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EXTENDED ABSTRACT 307

Source rock potentiality of the late Miocene sapropelic layers of Gavdos Island, Greece, based on geochemical and stratigraphic data

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Introduction / Background

The island of Gavdos is the southernmost part of Greece and at the same time represents the southernmost island of whole Europe. It is located in the eastern part of central Mediterranean Sea, south of the western Crete Island (Figure 1, left). It is rather considered a small island with an overall size of ca. 33 km^2. Based on the general geological framework, the island is directly connected to the subduction of the African lithospheric plate beneath the European one, precisely the Aegean microplate. It is placed right at the north of the Hellenic trench, that is developed due to the subduction, with a peculiar position, where the latter bends from a NNW-SSE to a NNE-SSW direction. Gavdos may have been related to the late N-S shortening that followed the N-S extension and graben formation and created the accretionary wedge of the Mediterranean ridge commencing by 11 Ma (Ring and Yngwe, 2018).

Mesozoic limestones, Eocene flysch, a few ophiolites (Sarakiniko Bay, located at the north-northwest) and Neogene to recent carbonate to clastic deposits build the island. The limestones occur at the south, southwestern part of the island, and are developing along a NNW-SSE direction, parallel to the general Hellenides trend of western Greece and Peloponnesus, while flysch is present in spot locations.

The Neogene unconformably overlies the pre-Neogene rocks and covers most of the central and northern part of the island, while a Pleistocenic marly limestone marine terrace (detailed literature review in Antonarakou, 2001; Tsaparas, 2005) and recent-subrecent aeolianites are among the youngest strata of the island. According to Anastasakis *et al.* (1995) in (Antonarakou, 2001), the Neogene deposits consist of two formations, namely these of Potamos and Metochia. Based on biostratigraphic data, Potamos Fm represents the oldest strata of Middle Serravallian to lower Tortonian age, while sedimentation in Metochia developed from the Middle/Lower Tortonian and ranged up to the Messinian (Triantaphyllou *et al.*, 1999) in (Antonarakou, 2001). The Metochia section was initially studied by (Postma *et al.*, 1993: Metochia-B), (Krijgsman *et al.,* 1995: Metochia-B/C) and (Postma and Ten Veen, 1999: Metochia-B/C). Based on the mostly regular alternations of brownish, organic rich layers and grey to blue hemipelagic marlstone, they first recognized consistent sedimentary cycling of late Miocene, and connected them to the Earth's orbit, and more precisely to the precession cycles, while by applying magnetostratigraphy they assigned an age of 9.642 Ma to the sections' basal strata. Initially, fifty-eight (58) such sapropelic layers (i.e. successive cycles) were distinguished in Metochia-B (56 in Krijgsman *et al.*, 1995), while additional forty (40) cycles were documented in Metochia-C, which represents the upper part of the section (Krijgsman *et al.,* 1995). Based on the later author's samples from the Metochia sections, Schenau *et al.* (1999) investigated the mechanism of formation for specific sapropelic layers, while Köhler *et al.* (2008) studied provenance changes of the material during the late Miocene The later authors concluded on changes a) from arid to more humid conditions (paleoclimatic) and b) from terrigenous input material to marine dominated (base to top of the section, respectively). By studying paleoflora from Gavdos locations of Tortonian age, Mantzouka *et al.* (2015) suggested that rather the paleogeographical setting than (paleo-)temperature changes affected the island during that time. Recently, Zachariasse and Lourens (2021), by studying the uppermost part of Metochia section (namely part D) concluded that the intercalated limestones are evaporitic, and that their formation onset is placed at 6.00 Ma, indicating abrupt sedimentation changes and a distinct rise in salinity, which in turn is connected to the MSC onset.

