



Technical University of Crete
School of Mineral Resources Engineering
Petroleum Engineering MSc

MASTER THESIS

“Oil and gas potential of the Neogene clastic formations in the sedimentary basins of NW Crete”

EXAMINATION COMMITTEE

Emmanouil Manoutsoglou

Spyridon Bellas

Ioannis Oikonomopoulos

Telemenis Dimosthenis

Chania 2022

A MSc thesis submitted in partial fulfilment of the requirements for the degree
of Master of Science in Petroleum Engineering

The MSc Program in Petroleum Engineering of the Technical University of
Crete was attended and completed by Mr. Dimosthenis Telemenis due to the
HELPE Group Scholarship award

ACKNOWLEDGMENTS

This dissertation has been completed at TUC (Technical University of Crete) and FORTH/IG (Institute of Geoenergy). I would like to express my gratitude to my scientific advisor, Principal Researcher Spyridon Bellas for his valuable guidance and assistance throughout the whole project. We had a wonderful collaboration both on the field and at the lab.

My sincere thanks extend also to Prof. E. Manoutsoglou TUC (Technical University of Crete) who kindly provided with hints to the diatomites of western Crete. Moreover, I would like to thank the team of the Institute of Geoenergy (FORTH/IG), with Head Prof. Nikolaos Pasadakis and further the technical stuff.

Moreover, my gratitude to Miss Vayanna Makri, (MSc, doctoral candidate), who was always willing to help with advices and explanations, not only during the required geochemical analyses but also for every technical problem that could occur.

In addition, I would like to give my gratitude to my colleague Zafeiria Makridou for the cooperation we had to achieve our master thesis projects.

Finally, I am deeply indebted to my family for their patience, support and encouragement throughout my master studies.

ABSTRACT

Crete is one of the largest islands in Mediterranean Sea, located in the Eastern part of it and it is considered of great geological aspects.

The geological evolution and conditions that shaped the Neogene paleoenvironmental history of the Mediterranean Sea, have been investigated so far by numerous researchers. The Upper Miocene particularly (late Tortonian and early Messinian) was generally characterized by the rapid building of extensive carbonate platforms and basins which included hemipelagic formations (marls/mudstones, sapropels), as well as shallow-marine deposits (evaporitic formations, coral reefs, bioclastic and red algae limestones).

This study focuses on three sedimentary sections in those (marginal) Neogene basins on NW part of Crete in the Prefecture of Chania and their hydrocarbon prospectivity.

More specifically, these Neogene basins, in which the sections are contained, are Apokoronas (Kalyves), Kalydhonia and Afrata basins. A macroscopically description of lithologies and sediments has been occurred in all three outcrops and also a geochemical analysis has been conducted.

The studied outcrops pinpoint an Upper Miocene (Tortonian/Messinian) pre-evaporitic age of the deposits. Kalyves section is well-laterally extended, presents adequate thickness and is subdivided into three subsections and four profiles (due to dense vegetation and steepness), while the other two are clearly more narrow and continuous. Stratigraphic analysis of the outcrops illustrates clear alternations of fine sands, siltstones/mudstones and laminated diatomaceous beds from bottom to top in each subsection in Apokoronas basin, mudstones alternating with sandstones in Kalydhonia Basin and mud/clay/siltstones beds interchanges with sandstones in Afrata Basin.

Bulk sampling of 48 samples has been carried out in the three outcrops. In more detail, 28 samples in the synthetic section of Kalyves, 9 samples in the section of Kalydhonia, 7 samples from Afrata section and 5 extra samples from area near Kalyves section were collected. For this set of samples, geochemical analysis has been fulfilled by the means of Rock-Eval 6 pyrolysis to facilitate the understanding of hydrocarbon potential. Total organic carbon (TOC) values of the samples reach up to 3.3 %. As a result, a kerogen type of II-III, leaning towards type III is documented by the analyzed samples of Kalyves section. The sets of samples of the other two sections indicate a kerogen type IV in both of them.

Based on the analysis several outcomes have been made. This study supports and reports the extent of Messinian Diatomites in Western Crete. The stratigraphic analysis of the Kalyves section establishes System Tracts (ST), with a transgressive ST in the bottom part of the section, followed by a Highstand to Regressive ST in middle and top parts. Moreover, it is indicated the potential of Diatomites as source rock for hydrocarbon generation. In addition, a distribution of new potential gas/oil sources in different areas of District of Chania (Western Crete) is demonstrated. That also declares the high significance for the offshore hydrocarbon exploration in the Eastern Mediterranean, and especially in offshore Western Crete.

Data

INTRODUCTION.....	7
CHAPTER 1	9
1.1. Study Area	9
1.1.1. Neogene Formations in studied areas	11
1.2. Kalyves Neogene Basin.....	15
1.2.1. In general.....	15
1.3. Kalydhonia Neogene Basin.....	18
1.3.1. In general.....	18
1.4. Afrata Neogene Basin	19
1.4.1 In general.....	19
2. CHAPTER 2: MATERIAL AND METHODS.....	21
2.1 Geology	21
2.1.1. Kalyves Section	21
2.1.2. Kalydhonia Section.....	29
2.1.3. Afrata Section	34
2.2 Geochemistry	40
2.2.1. Methodology	40
2.2.2 Results	42
2.3. Type of Kerogen and abundance of samples	47
CHAPTER 3	54
3.1 Conclusions/ Discussion.....	54
REFERENCES.....	56

INTRODUCTION

Crete is the largest island of Greece (Figure 1) and one of the larger of Europe and is located in the Southeast Mediterranean Sea. It is positioned to the southernmost part of the Hellenic arc (around 90km away) between the south Aegean volcanic arc and the south Ionian trench. (Kontopoulos, Zelilidis 1997). Geologically it belongs to the outer (external) Hellenides. There is also an Uppermost Unit, which is placed to the Pelagonian Zone (Internal geotectonic zone of Hellenides) (Martha et al., 2017 and references therein, i.e. Bonneau, 1972). Crete includes Neogene deposits, Quaternary sediments and several nappes of Triassic to Cenozoic rock units that are correlated to different geotectonic zones (Figure 2). The nappe pile of Crete is roughly divided into two members:

- a) A lower one, that contains high pressure and low temperature (HP-LT) metamorphic rocks and
- b) An upper one with no metamorphic rocks.

It is thought that these nappes have been placed together through south-directed subduction and/or collision and accretion to the northern Gondwanan edge. The pre-Miocene basement rocks were tectonically cracked into numerous parts because of uplift and exhumation of the nappe masses (Thomson et al., 1999) and were responsible, in combination with the activation of N-S extension in the Early to Middle Miocene (van Hinsbergen, Meulenkamp, 2006) for the creation of Middle to Late Miocene sedimentary basins. (Maravelis et al. 2022).

The main Geological aspect that we will deal with in this project is the Neogene lithologies and the sedimentary (Miocene) Basins that are being contained. More specifically, we investigate/explore the Oil and/or gas potential of these Neogene formations.

