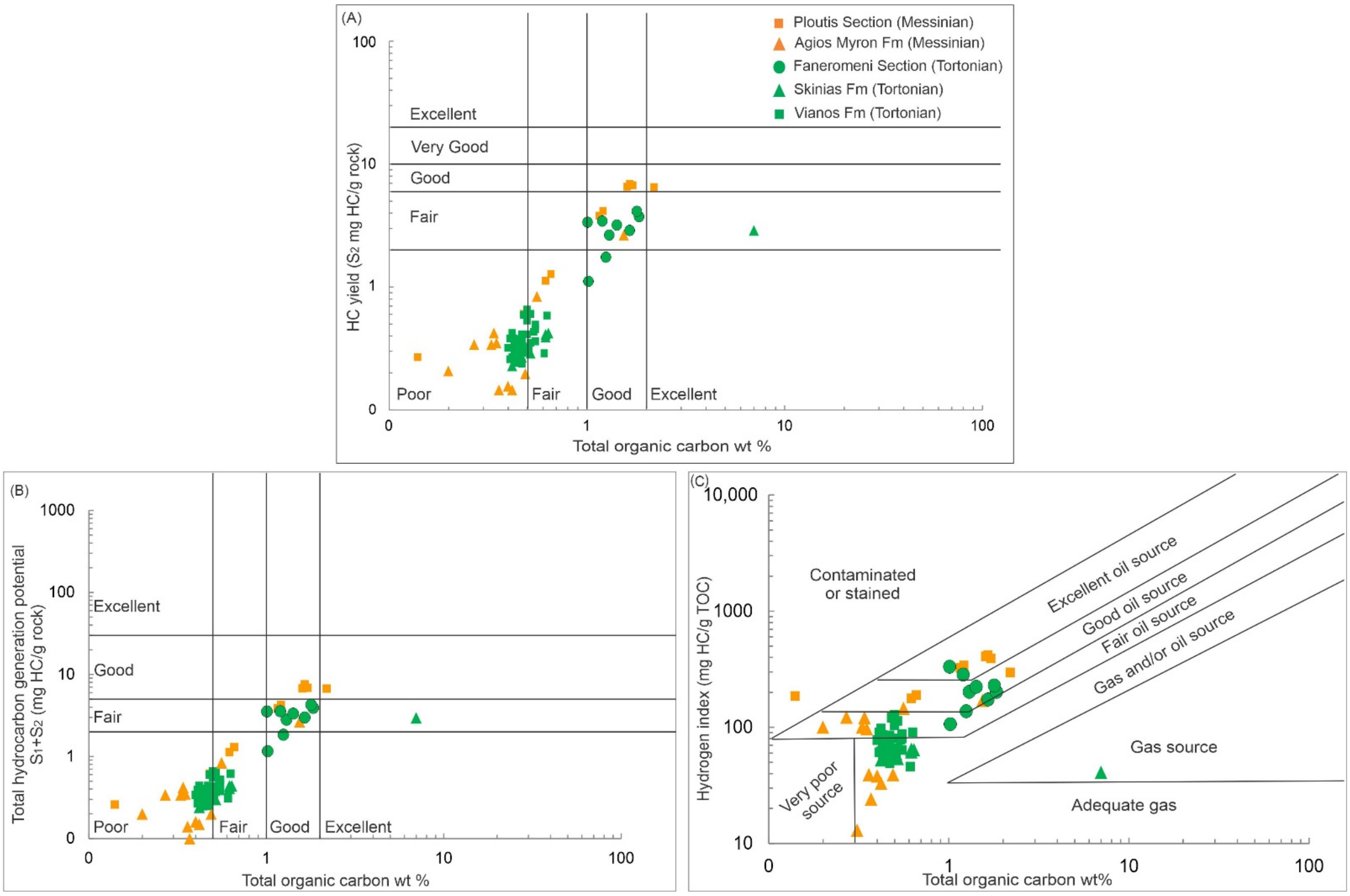

Figure 4. Evaluation of hydrocarbon generative potential of the examined samples from Crete Island. (**A**) Cross-plot of S2 vs. total organic carbon, (**B**) Classification diagram of total hydrocarbon generating potential vs. total organic carbon and, (**C**) Cross-plot of hydrogen index vs. total organic carbon. These diagrams suggest that the most promising samples come from Moulia Fm (at Faneromeni) and Ploutis section, whereas Viannos, Skinias Fm and Agios Myron Fm exhibit little hydrocarbon generative potential. Green color refers to samples that are Tortonian in age, whereas orange color refers to samples that are Messinian in age.