Objectives

By using Rock-Eval pyrolysis, this study focuses on the geochemical analysis of two sets of sapropelic layers from Gavdos Island (Figure 1, right): a) The first set correlates to the lowermost eight of those (L1-L8) described by Postma *et al.* (1993) and represents the lateral equivalent of the basal part of Metochia-B (compare Pyliotis *et al.*, 2013), and b) the second sampling set comes from the uppermost part of these sapropelic successions, located just below the sandstones of the MSC, which has never been geochemically studied up to now. The aim is to unravel the hydrocarbon generation potentiality of the late Miocene sapropelic deposits of the eastern Mediterranean, closing the gap between the basal (Tortonian) and the top sapropelic layers deposition (Messinian) of Gavdos and further to investigate the development of lateral continuity or differentiation of the geochemical properties of these strata relevant to gas prospectivity south and southwest of Crete, that is currently under way in two major offshore blocks southwest and south of Crete.

Figure 1. Gavdos Island with the investigated outcrops position.

Material and Methods

Two outcrops were investigated for this study. The first one is GL# outcrop and is located north of the main Metochia-B outcrop (Postma *et al.,* 1993). It consists of alternations of sapropelic layers and marlstones (silty mudstones) and specifically 8 levels/intervals of sapropels (approximately 7 m thick). In the basal part of the outcrop, a 2.4 m marly sandstone prevails and underneath of it, a 1-m-thick, grey to green muddy siltstone (GL#1 and GL#2 samples) was monitored, with noticing oxidations occasionally. As we proceed to the uppermost levels, thick sandstones (over 5 m) close the section. Regarding the second section, which is named GC#, it is situated south-east from Metochia section near the buildings of University of Crete. The total thickness of the outcrop is almost 16.5 m. Its bottom part (GC#0 sample) is a few meters eastern from the main body of the section and is considered as its base. Furthermore, a 12-m-thick section with similar alternations of sapropelic levels and marls is observed. The main issue in this section is the presence of oxidation levels in some of the intervals, which renders the distinction of the lithologies more difficult. Proceeding to the top part, bioclastic sandstones over 2.5 m thick close the outcrop.

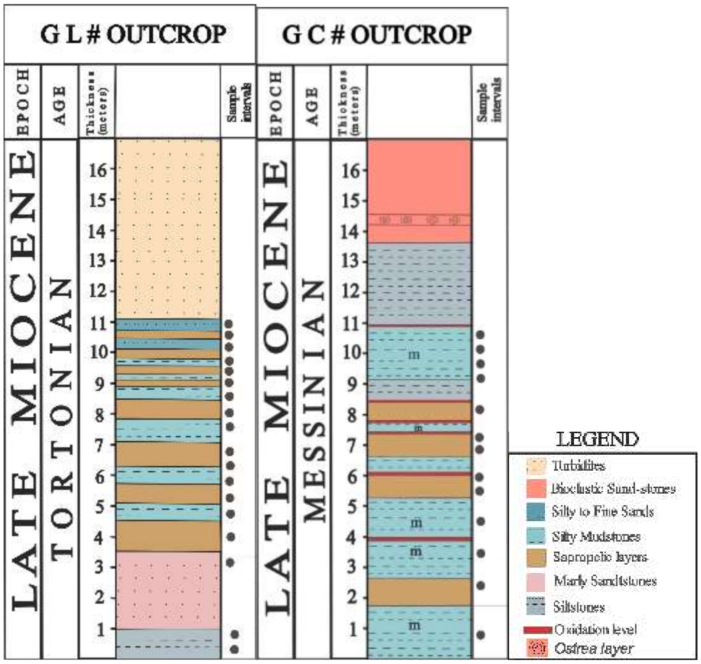

Figure 2. Lithostratigraphy of the studied GL and GC outcrops from Gavdos Island.

Bulk sampling was carried out in both outcrops. The total number of samples is fifty-nine (59). Thirty-five (35) come from the GL# outcrop and twenty-four (24) from the GC# outcrop. Both sapropelic layers and marlstones (mudstones, siltstones etc.) were collected. Rock-Eval pyrolysis was conducted to those samples, utilizing a Rock-Eval VI® (RE6) anhydrous open system pyrolyzer (Vinci Technologies; Lafargue *et al.,*1998) following the standard organic matter (OM) analysis setup (Behar *et al.*, 2001).