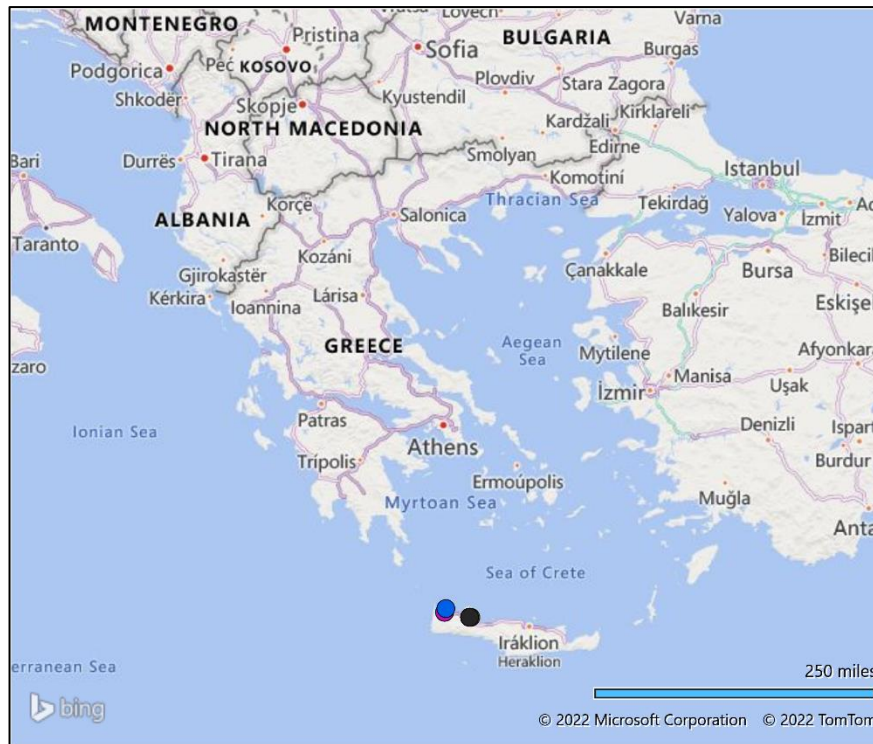


Figure1. Map of Greece, dots pinpoint the positions of the investigated areas

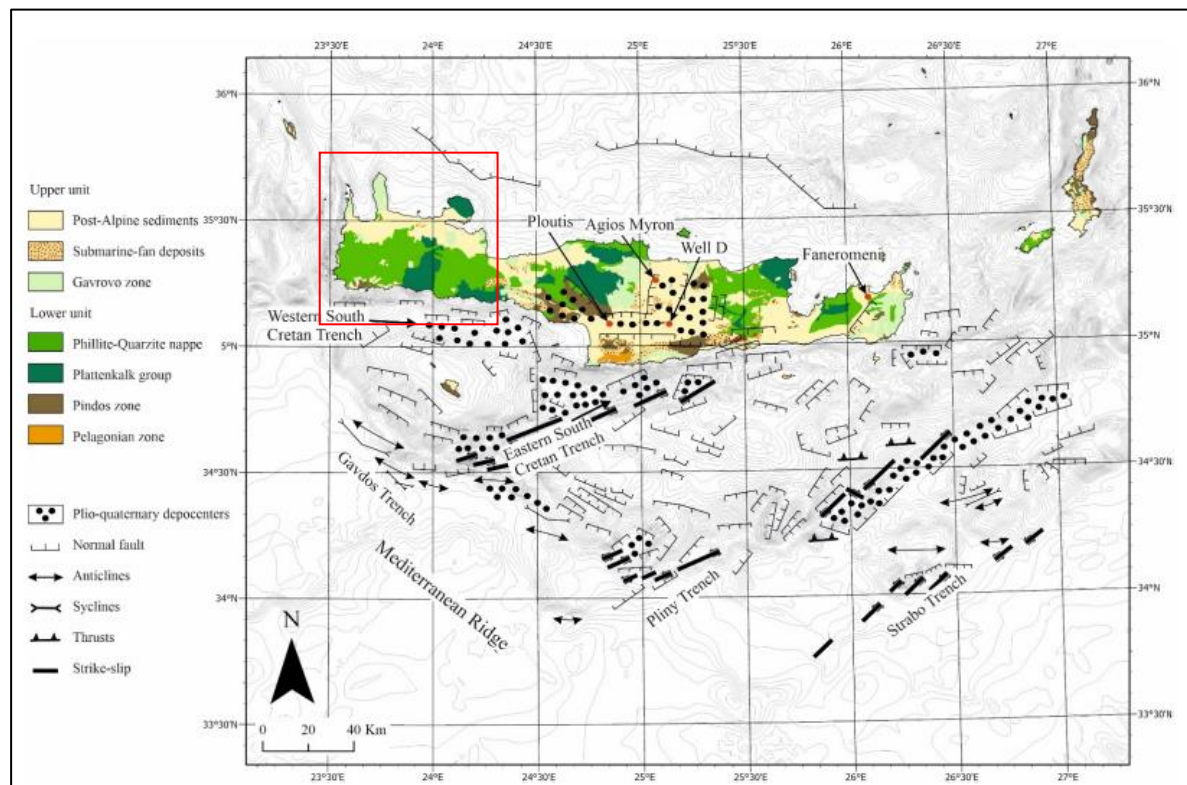


Figure 2. Figure by Maravelis et al 2022, main geotectonic zones of Crete Island (Modified)

CHAPTER 1

Twelve (12) Neogene formations exist in the wider Chania area and have been originally described by Freudental (1969): Namely the Mesonisi Formation, Roka Formation, Koukounaras Formation, Kissamou Formation, Khairitiana Formation, Khatzi Formation, Tavronitis Formation, Ayios Yeoryios Formation, Akrotiri Formation, Soudha Formation, Keramia Formation and Gavdos Formation.

These formations represent the Neogene basins' infill, from middle Miocene onwards, not including the Quaternary marine and non marine depositional sequences of the area.

1.1. Study Area

In this study, we investigate three sedimentary deposits/outcrops, in the prementioned Neogene Basins of western Crete. More precisely, their locations are in the North-Western Crete, in the prefecture of Chania. The three different locations are depicted in the next figure (Figure 3). All three outcrops were analyzed both geologically (macroscopically, lithologically and sedimentologically) and geochemically (in the laboratory). The total number of samples that were taken for those analyses is forty-eight. It should be noted, that the descriptions of the sediments / layers of the studied outcrops, are based on field review/observations and not extracted by lab analysis.

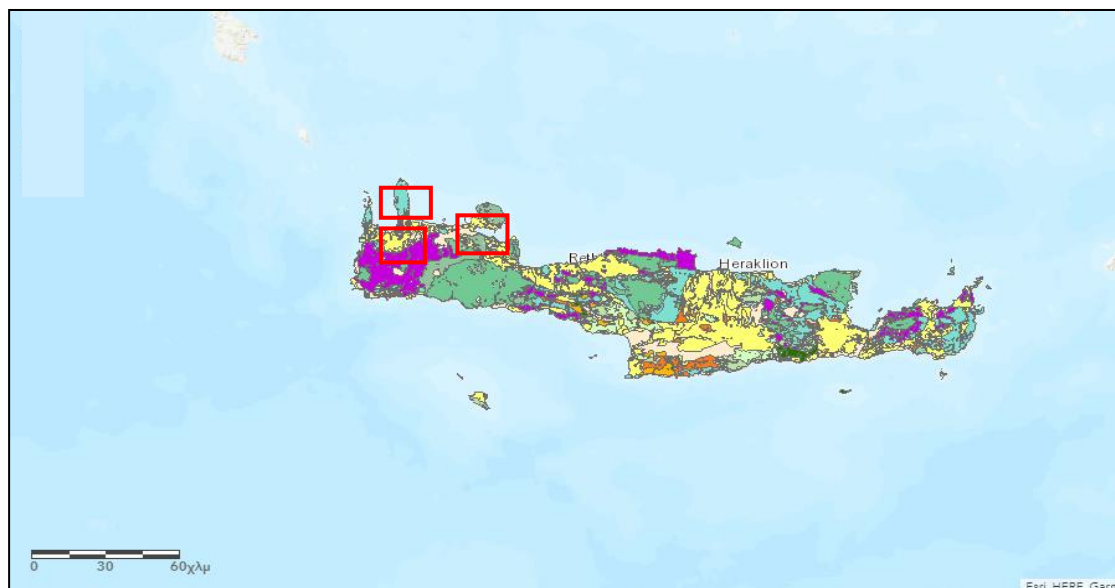


Figure 3. Map by <https://geoportal.apdkritis.gov.gr/> (modified)

It is worthy to mention that two of the investigated sections (Kalydhonia and Afrata) have already been studied geologically (and mainly biostratigraphically) in the past but they were never studied in a geochemical aspect. Moreover, the third (in Kalyves Basin) has not ever been reported before out of a short note talking generally on laminated sediments (marls) by Freudenthal (1969: p. 36) and it is the first time that is described and investigated in detail (co. also Telemenis et al., 2022). The Neogene lithologies (according to Freudenthal, 1969) that the studied deposits include are:

- the **Kissamou** formation- reported also as **Tefelion** Group (in Kalydhonia and Afrata) and resemble those of
- **Khairitiana**- placed probably to the **Vrysses** Group, described as including alternations of laminated and homogenous marls (in Kalyves).
- Afrata and Kalydhonia sections also include the **Roka** formation deposits (i.e. the **Vrysses** Group) (Figures 3a and 3b with both concepts).

The prementioned (lithostratigraphic) Groups assignments (i.e. Tefelion and Vrysses) are reported by Hinsbergen & Meulenkamp (2006), but it has to be pointed out that these authors refer to the whole island and not specifically to the western part of it which is currently investigated.

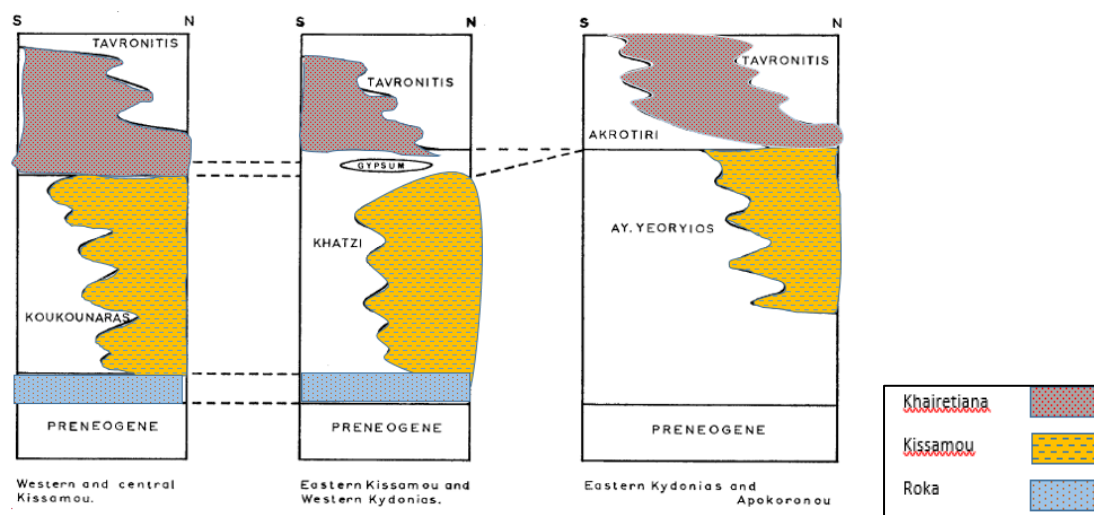


Figure 3a. Neogene Formations of western Crete by Freudenthal 1969 and legend to the right (modified)

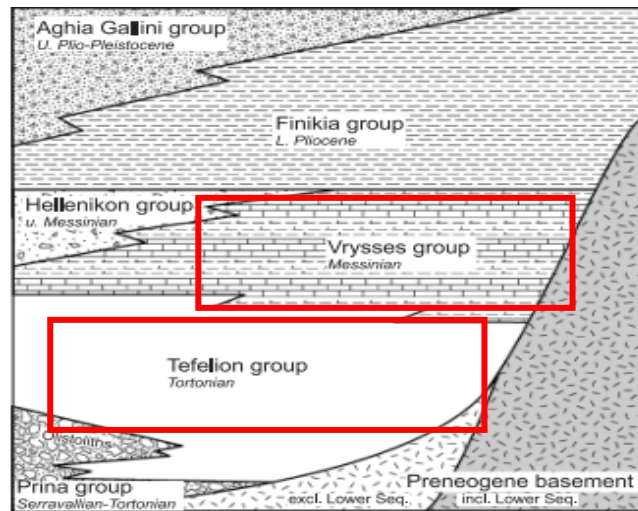


Figure 3b. Lithostratigraphy of Crete: the major facies groups by Hinsbergen & Meulenkamp (2006) (modified)

1.1.1. Neogene Formations in studied areas

The Roka Formation

Three different lithologic units have been described within the Roka Formation (Freudental 1969). From bottom to top they are: a) Conglomerates, b) sands-sandstones (with *Heterostegina* and other fossils) and c) organic limestones.

a) Coarse, angular, red or brown conglomerates. They become more finely grained in their upper part and may then contain molluscs, such as *Ostrea*. The thickness of those beds is between 1 and 60 meters, but it rarely exceeds a few meters.

b) Coarse /fine grained, red or brown sands. Locally they are cemented by calcareous matrix, giving rise to strongly indurated calcareous sandstones. At many districts, macro- and microfossils can be observed in the sands, most frequently *Clypeaster*, *Pecten*, *Ostrea* and *Heterostegina*. Exposures with a good macro- and microfauna have been found in a lot of different areas like Nokhia, Afrata, Platanos, etc. Maximum thickness of those sands reaches 30 meters in the area of Platanos. In two localities (Potamidha and Gribeliana) cross-bedded sandy layers have been reported. These fairly strongly dipping sand layers are cut off by more horizontal, overlying sands.

c) Thick-bedded or unbedded, yellow or orange, marly biogenous limestones. Macro- and microfossils appear in abundance, with *Pecten* and Echinoids such as *Clypeaster* being the most common while at some places *Heterostegina* can be detected. The thickness of this unit varies between 0.5 and 50 meters, but it does not exceed 10 m most of the times. These

limestones occur almost in every locality-area where the Roka Formation is exposed, and sometimes they overlie the other two prementioned lithologies.