6.3. Eastern Mediterranean Petroleum Plays Related to the Messinian Evaporites

The seismic profiles illustrate the occurrence of numerous normal faults that crosscut the Tortonian—Pleistocene succession and develop smaller-scale graben, horst, and domino structures [88]. These tectonic configurations are highly prone to form migration paths terminating in structural traps constrained by evaporitic cap rocks and sealing faults. Similar trap styles are recognized in the Levantine and Herodotus Basins, where a combination of normal and reverse faults developed several large four-way closure structures, as well as Oligocene—Miocene tilted fault blocks [12]. These active basin tectonics promoted the development of regional-scale unconformities [88] that can form stratigraphic traps [14,91]. In this situation, hydrocarbon plays could exist both beneath and above the unconformity. The regional deepening that followed the accumulation of the Messinian evaporites likely provided the conditions for the accumulation of coastal, sand-dominated deposits. These deposits are often covered by finer-grained transgressive facies and can trap oil and/or gas above the unconformities. Apart from these mud-rich deposits that can prevent the upward movement of fluids (oil and/or gas), Messinian salt deposits constitute the principal regional seal rocks. Despite the mode of formation (e.g., shallow-water deep-basin vs. deep-water, non-desiccated scenario; [92,93]), these deposits are thick, potentially offering sufficient seal capacity. Further, they are laterally continuous, influencing the size of the potential plays. It should be noted that the thick evaporitic layer can hold fluids within the underlying sedimentary successions and cause increased overpressures, stimulated by sediment unloading ascribed to the relative sea level fall that occurred in the Mediterranean, and can increase overpressures and deteriorate the quality of the seal rock [94].