Samples, finely ground (<250 μm or 60 mesh) and dried at 60°C (overnight drying), were subjected to sequential pyrolysis and oxidation (Espitalie *et al.,* 1984). Various authors have provided analytical details of the RE VI methodology and interpretations of the resultant data (Behar *et al.,* 2001; Lafargue *et al.,* 1998, and other researchers). The volatile hydrocarbons produced were identified and quantified using a flame ionization detector (FID). Pyrolysis was conducted isothermally, commencing at 300 ◦C and escalating with a gradient of 25 ◦C/min until reaching a peak of 650 ◦C. Subsequent to pyrolysis, oxidation was performed from 300 to 850 ◦C at a heating rate of 20 ◦C/min. Consequently, key parameters such as S1 (mg HC/g rock), S2 (mg HC/g rock), S3 (mgCO_2/g rock), Tmax (◦C), TOC [(total organic carbon content) (%wt)], Hydrogen Index [(HI) (mg HC/g TOC)], and Oxygen Index [(OI) (mgCO_2/g TOC)] were determined (Espitalie *et al.*, 1984; Lafargue *et al.*, 1998). The evaluation of the data relied upon the studies by Tissot and Welte, (1984) and other researchers.

Results and Discussion

Based on the Rock-Eval pyrolysis data (RE-VI), all important parameters that measured and calculated, such as TOC, S2, HI and OI are presented in Figures 3 and 4 (for the studied outcrops GL# and GC#, respectively), from bottom to the top, according to the stratigraphic development of the deposits from older to younger.

A. GL# outcrop (lateral equivalent to the lower part of Metochia-B).
   The TOC content of the sapropelic layers fluctuates from 0.06%wt (GL#8b) up to 0.5%wt (GL#14). The rest lithologies' samples (silty mudstones, siltstones and sandstones) provide similar TOC results with a minimum of 0.03%wt (GL#5) and a maximum of 0.44%wt (GL#9). The average TOC content of this studied section is 0.24%wt with maximum S2 value of 0.52 mg HC/g rock at the basal samples. Additionally, the HI and OI values range between 0-130 mg HC/g TOC and 133-917 mg CO_2/g TOC.
B. GC# outcrop (uppermost part of Metochia-C).
   The TOC content varies from 0.13%wt (GC#7) to 0.43%wt (GC#4b) with an average value of 0.28%wt for the whole studied section. The HI and OI values found to range between 6-115mg HC/g TOC and 365- >1000 mg CO_2/g TOC.

Considering all above values distribution for both studied outcrops of the late Miocene (Tortonian and Messinian) of Gavdos Island, it can be concluded that they are indicative of a rather poor to fair H/C potential generation.

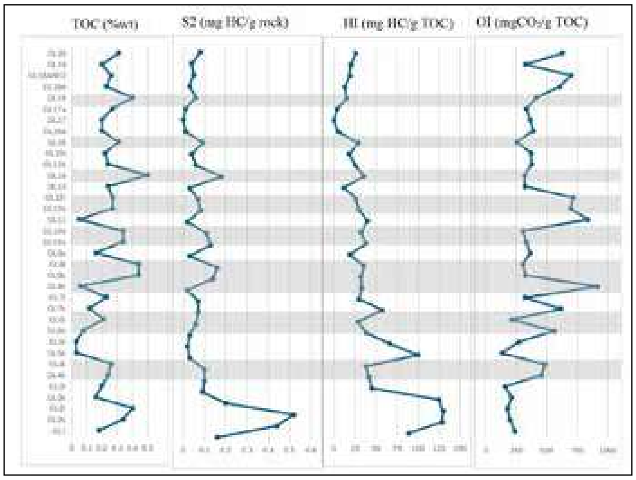

Figure 3. GL# outcrop; Vertical distribution of the main Rock-Eval VI parameters that have been recorded. Shaded intervals correspond to the sampled sapropelic layers.