In general, one or two of these lithologic units appear at the same time at a single locality-area.

The Khairitiana Formation

The formation is mainly consisted by amorphous yellowish marls in alternation with laminated brown or yellow marls/clays/silts. The thickness of one sequence of this alternation, usually does not exceed 5 meters. In addition, in some areas gypsum deposits appear. Some graded beds also are present, but rare, in different districts with their thickness being less than 0.5 meters. Coarse, graded intercalations are also rare.

Macrofossils/molluscs are rarely come across the amorphous marls, but microfossils like *Discospirina* occur in plethora. Such kind of fossils were not found in the laminated beds, which contain a lot of plant debris. Sponge needles and diatoms are frequently found in the laminated layers too. The graded beds display similar resemblance to those of other Neogene Formations like Kissamou, but their basal part is less coarse. The biggest components do not exceed 1 cm in diameter. *Heterostegina* specimens have been found in the coarse lower parts in some localities, but they are rare. In the Kissamou District, near the villages of Dhrapanias and Papadhiana, gypsum deposits exist in the lowermost part of the Formation. They are found in association with laminated marls with fish remains. Their thickness is most up to 1.5 meters.

At other areas, where bedding planes are not visible, the thickness can reach up to 50 m. At these localities, squeezed out gypsum masses or solved gypsum masses exist, which have been secondarily crystallized. Those kind of gypsum masses have been observed in areas like Papadhiana and Kaloudhiana villages.

In the Apokoronou District the lithology of the Formation is differentiated. "Here, laminated and amorphous white marls alternate with coarser, organic, detritic limestones, in which never any gradation could be observed."

A major observation is that the laminated marls are softer than the amorphous marls and detritic beds. This difference led to a terraced character of the morphology. These laminated marls alternate with thinly bedded cemented limestones with *Pycnodonta*. Sponge needles

are also in abundance. The marls demonstrate similar resemblance to the Italian "Tripoli" and "Spanish moronitas". The maximum thickness of the Formation reaches up to 100 meters.

The Tavronitis Formation

It is divided into three parts a, b and c (Freudenthal, 1969). In the lower part amorphous marls of white colour is the dominant lithology. In the middle part, graded beds of gravels "*slumped into similar looking marls*" have been reported. Lastly, in the upper part sandy beds, slightly graded, alternating with amorphous marls again are the lithologies of the formation. Many slumps of coarse material occur in the marly levels.

The succession of those lithological units is mainly exposed along the flanks of the Tavronitis River.

a. The lower part of the Tavronitis Formation is exposed in the area 'Moulete' of Kissamou. It consists of amorphous, unbedded marls of white colour and with no macrofossils. A lot of unoriented tubular worm tracks have been observed. They have a lighter colour than the surrounding marls. In the basal part several non-graded coarse gravel layers are interbedded. They contain well rounded shale and quartzite components. The contacts with the underlying and overlying marly beds are irregular and waving.

b. The middle part of the Tavronitis Formation consists of the same marls, but with the difference of numerous unoriented worm tracks. Large masses of coarse bearing material (with macrofossils) have slumped into these marls. They have eroded the underlying marls, again creating waving lower contacts. The material of the marls has been mixed with the other displaced material. The upper contact of the layers contains slumped material too, with the overlying marls being generally straight. The slumped material consists mainly of sand but also a small amount of gravel is included, with a maximum bed thickness of 3 meters. Plenty macro- and micro-fossils such as *Pecten* and *Elphidium* have been found. Graded bedding has not been monitored.

c. The upper part is characterized by marls with slump structures that underlie well bedded, slightly grading (medium- to fine-grained) brown, sands of 25-50 cm, alternating with cemented, amorphous white marls with numerous unoriented worm tubes. Furthermore, within the marls, vertically running spurs with diameter between 2 to 3cm are present. They are apparently burrows of animals (like crabs), which are filled with sandy material of the overlaying graded layer. Macrofossils are mainly in lack in the graded beds.

The total thickness of the Tavronitis Formation in the Tavronitis River valley is almost 80 meters.

The Kissamou Formation

Kissamou Formation is one of the most widespread formations. The type section is ca. 300 m E of the village of Potamidha Kissamou. It mainly consists by amorphous, but also very thinly to medium bedded (sometime laminated) clay/mudstones of blue grey color. Interbedding boundaries are usually difficult to recognize. Fine clastic layers are also intercalated, which are rarely graded, particularly near the basin margins. Slump structures with shell fragments and mudstone balls occur as well. This formation overlies or laterally interfingers with the Roka Formation, but generally the basis of Kissamou Formation is not exposed. The overlying strata are consisting of the more or less sandy Khairethiana Formation mainly in the eastern part of the Kastelli Basin. Transition is usually gradual, although a change in color from blue to yellow is recognizable. A report of Freudenthal (1969) that to the southeast margin of the Kastelli Basin the Kissamou Formation is conformably overlain by the Khatzi Formation could not be confirmed. A rather deep marine, depositional environment is postulated, compared to the Deep Water Facies (DWF).

At the type locality the transition from Kissamou Formation to the overlying Khairitiana Formation is not exposed. In the Apokoronou area, there is a small, isolated occurrence of the Kissamou Formation near Vryses which is overlain by the Khairitiana Formation, but unfortunately the contact is not exposed. The Kissamou Formation is almost completely geographically restricted to the Kissamou District, where it laterally passes into the Koukounaras Formation. Isolated occurrences as mentioned above can be found in the vicinity of Vryses Apokoronou.

Lithologically the main body of the Formation consists of blue, purple or grey mostly amorphous clay/mudstones, where in some districts they are laminated. Within these formations strongly indurated, graded and ungraded, sandstones, calcarenites and organic limestones occur at various stratigraphic levels. Three lithological types are the main ones:

1. Blue or purple, generally amorphous, sometimes laminated clays. Macrofossils' are abundant, but only at a few localities (have been described by KOLIOPOULOS 1952). Among them *Pycnodonta*, *Amussium* and *Ephippium* are the most common with a lot more like *Dentalium*, *Cardium*, *Chlamys*, *Spondylus* etc. to exist less frequent. In some districts like Ayia Marina the Kissamou Formation mainly consists of laminated, sandy clays. At other areas, at

the upper part of the Kissamou Formation the laminated clays are being transitional to the laminated clays and marls of the overlying Khairitiana Formation.

2. Graded, clastic intercalations. In almost all sections studied the main mass of blue and purple clays is interrupted by indurated coarse- to fine-grained graded beds at various stratigraphic levels. Their thickness ranges between 5 cm and 10 m. In general, the basal parts of these graded beds consist of gravel, and in some cases are mixed with large clay balls derived by the erosion of underlying formations. To add up, algal balls and *Heterostegina* specimens are also present in these coarse basal parts. Periodically there is a narrow, transition (laminated again) between the sandy parts of the graded beds and the overlying amorphous clays. Sometimes the erosion that is caused by the overlying graded beds to the underlying beds is so strong, that the underlying sequence has been completely eroded away, even parts of the fine-grained top. Most of the times, the thickness of the graded intercalations does not exceed 2 m.

3. Non-graded sand, gravel and limestones. At several localities sand or gravel layers, occur within the blue/purple amorphous clays at different stratigraphic levels. Graded bedding is not very clear in these formations. Furthermore, they are compacted by calcareous matter and in several areas they mix up with the sandy beds. In some localities, these beds are present in the top of the Kissamou Formation. Bryozoa, coral debris and *Heterostegina* are being contained in these beds. That kind of limestones are formed nowadays in different areas (big distances). They are probably of similar origin, but have been displaced and cemented. The total thickness of the Kissamou Formation reaches up to 175 m.

Further details on the macroscopic fauna is out of the scope of this work. (see detailed work in Freudenthal 1969 and references therein).

1.2. Kalyves Neogene Basin

1.2.1. In general

In this studied area, a synthetic outcrop that includes new diatomitic occurrences in the marginal Neogene basin of Apokoronas is reported and studied both stratigraphically and geochemically. It is located south of Souda port, in Chania province. The studied section is well-laterally extended and presents adequate thickness in relation to other diatomitic occurrences in Crete. We subdivided it into three subsections and four profiles, the lower

(includes 2 profiles), middle and upper one, separated by not recorded parts due to high vegetation density and steepness. Their precise locations are: Lower Part (N35°27'27"E24°10'0.2"), Middle Part (N35°27'24" E24°09'55"), Upper Part (N35°27'18" E24°10'03") (Figure 4). Twenty-eight samples were taken in total from this section and five more from isolated areas (Figures 5,6) with bulk sampling (not lamina scale).

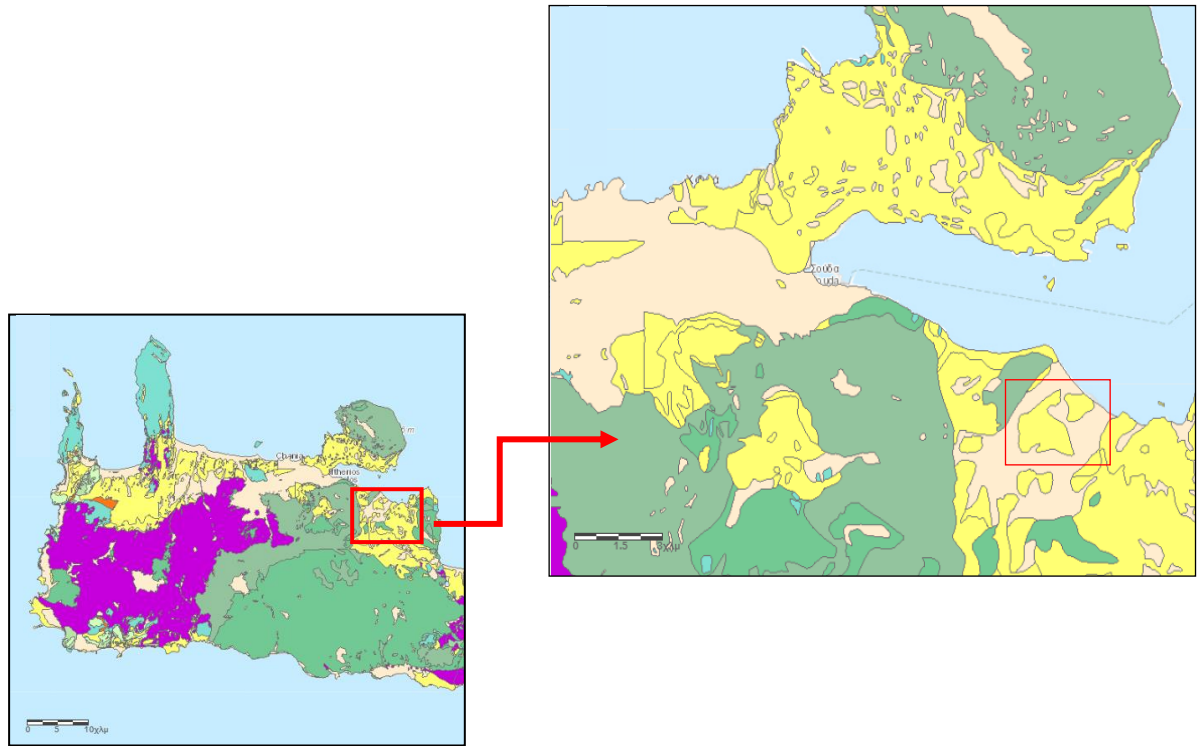


Figure 4. Neogene Basin in Apokoronou District (Map by <https://geoportal.apdkritis.gov.gr/>(modified))