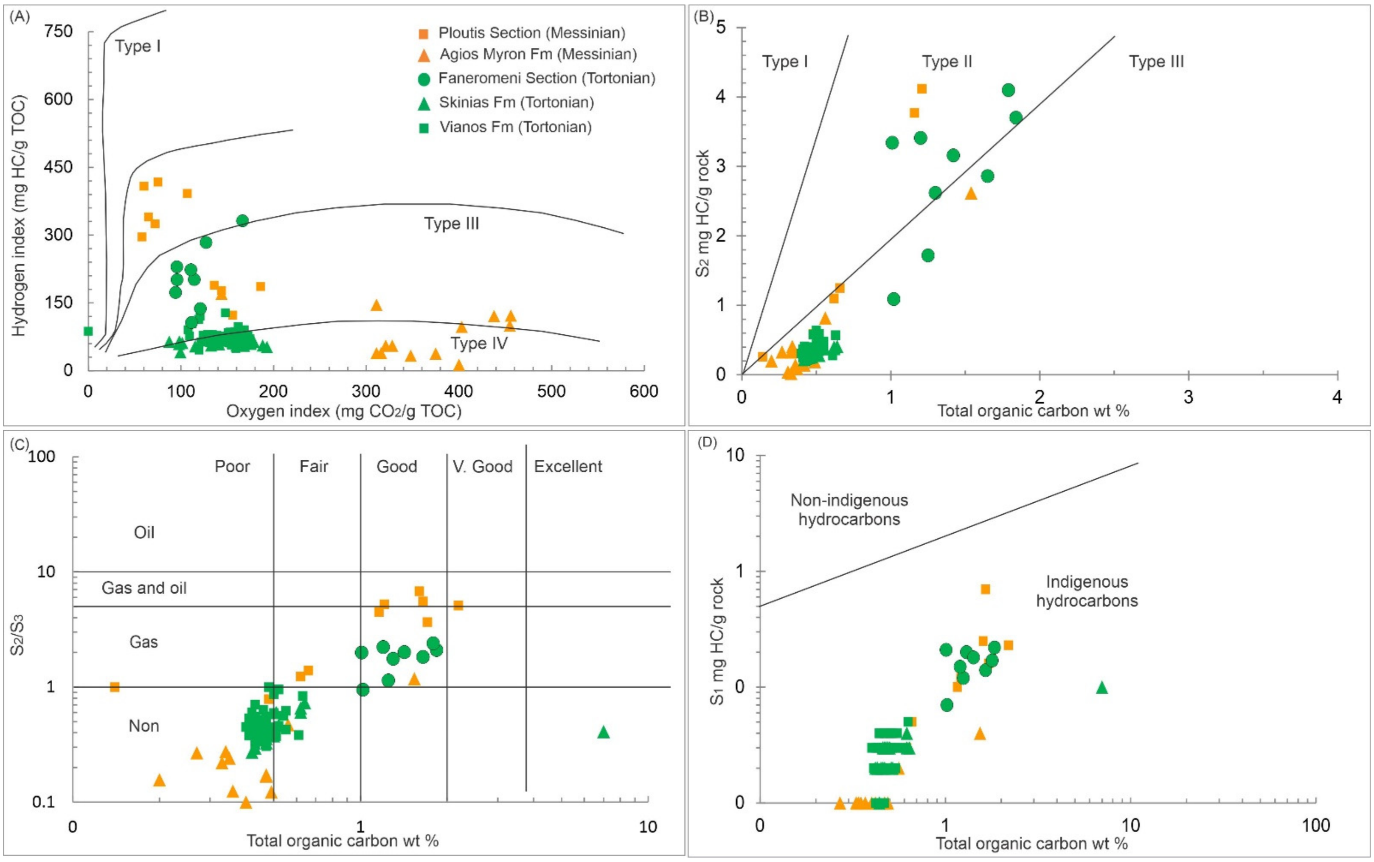

Figure 5. Evaluation of the kerogen type in the examined sedimentary rocks: (**A**) Classification diagram of hydrogen index vs. oxygen index kerogen, (**B**) Bi-plot of S2 vs. total organic carbon, (**C**) S2/S3 vs. total organic carbon, and (**D**) S1 vs. total organic carbon cross-plots. These plots suggest that Moulia Fm (at Faneromeni) and Ploutis section could represent source rocks with potential to generate gas. In contrast, Viannos Fm, Skinias Fm and Agios Myron Fm contain principally organic matter of kerogen IV, with no or little hydrocarbon generative potential. Green color refers to samples that are Tortonian in age, whereas orange color refers to samples that are Messinian in age.