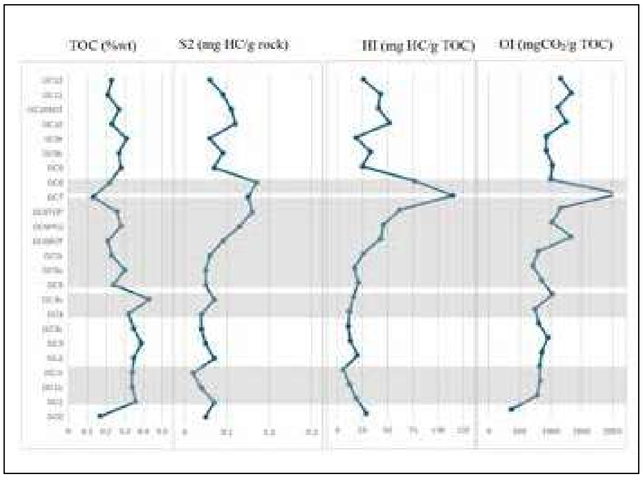

Figure 4. GC# outcrop; Vertical distribution of the main Rock-Eval VI parameters that have been recorded. Shaded intervals correspond to the sampling positions of the sapropelic layers.

Following the laboratory analysis and based on all RE-VI pyrolysis data, and in order to evaluate the maturity and hydrocarbon potentiality of the samples, a number of XY-diagrams were created, where all values obtained have been plotted. In the present work only two of them are presented, namely a) the HI vs Tmax diagram and b) the TOC (log) vs S2 (log) diagram.

The first one (Fig. 5, left), is representative of the kerogen types of the analyzed samples. As it is clearly shown, the majority of the plotted samples' values reveal a Type IV kerogen, while a small amount of them tends to a Type III kerogen and a possible gas-prone source rock.

The second diagram (Fig. 5, right) indicates the hydrocarbon generation potential of the rocks. All values are plotted in the lower left quadrate of the diagram, therefore, as we mentioned before, the analyzed samples exhibited a poor to fair H/C potential generation for both outcrops. A slightly poorer indication is apparent for the GC#, which represents the Messinian samples, where a number of oxidized layers occurred at various stratigraphic levels (Fig. 2: GC#). Despite the careful sampling procedure, being conducted to minimize the effects of weathering and oxidation, it is highly likely that the analyzed samples could display more favorable organic geochemical signatures.