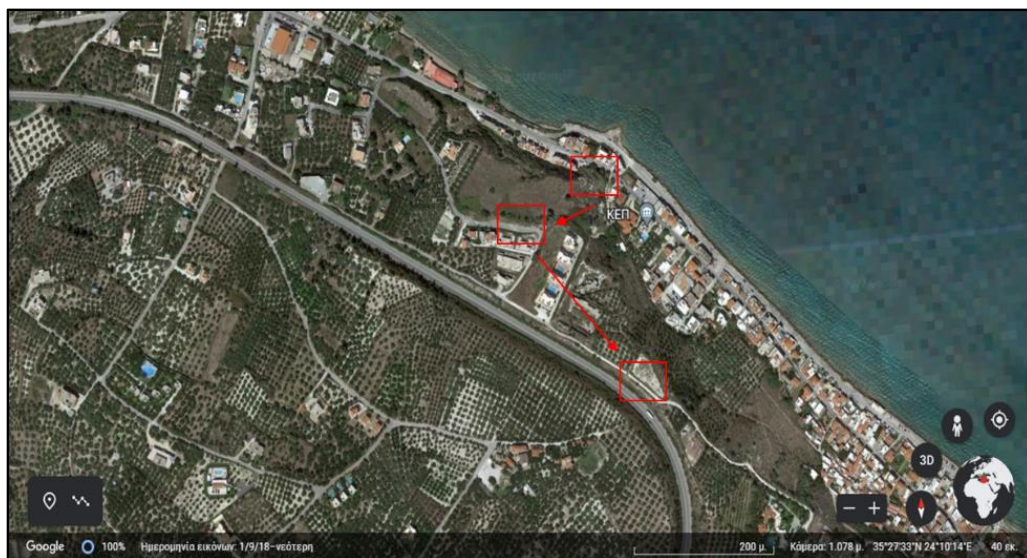


Figure 5. The three subsections of the synthetic section, modified map by Google earth



Figure 6. From left to right the three subsections : Bottom , Middle and Upper Part

In addition, we located a small section about 1km away from the main outcrop (Figure 7.). We clearly noticed that the beds were slumped and we collected four samples, to make comparisons with the results of the main section.



Figure 7. Slump, area near the main section, see the geologic hammer for scale.

1.3.Kalydhonia Neogene Basin

1.3.1. In general

The Kalydhonia Basin is a sedimentary basin (or sub-basin), located on the NW Crete and situated directly on the foot of Rodopou peninsula in Chania Province (Figure 8). Kalydhonia section is located on the national road (Figure 9), about 20-25 kilometers to the west of Chania city. Basin's boundaries are situated between Kastelli Basin to the west and Voukolies Basin to the east respectively (Keupp and Bellas in collab. with Frydas and Bartholdy 2000). The precise location of it is given as: N35°31'38'' E23°45'24'' and it is found on the left part of the national road (driving from Chania to Kissamos Town) and in the opposite side of the road there is the cement industry "Heracles". This section has already been described geologically (Keupp et al. 2000; Bellas. et al 2007) in detail. For that reason, the bulk sampling that we accomplished was for mainly analyzing the samples geochemically. In addition, a description of the area of the sampling has been done. A total number of nine samples has been collected, all in the right part of section but in three different levels.

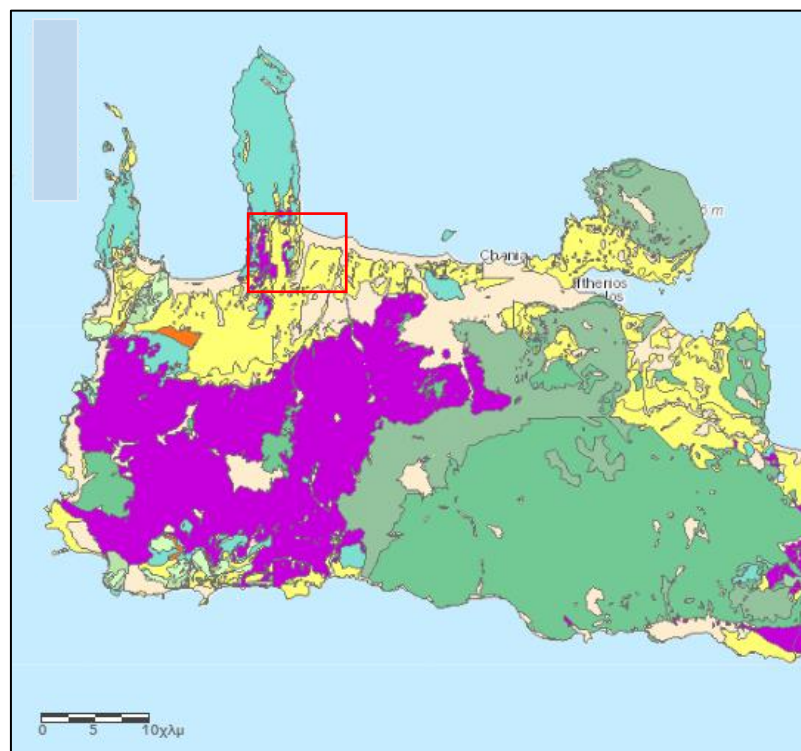


Figure 8. Neogene Basin in Kalydhonia (map by <https://geoportal.apdkritis.gov.gr/>(modified))

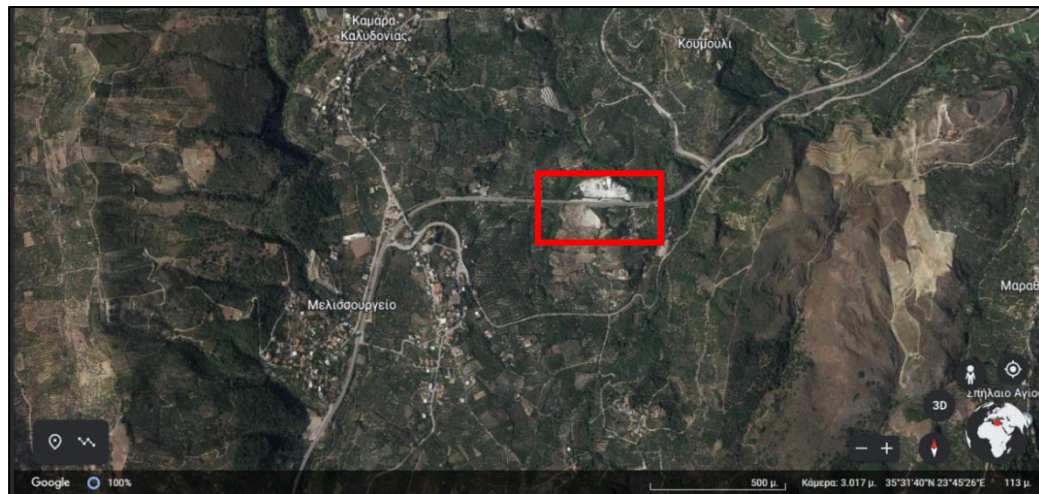


Figure 9. Location of the section, modified map by Google earth

1.4. Afrata Neogene Basin

1.4.1 In general

Afrata section (Figure 10) is a composite section composed by two parts (A, B), located in the Afrata village, on Rodopou Peninsula. Two major theories indicate either it was partially connected to the Kalydhonia basin to the east or it could be a small, narrow but elongated (north-south oriented) independent Neogene basin, following the N-S faulting system (W-E opening) that developed the two peninsulas (Gramvousa and Rodopou) as well. Its location (Figure 11) is N 35°34'23\"

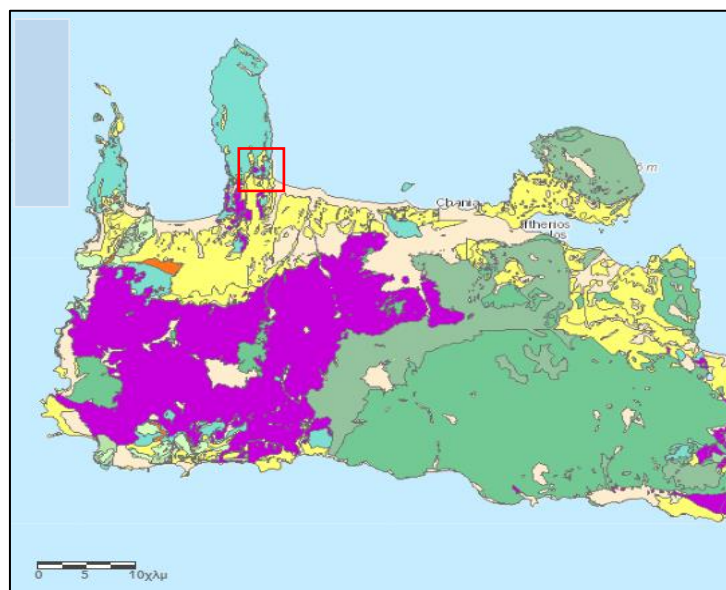


Figure 10. Neogene Basin in Afrata (map by <https://geoportal.apdkritis.gov.gr/>(modified))

A detailed geological study has already demonstrated too (Keupp, et al., 2000). Therefore, bulk sampling of seven samples and a brief description of the whole section (both parts) has been conducted in order to analyze geochemically and have a general view of the section.