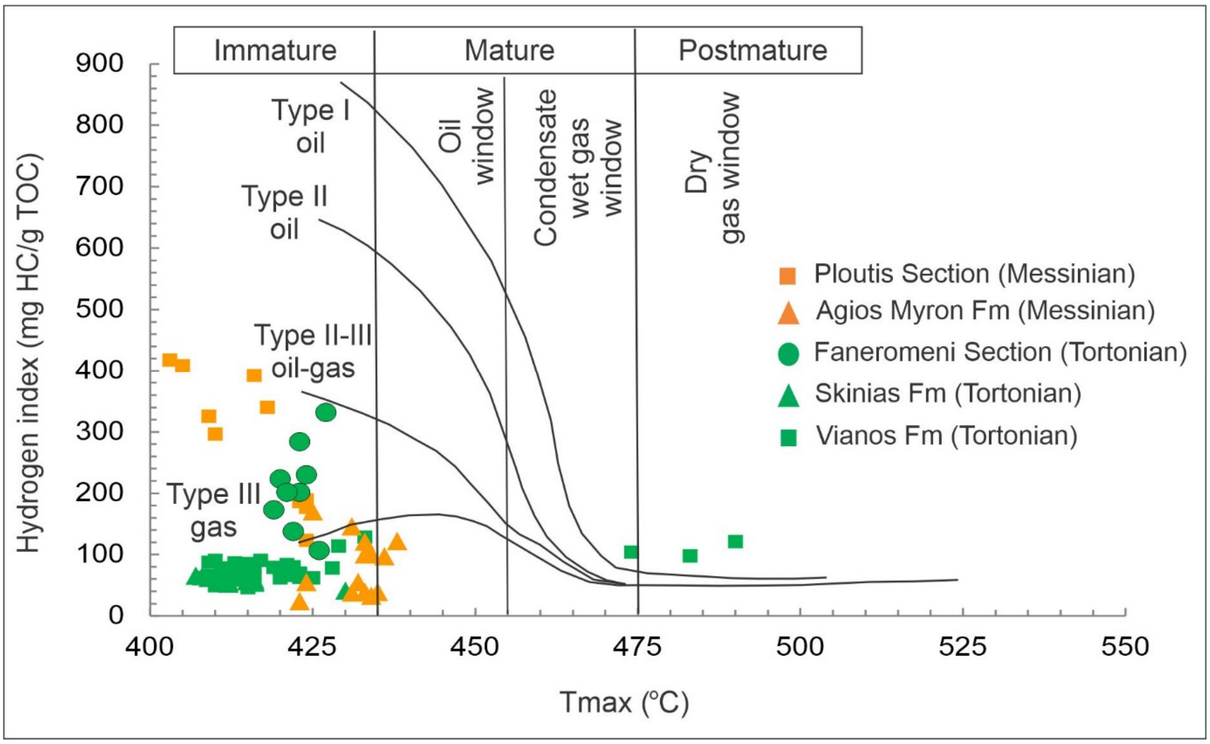

Figure 6. Assessment of maturation status of the examined samples, based on hydrogen index vs. Tmax cross-plot. The samples derived from all formations are thermally immature. Green color refers to samples that are Tortonian in age, whereas orange color refers to samples that are Messinian in age.

7. Conclusions

The Tortonian—Messinian sedimentary succession onshore Crete Island (eastern Mediterranean, Greece) was examined to assess the quantity, quality, and maturation level of organic matter as a source rock. Several samples yielded TOC values above 0.5 wt%, suggesting some hydrocarbon generating potential. The studied succession included samples that are likely to be interesting (TOC between 0.5 and 1.0%), and samples that are very promising (TOC above 1.0%). The organic geochemical analysis illustrates the presence of source rocks that exhibit poor to good potential to generate hydrocarbons. Rock units with fair to good geochemical values include the Moulia Fm (at Faneromeni, Tortonian) and Ploutis section (Messinian), whereas Viannos Fm, Skinias Fm, and Agios Myron Fm exhibit little hydrocarbon generative potential. Most of the samples contain organic matter that is of type III and IV kerogen, suggesting gas-prone source rocks. Maturity parameters (Tmax and PI) suggest that the analyzed samples have not reached the oil window. Despite the low levels of maturation, the offshore equivalents of the studied succession (in the western and eastern south Cretan trenches) could possibly have reached the oil and/or gas window because of tectonic subsidence and thicker sedimentary overburden. The hydrocarbons, possibly expelled by these mature source rock units, could be trapped in the hanging walls of normal faults, in the margins or the corners of tilted fault blocks, and below (and/or above) unconformities. The study region is a promising frontier basin with potential future exploration opportunities. As technological advances in the petroleum industry allow for the more precise evaluation of vintage geological, geochemical, and geophysical data, as well as the acquisition of high-quality new data, an updated re-evaluation of the regional geotectonic models is suggested. A better understanding of the regional geology can be achieved by refining the data from vintage seismic profiles and wells, along with the surveying of additional seismic campaigns and the drilling of new exploration wells.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/jmse10091323/s1, Table S1: Experimental data of Rock Eval-TOC analysis.

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