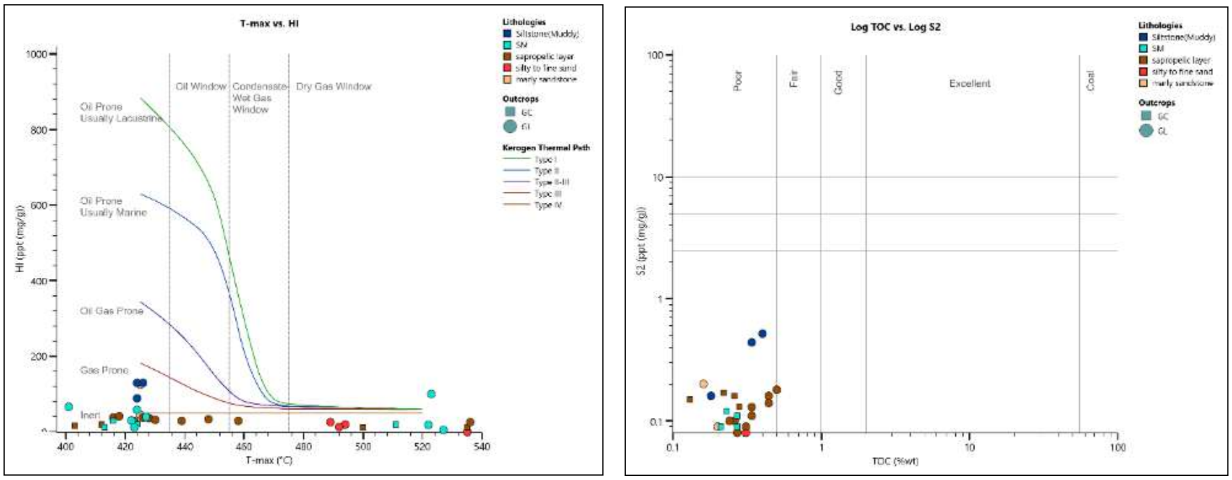

Figure 5. At the left: HI (mg HC/g TOC) versus Tmax (°T) showing idealized kerogen types and thermal maturity of the studied samples and (at the right) Logarithmic plot of TOC (%wt.) versus S2 (mg HC/g rock) illustrating the source-rock potential. As in the legend, squares represent samples of the GC# outcrop, while circles the GL#.

This study completes previous research for the organic-rich layers of Metochia [(Schenau *et al.*, 1999); who studied particularly three sapropelic layers of the basal section: L5-L7], the source rock potentiality of Gavdos (Pyliotis *et al.*, 2013), as well as the review work for the organic geochemistry signature of various Crete Neogene sediments of (Maravelis *et al.,* 2022) by contributing additional data to compare the geochemical analysis of the Gavdos Metochia-B lower part section with its lateral equivalent (GL#). The first set of samples of the present work (GL#), represents the sapropelic/mudstones interval that stratigraphically is situated below the turbiditic sequence (Krijgsman *et al.*, 1995). Furthermore, by extending this type of analysis to locations that have not yet undergone geochemical investigation (Metochia-C), the gap with the analysis of samples from the GC# outcrop is closed. The latter appears to correlate with the upper cycles of the Metochia-C section (M92-M96) as an equivalent. Gaining a comprehensive understanding of the entire area through its stratigraphic evolution is crucial for its paleogeographic development prior to the Messinian Salinity Crisis, and at the same time for the hydrocarbons exploration that is currently underway.

Conclusions

A geochemical analysis has been conducted on samples obtained from outrcrops on Gavdos Island to reveal new potential source rocks. Fifty-nine samples of two outcrops (GL# and GC#) have been studied by using RE-VI pyrolysis. These samples included mainly sets of sapropelic layers and mustones/siltstones alternations. GL# samples are of Tortonian age, while GC# samples are of Messinian age (Metochia-C, upper part).

1) The RE-VI results have shown that hydrocarbons generation potential varies from poor to fair in both studied outcrops.
2) The lateral equivalent GL# outcrop (to Metochia-B, basal part, cycles L1-L7/L8) provided lower values in relation to data from previous authors, indicating that the outcrop was located at a more marginal sector of the sedimentary basin.
3) Samples of the GC# outcrop, proved of poor H/C potential generation, indicating that locally, the productivity was rather decreased approaching the onset of the Messinian Salinity Crisis (MSC).
4) By studying these two outcrops, a research "gap" is partially covered, particularly in relation to the Messinian record (GC# outcrop samples). However, more analyses need to be conducted to get a better and more detailed understanding of the maturation of these rocks under proper burial conditions.
5) These analyses and their findings have enriched the hydrocarbon map of the Eastern Mediterranean and

made an additional contribution to the energy sector, which should expect enhanced results moving to the offshore area, due to better organic matter preservation.

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References

Antonarakou, A., 2001. Biostratigraphic and Paleoenvironmental Interpretation in Miocene Sediments of the Eastern Mediterranean (Gavdos Island). PhD Thesis, National and Kapodistrian University of Athens, Department of Geology and Geoenvironment, Athens, 176 p. (in Greek).

Behar, F., Beaumont, V., Penteado, H.L. De B., 2001. Rock-Eval 6 Technology: Performances and Developments. Oil & Gas Science and Technology-Rev. IFP 56(2), 111–34.

Espitalie, J., Marquis, F., Barsony, I., 1984. Geochemical Logging, in: Voorhees, K.J. (ed.) Analytical Pyrolysis: Techniques and Applications, 276–304.