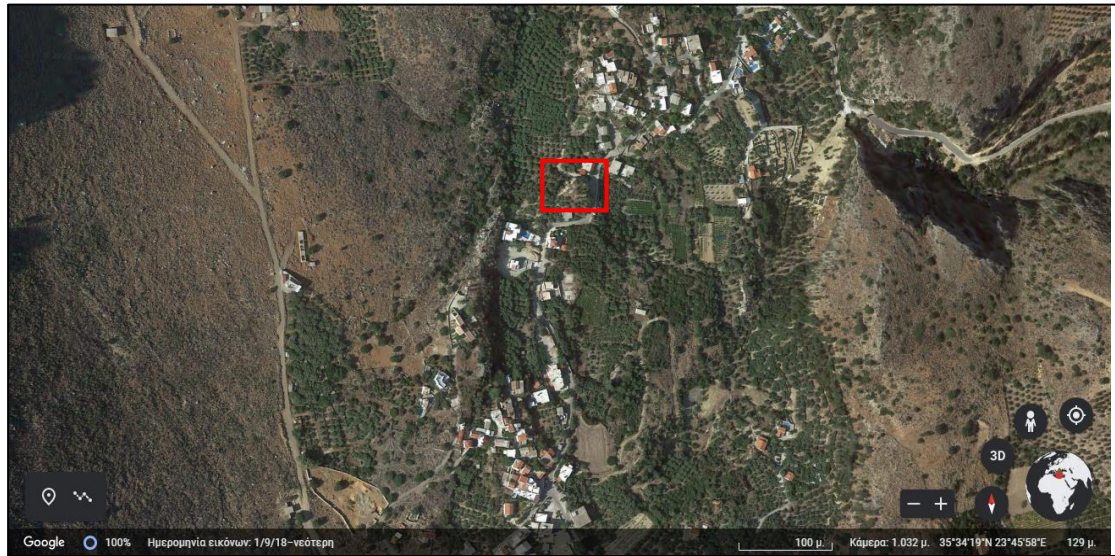


Figure11. Location of the section, modified map by Google earth

2. CHAPTER 2: MATERIAL AND METHODS

2.1 Geology

2.1.1. Kalyves Section

As it was mentioned before the section is located at Apokoronas Basin, in the District of Apokoronou (name of Basin was given by the surrounding area).

In this District, the Khairitiana Formation has a different lithologic character. Here as Freudental (1969) has reported “ *laminated and amorphous white marls alternate with coarser, organic, detritic limestones, in which never any gradation could be observed*”. However, after our examination in situ (Figures 12, 13), our bulk sampling and then, the observation in SEM microscope (Figures 14, 15) we clearly noticed well preserved circular & elongated Diatoms oriented parallel to the stratification, developing a clear lamination in the strata. Therefore, as a result we refer the laminated marls as Diatomites.

Diatomites are siliceous sedimentary rocks composed mainly of diatoms, silicoflagellates, sponge spicules and/or radiolaria, well-organized in cyclic light and dark color alternations (laminae), mostly connected to seasonality. Diatoms are autotrophic, silica-based, unicellular algae that form in marine and freshwater environments, and they have shown rapid evolution during Cenozoic and particularly during Oligocene - Miocene - Pliocene (Tulan et al., 2020). Among others, their significance relies on their high value on hydrocarbon exploration.

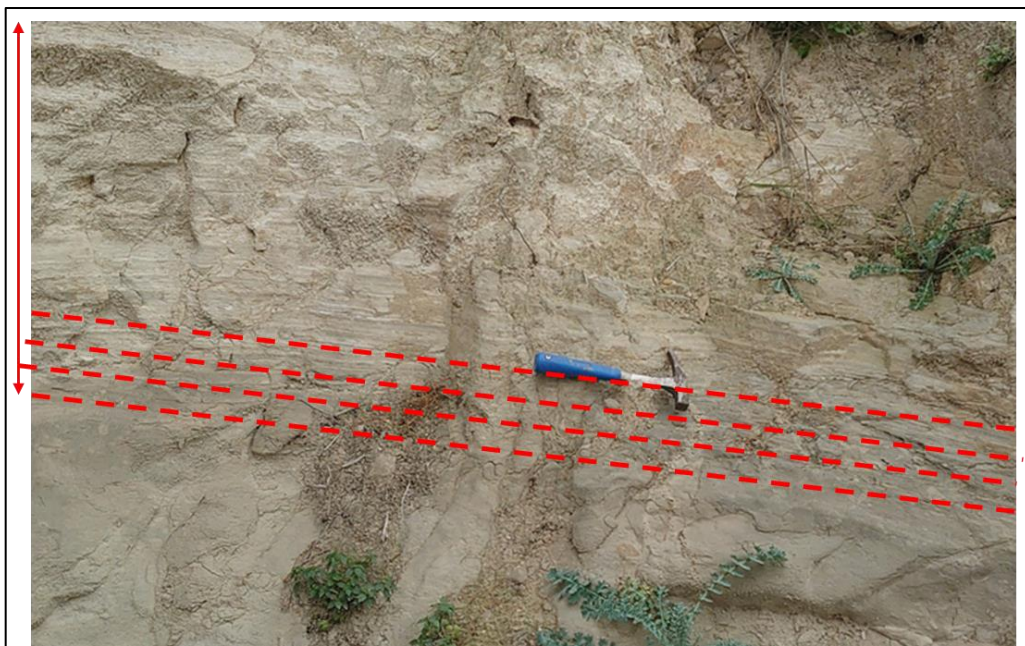


Figure 12. Diatomites layering in Profile 1. You may distinguish between the whitish “clear” diatomites”, dashed red lines and above and the grey siltstones, below.

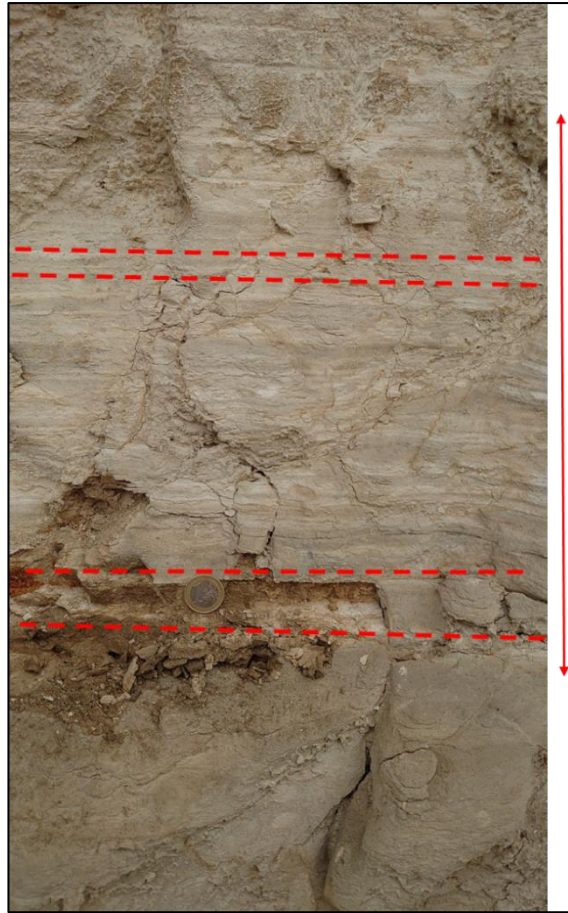


Figure 13. Fine laminae setting framework of diatomitic layers in Profile 1a

In the SEM microphotographs below you may observe that the round type of diatoms is the dominant one, while the elongated are the less observed. The frustules are very well preserved, pointing to rather in situ deposition and preservation is quite fine. Silica Spicules are also to be observed, as well as minor Silicoflagellates and small calcareous nannofossils. Note that we copy with a whole sample (rock fragment) and during sample preparation this was not washed with HCL, therefore the calcareous content was not diluted.

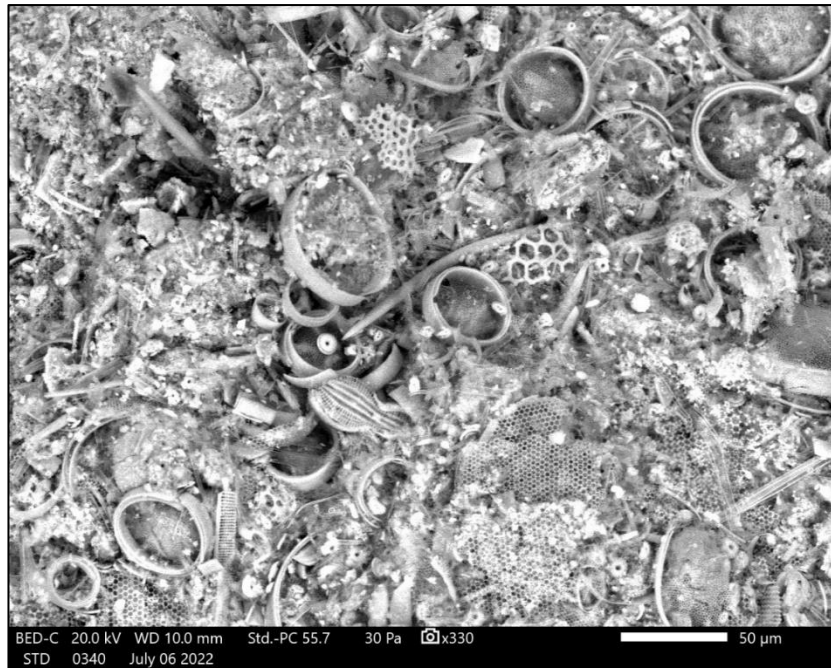


Figure 14. Sample 13: Well preserved circular & elongated Diatoms.

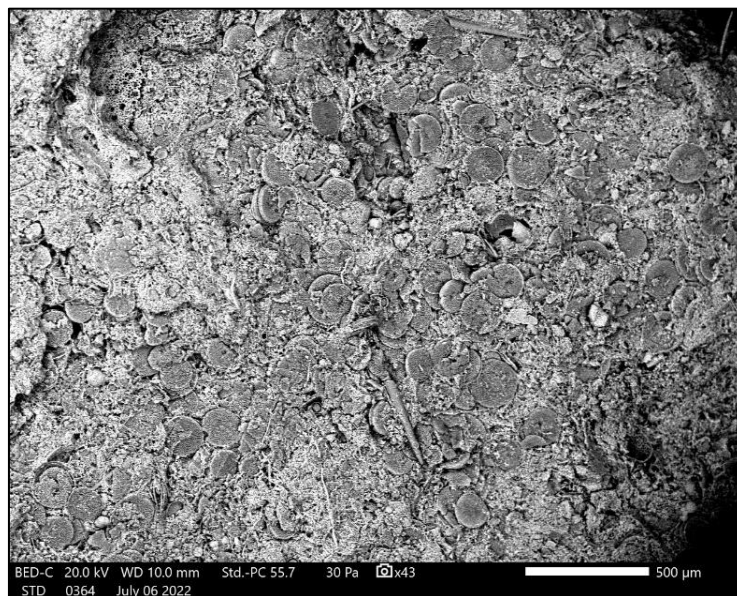


Figure 15. Sample 21: Diatoms, Sponge Spicules & Calcareous nannofossils

Our first results point to an Upper Miocene (late Tortonian/early Messinian) pre evaporitic age of the deposits. Each profile documents various levels with diatomites. Several alternations were observed between fine sands/siltstones/mudstones and laminated diatomaceous beds from bottom to top.

To continue with, the section is subdivided into three subsections and four profiles. The first subsection represents the base of the whole outcrop. Its total height is 5.60 meters. The lower 2.90m “belongs” to Profile 1 and the rest 2.70m to Profile 1a (Figures 16,17). In profile 1, the bottom part is consisted of grey/blueish bioturbated fine sand-to-siltstones moderately cemented, up to 1.80m. The following part is 1.10m consisting purely of Diatomites. Similar alternations exist in the Profile 1a, where the bottom sector (1.35m) consists mainly silty mudstones underlying of a 0.95m well-laminated white to slightly light grey diatomaceous deposit. The section “closes” with a 0.4m Sandstone layer, which is oxidized. Bioturbation was also observed in this subsection (Figure 18) indicating a marine environment. As a matter of fact, the Profile presents a lateral expansion, with the horizontal length (that has been studied) is almost 100meters. Moreover, *Pycnodonta* and other bivalve shells (slightly reworked) were found in the Profile (Figure 19) as pinpointed by other researchers before (Freudental 1969).

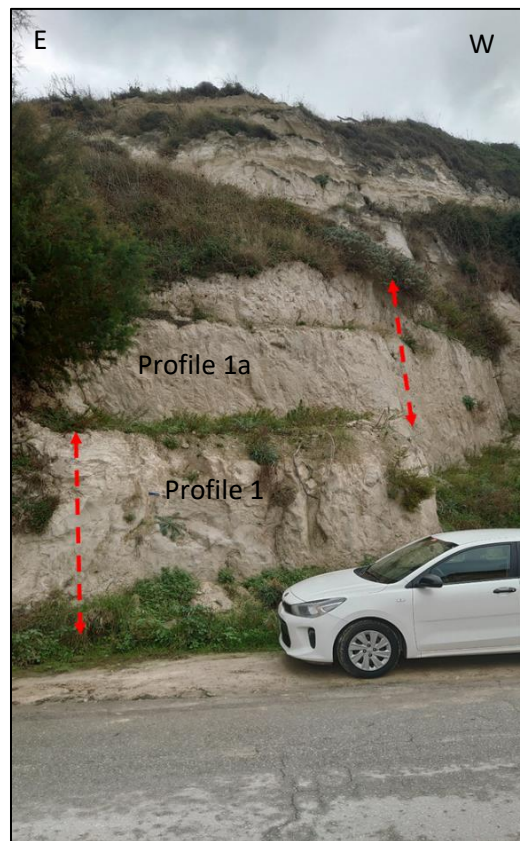


Figure 16. Bottom part of the section

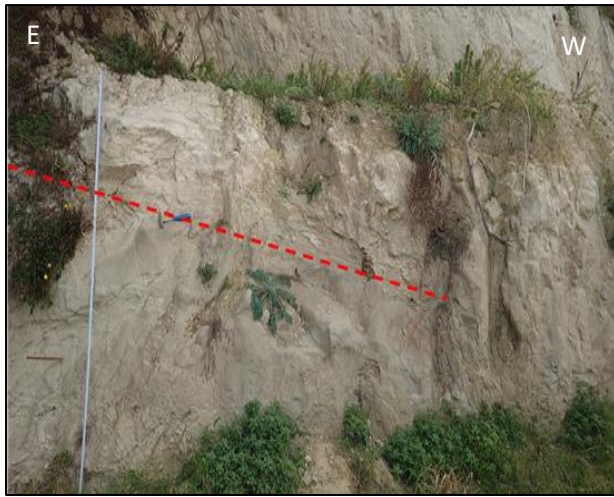


Figure 17. Left is Profile 1, Right is Profile 1a



Figure 18. Burrows and bioturbation of the basal package



Figure 19 Rare Pycnodonta shells in lower part of the whole section

Profile 2 is the middle package of Diatomites. Unfortunately, the whole profile is inside of a construction site, so the available data are in lack. The measured sector is approximately 3 meters, while the whole subsection has a thickness of about 7,60 meters. Silty mudstone at the bottom part, followed again by a diatomitic occurrence (Figure 20). In one sample fish rests were found but not identified, indicating again the marine environment existed in the area.



Figure 20. Profile 2-middle part of the synthetic section

Profile 3 is the upper package of mudstones and Diatomites with a total length of 3.60 meters. Towards the top part silty mudstones underlie the diatomitic beds. The section closes at the top with thick, cemented sandy mudstone beds and it is the closure of the synthetic section in the studied area. (Figure 21).

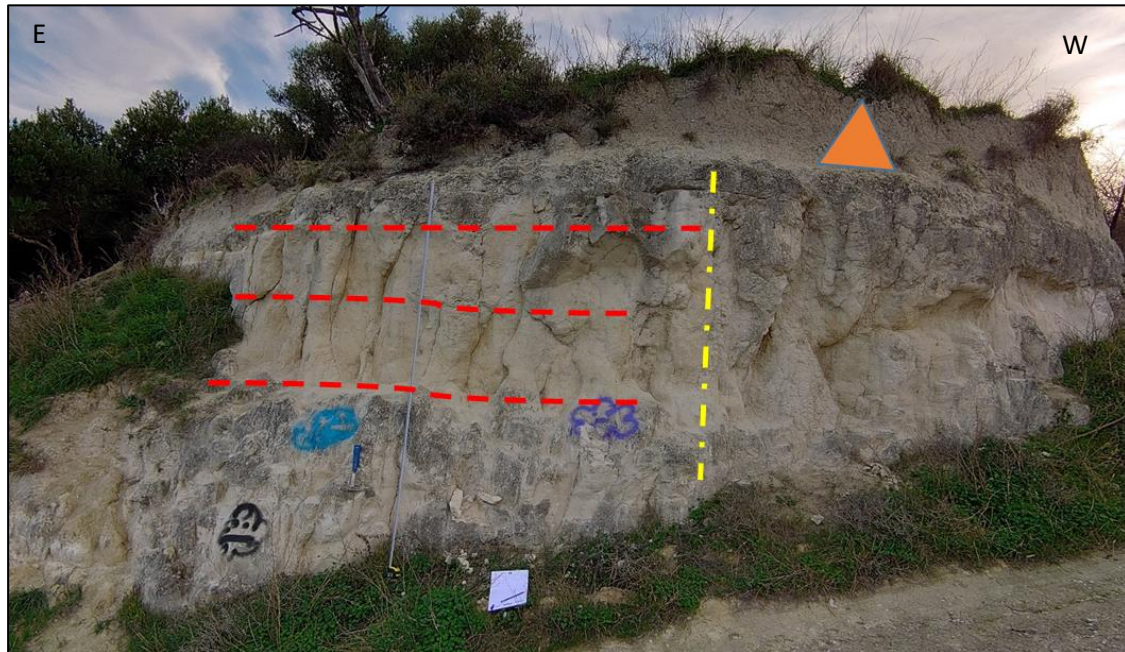


Figure 21. Profile 3 – Upper package of Diatomite-mudstones

In contrast with other sections in the general area of Chania, Gypsum was not found in or near the outcrop.

Sequence Stratigraphy

The major part of the sections' strata was deposited during a transgressive system tract (TST) (profiles 1, 1a) approaching also a High stand System Tract (HST) in profile 2, which was developed following the Tortonian deepening to the early Messinian. It seems to be part of the first sedimentation cycle (Transgressive cycle A) of Late Miocene age (Keupp and Bellas in collab. with Frydas & Bartholdy, 2000). However, at the top part (profile 3), shallowing of the water depth took place, pointing to a regressive system tract (RST) with minor interruptions. Upwelling seems to have been developed in distinct stratigraphic levels illustrating significant changes in the paleo-water-circulation and may well be correlated with the increased variability in climate of Phase 3 described in Kontakiotis et al. (2022).

The sequence stratigraphy of the whole section is given in the next figures (Figures 22-24). Relevant evidence of upwelling during lower Messinian (Late Miocene) in central Crete has also been documented by stable isotope data applied on microfauna by Brachert et al. (2015).