Köhler, C.M., Heslop, D., Dekkers, M.J., Krijgsman, W., Van Hinsbergen, D.J.J., Von Dobeneck, T., 2008. Tracking Provenance Change during the Late Miocene in the Eastern Mediterranean Using Geochemical and Environmental Magnetic Parameters. Geochemistry, Geophysics, Geosystems 9(12), 1–14.

Krijgsman, W., Hilgen, F.J., Langereis, C.G., Santarelli, A., Zachariasse, W.J., 1995. Late Miocene Magnetostratigraphy, Biostratigraphy and Cyclostratigraphy in the Mediterranean. EPSL Earth and Planetary Science Letters 136, 475–494.

Lafargue, E., Marquis, F., Pillot D., 1998. Rock-Eval 6 Applications in Hydrocarbon Exploration, Production, and Soil Contamination Studies. Revue de l'Institut Français Du Pétrole 53(4), 421–37.

Mantzouka, D., Kvaček, Z., Teodoridis, V., Utescher, T., Tsaparas, N., Karakitsios, V., 2015. A New Late Miocene (Tortonian) Flora from Gavdos Island in Southernmost Greece Evaluated in the Context of Vegetation and Climate in the Eastern Mediterranean. Neues Jahrbuch für Geologie und Paläontologie - Abhandlungen 275(1), 47–81.

Maravelis, A., Kontakiotis G., Bellas, S., Antonarakou, A., Botziolis, C., Janjuhah, H.T., Makri, P., Moissette, P., Cornée, J.J., Pasadakis, N., Manoutsoglou, E., Zelilidis, A., Karakitsios, V., 2022. Organic Geochemical Signatures of the Upper Miocene (Tortonian—Messinian) Sedimentary Succession Onshore Crete Island, Greece: Implications for Hydrocarbon Prospectivity. Journal of Marine Science and Engineering 10(1323), 1-17.

Postma, G., Hilgen, F.J., Zachariasse, W.J., 1993. Precession‐punctuated Growth of a Late Miocene Submarine‐fan Lobe on Gavdos (Greece). Terra Nova 5(5), 438–44.

Postma, G., Ten Veen, J.H., 1999. Astronomically and Tectonically Linked Variations in Gamma-Ray Intensity in Late Miocene Hemipelagic Successions of the Eastern Mediterranean Basin. Sedimentary Geology 128, 1–12.

Pyliotis, I., Zelilidis, A., Pasadakis, N., Panagopoulos, G., Manoutsoglou. E., 2013. Source Rock Potential of the Late Miocene Metochia Formation of Gavdos Island, Greece. Bulletin of the Geological Society of Greece 47(2), 871–79.

Ring, U., Yngwe, F., 2018. To Be, or Not to Be, That Is the Question' - The Cretan Extensional Detachment, Greece. Tectonics 37(9), 3069–3084.

Schenau, S.J., Antonarakou, A., Hilgen, F.J., Lourens, L.J., Nijenhuis, I.A., Van Der Weijden, C.H., Zachariasse, W.J., 1999. Organic-Rich Layers in the Metochia Section (Gavdos, Greece): Evidence for a Single Mechanism of Sapropel Formation during the Past 10 My. Marine Geology 153, 117–35.

Tissot B.P., Welte D.H., 1984. Petroleum Formation and Occurrence. 2nd ed. Springer-Verlag Berlin Heidelberg New York Tokyo.

Tsaparas, N., 2005. Contribution to the Sedimentation History of Marine Formations of Upper Cenozoic of Gavdos Island. PhD Thesis, National and Kapodistrian University of Athens, Department of Geology and Geoenvironment. Athens, 210 p. (in Greek).

Zachariasse, W.J., Lourens. L.J., 2021. The Messinian on Gavdos (Greece) and the Status of Currently Used Ages for the Onset of the MSC and Gypsum Precipitation. Newsletters on Stratigraphy 55(3), 333–60.