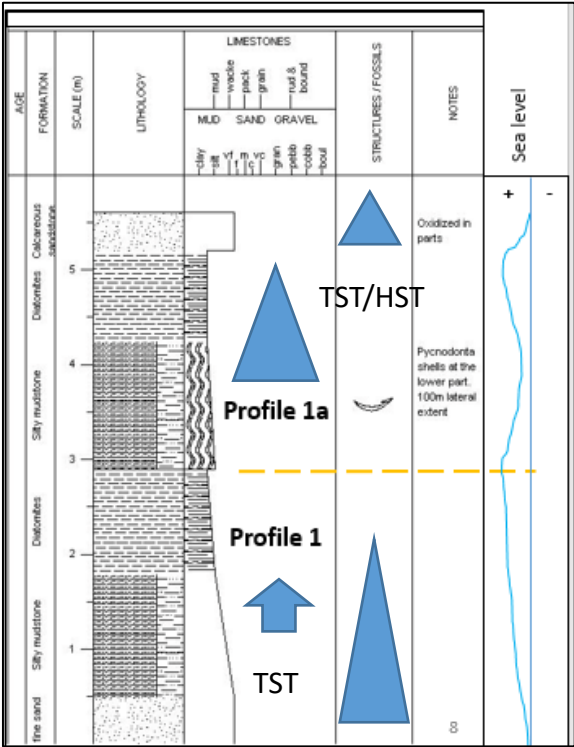


Figure 22. Sequence and Lithostratigraphy of basal part

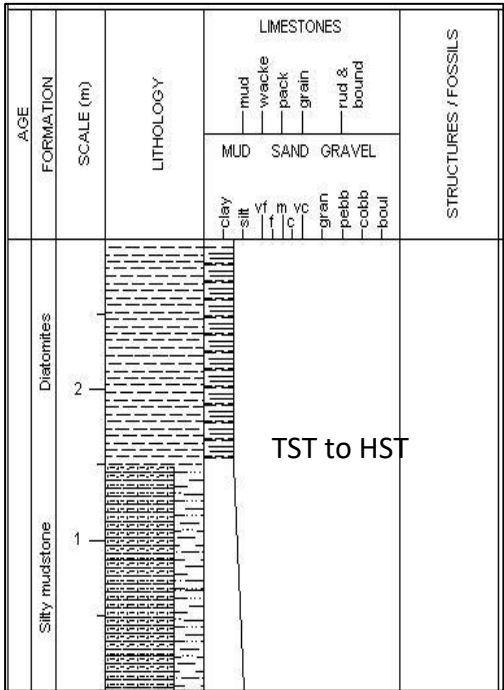


Figure 23 Sequence and Lithostratigraphy of middle part

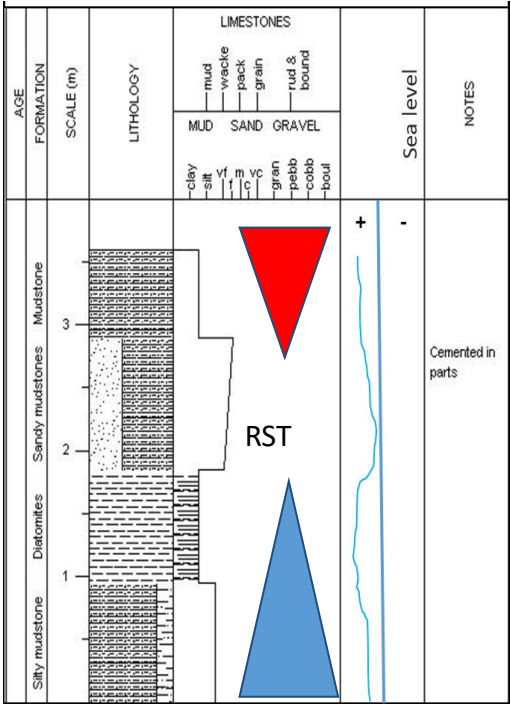


Figure 24. Sequence and Lithostratigraphy of upper part

2.1.2. Kalydhonia Section

This section is considered as the type section of the Kalydhonia sedimentary basin (Bellas et al., 2007). Due to the existing good material quality, the exposure possibilities and preservation of the microfossils and nannoflora, the Kalydhonia section is treated as a sub-typus locality for the Deep Water Facies (DWF) (i.e. the "Kissamou Formation").

Three are the main lithofacies constrain the whole section:

1) Grey, amorphous, homogenous, slightly sandy marls about 17 meters thick are overlain by 8 meters of slightly laminated marls and claystones of middle/outer shelf to slope or mesopelagic environment (Deep Water Facies, DWF), which consists most of the section's sediments). *"When alternate, the former marls are generally considered to correspond to insolation minima, while the later one to insolation maxima "* (Krijgsman, et al. 1999).

2) Yellowish marls about 2 meters thick and sandy marls with 1 meter thickness, of transitional origin to a rather neritic environment (Transitional Facies, TF) with abundant *Pectenidae* (the "Khairithiana Formation"). Furthermore, important fossil elements, like Brachiopods and an important bio horizon of the benthic foraminifer *Heterostegina* sp. firstly reported by Freudenthal (1969).

3) A kind of caprock, consisting of the reefal bioclastic limestones facies (RF) or the upper regressional, littoral facies Type A (Bellas et al., 1998) is the top-closure- upper part of the section, with a thickness of about 3.5meters (partly correlated to the "Roka Formation") (Figure 25).



Figure 25. Kalydhonia Section with lithofacies-levels

The reefs (upper part ellipses) are rich in a variety of fossils, like Corallinaceae (*Lithothamnium*), scleractinian corals (*Tarbellastrara*, *Porites*), tentaculats (cyclostome *Bryozoa*, *Terabratula sinuosa*), cirripeds (*Pyrgomma*), molluscs (*Glycimeris*, *Lithophaga*, div. pectinids and molds of gastropods), (Figure 26), and echinids (*Schizechinus*, *Clypeaster*). (Figure 27)



Figure 26. Fragmented *Pecten* macrofossil we found approaching the upper part of the section



Figure 27. Macrofossils, mostly isolated Molluscs detected at the base of the right reefs' stratigraphic sequence

Pre-Neogene strata, mostly represented by the P-Q Group (Phyllites-Quartzites) separate the Neogene successions of Kalydhonia Basin, by those of the other basins. Remnants of Neogene deposits of the section have been observed in various localities along the Rodopou peninsula. Late Miocene sediments by Afrata basin could be the connection of the Kalydhonian paleobasin with the eastern part of the sea during the time of deposition and basin development.

Despite its isolated character and small size, the Kalydhonia basin Neogene section present similar lithostratigraphic facies and biostratigraphic history with other basins along Crete island (i.e. Meulenkamp et al. 1979), pointing to a rather more or less common development of them all.

For our project sampling was conducted at the right edge of the section (Figures 28 and 29) and at the same time we made in situ observations (like the fossils in the previous figures) in the same area. This part of the sections is consisted of a ca. 4 meters grey mudstone, following by an approximately 1.5 meter grey sandy siltstone. Then a narrow level (a few centimeters) of yellowish marls is observed before the ground – soil appearance. It is obvious, that these formations are the lateral continuities of the basal lithofacies of the main Kalydhonia section, the DWF and TF. We, also, observed two small sandstone alternations (a few centimeters too) between the mudstones, one at 2 meters and one close to 3.5 meters.

As it is already mentioned, bulk sampling of 9 samples was accomplished. The three different spots, where the samples were collected, are circled in Figure 28. Five samples were taken from the aforementioned mudstones, two from an area a few meters above and two from the right corner of the reef. The second area was chosen, so as to find a part of the section that was the continuity of the RF lithofacies. The sampling was done in such a way, that all three different lithofacies of the section to be included, in order for the results to lead to comparisons (similarities/differences) between them, after the geochemical analysis.



Figure 28. Right Part of the section, where sampling (circles) has been conducted



Figure29. Bottom part, approximately 5-6 meters thick

A lithostratigraphic profile of this part of the section is depicted in the next figure (Figure 30).

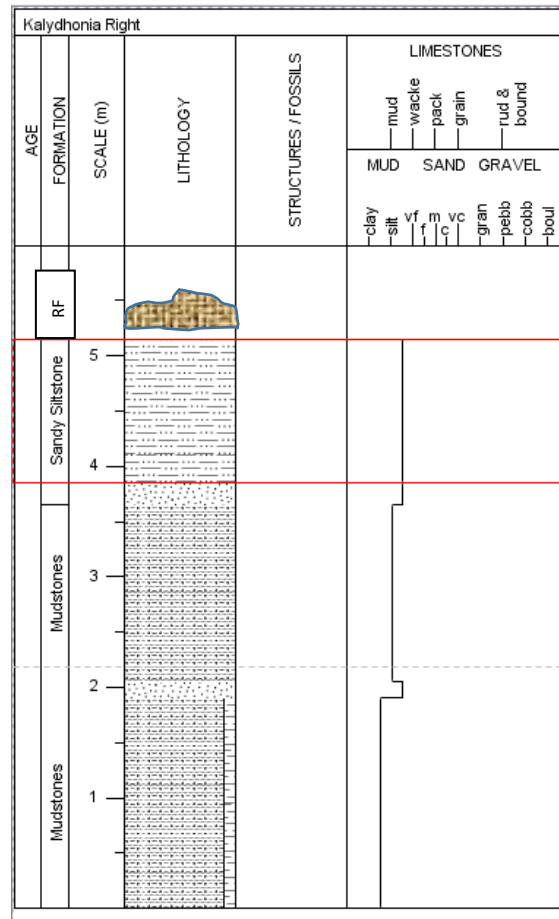


Figure 30. Lithostratigraphy of right part of Kalydonia section

Sequence Stratigraphy

These facies are characteristic for deposition during the beginning of the Mediterranean Messinian Salinity Crisis (MSC), which mainly occurred at the margins of the basins in the studied area. The whole succession of the three lithofacies points to a regressive sequence, from deeper marine at the base to pure shallow-water/littoral deposits at the top. It belongs to the first sedimentation cycle (A) of Late Miocene age.

The middle part is placed in the Transitional Facies (TF). Lamination of the beds is produced due to locally increased amount of fine sand. The middle is interpreted as nearshore, shallow water depth sands of the Littoral Facies Type A (LF-A), pointing to the transition from shelf sediments to shallow-water, neritic environment. In addition, the frequent occurrences of *Heterostegina* bio event recorded in this part of the section, preludes the so-called "Messinian Event" of middle-upper Messinian age. This part characterizes the **Basal Sandstone Subfacies (BSS)** of Keupp and Bellas in collab. with Frydas and Bartholdy (2000). The last sequence of carbonatic sandstones (reef like) closes the section at the top, revealing a regressive, littoral

character. The RF is characteristic for deposition during onset of the MSC, which mainly affected the margins and the highly uplifted blocks of the basins in the general area. Similar marine algal limestones were reported from the marginal Late Messinian Sea in several countries like Spain, Tunisia, western Sinai (Sonnenfeld, 1985; Bellas et al., 2007).

Below is given a similar sequence stratigraphic analysis (Figure 31). This model has been constructed for the Kissamos/Kastelli sedimentary basin which is one of the boundaries of Kalydhonia basin (at the west).

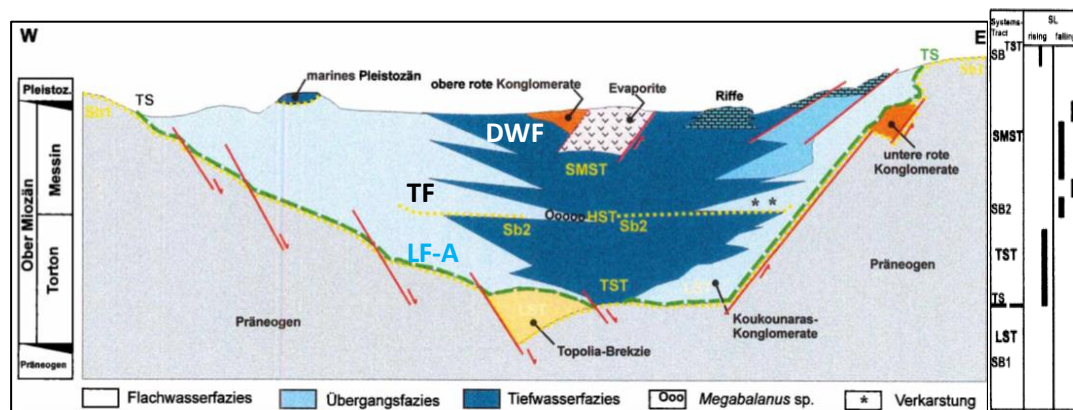


Figure 31. Sequence stratigraphic model by Keupp & Bellas (2000) (Zur Paläontologie der Jungtertiär-Becken in NW-Kreta (Prov. Chania, Griechenland)) (modified)

According to this concept the three depositional lithofacies, that have already been mentioned, are all recognized in the studied section; namely the DWF, the TF and the LF-A/RF.

2.1.3. Afrata Section

Although we are not sure for the origin of the section, the two scenarios we mentioned before are the most dominant.

This composite section is consisted of two parts (Part A and B). Total thickness amounts at 8.5-9 meters (without decompaction). Horizontal bedding with a slightly dip to NW is clearly present along the section.

Part A, which is the lower one, rests transgressively on the slightly deformed limestones of the Tripolitza nappe. It consists of 1 m fine to medium grained sandstones and the fauna assemblage of it is mainly composed by bivalves, gastropodes, bryozoa and echinoids. An indurated carbonate sandstone of 2 meters in thickness is overlying the bed, with *Clypeaster* sp. found on it and in a locality about 200 m to the north, dish-corals reef was detected on a

similar formation. Laterally to the west, sandstones packs are to be found, of 2 meters in thickness, rich in *Heterostegina microfossils*. A covered interval of about 5 m with buildings and roads of Afrata village lies stratigraphically between the two parts of the section.

Part B is subdivided into three units). 1) At the base 5 m of fine-bedded grey to blue marls lie, which include solidary corals (*Caryophylla emacinata* Reuss), a few gastropod and pectinids and is very rich in calcareous micro- and nannofossils. 2) Up next, grey, very fine to fine-grained, indurated sandy mudstones, alternating with grey to blue homogenous marls are observed. 3) Yellowish/grey, fine to medium-grained marly sandstones in alternation with coarser ones constitute the last bed. In addition, a micro- conglomerate is observed at the top.

For our project we investigated a part of the section, that was located inside the village of Afrata.

This section is mainly consisted from silty marls, alternating with sandstone beds. The basal part is grey – blue silty marls and reaches 4.45 meters height. It is overlaid by a 1.17m sandstone pack. This kind of alternation is being repeated two more times with two silty beds of 1.1 and 0.6 meters and two sandstone facies of 0.4 and 0.7 meters respectively. This is the main part of the section (Figures 32, 33), from where 7 out of the 8 samples were collected. A lithostratigraphic profile has been constructed, to present a thorough view of the section (Figure36).

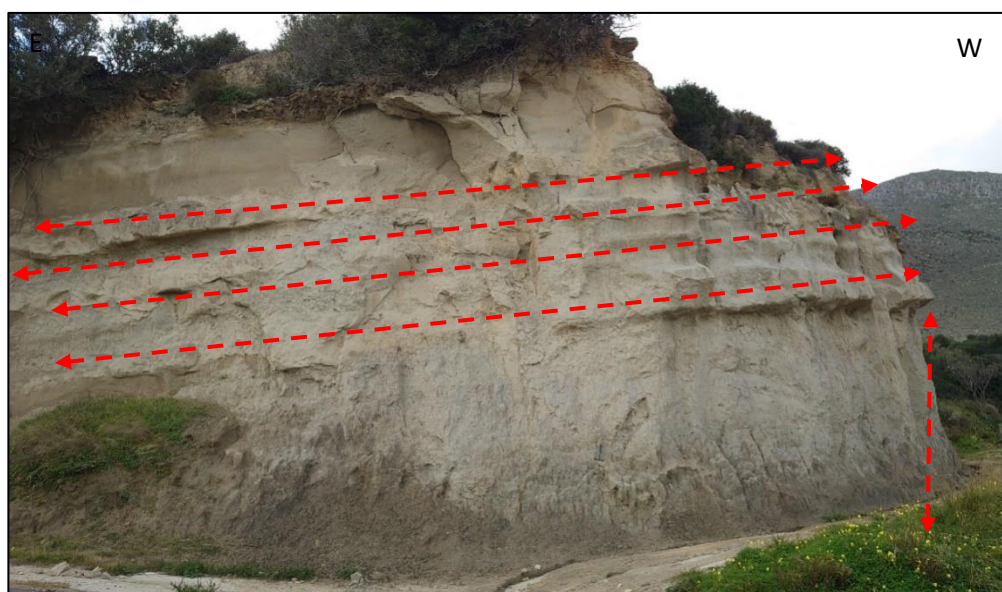


Figure 32. Main body of Afrata section



Figure 33. Alternations between mud/siltstones and sandstone beds

Sparse macrofossils, mainly deeper water bivalves were detected (Figure 34) within the beds of the section. Moreover, as it is noticeable in the figure below, vertical fracturing prevails in the layers, which also includes iron oxides, which probably have a secondary origin.



Figure 34 Bivalve macrofossil found in the bottom part of the section

As we proceed to the left part of the section (eastern), we notice that the basal part is almost disappeared and the first level we clearly observe is the 1st sandstone pack (Figure 35 below). The same alternations continue in the upper stratigraphic levels, with two silty clay deposits of 1 m each in thickness and two sandstone facies of 1.8 and 1.5 meters respectively. Furthermore, between the last sandstone pack and the ground-soil, a bed with silt mixed with bioclastic sandstone has been observed. The whole bed is 1.5m in thickness, with its bottommost part the silts, which decrease as we move upwards, and the last 0.5 meters is mainly composed by the bioclastic sandstones. A notable observation at this uppermost level is the existence of abundant fossil rests. (We have a fining upward cycle).

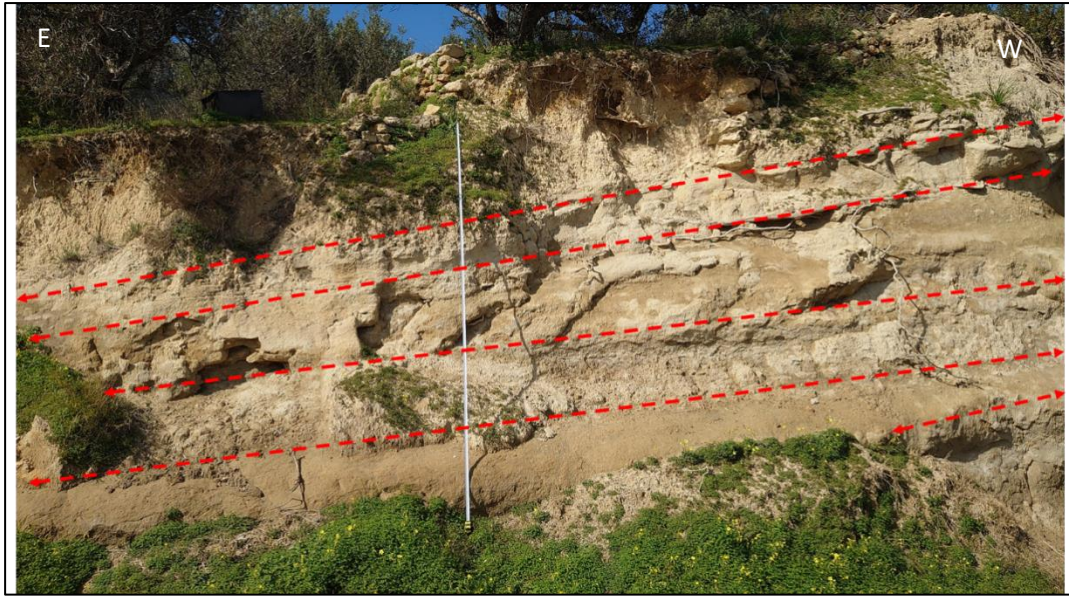


Figure 35. Left part of the section

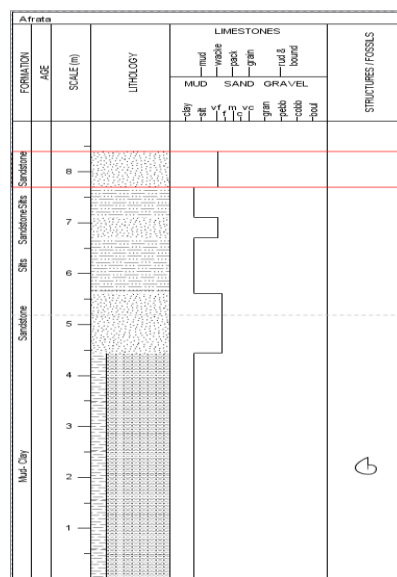


Figure 36. Lithostratigraphy of the main part of Afrata Section

It is also worthy to mention, that below the height of the main road the silty clays formation seems to continue for at least 2 meters in depth. Any other observations were not possible, due to the existence of buildings and the road construction in the area around the section. Moreover, a notable observation in an area 500 meters to 1 kilometer west of the village is corals in a basal Roka formation, we managed to detect (Figure a below).



Figure a. Coral in the formation

Sequence Stratigraphy

The succession of sediments of Afrata section represents a complete deposition through a marine sedimentation cycle (Frydas and Keupp 1996). Part A is a product of increasingly deepening sea, while the upper part is interpreted as a shallowing upwards sequence. Part A starts with transgressive shallow shelf marine facies (LF-A, Basal Sandstones Subfacies, BSS), then the depositional environment is deepening (Part B, Deep Water Facies, DWF). Further, the accommodation area decreases, with subsequently shallowing of sea-water paleodepth and we have the deposition of the Transitional Facies (TF). Within this unit, at least three subcycles of higher frequency flooding events may be distinguished. At the top part of B, the coarse-grained, regressive sandstones point to a littoral facies zone (LF-A), while at the top a pebbly, shore-facies closes the section.

2.2 Geochemistry

2.2.1. Methodology

The Rock-Eval (RE) pyrolysis method developed by the French Institute Petroleum (IFP) in 1997 has been widely used for oil exploration and gas in sedimentary basins around the world. It is one of the most important methods in organic geochemical analysis for its evaluation productivity of source rocks and the estimation of the thermal maturity of sediment organic matter. (Pasadakis 2015)

The main aspect-goal of it is the determination of TOC (Total organic carbon) of the samples. We performed this procedure in the department's research Centre. (Figure 37)



Figure 37. Rock Eval 6 in the lab

We weighted the samples, then shattered into until they are fine-grained, to perform pyrolysis with Rock-Eval 6. For every sample (Figure 38), we need 50-70mg to perform the pyrolysis procedure. We used a mortar and pestle to turn our samples into powder and they could be permeable from a sieve of 250 Micron (or 60 Mesh) (Figure 39). The next step was to put them into oven for 24-48hours in low temperatures between 50-60 °C, so as to make them dry and they can be ready for use into Rock Eval 6 tool-machine. Last step is to insert the samples (through crucibles) to the Rock Eval 6 so the procedure could start. Two basic stage occur into a RE: 1) pyrolysis, heating in an oven in the absence of oxygen, 2) oxidation.



Figure 38. Different angles from a sample before it is shattered



Figure 39. Sieved sample, ready for pyrolysis use

The main parameters measured through the pyrolysis include the TOC, the free hydrocarbon in the sample (S1), the remaining hydrocarbon generative potential of the sample(S2) in $\text{mg}(\text{HC})/\text{g}(\text{TOC})$, the temperature (Tmax) reached during the maximum hydrocarbon pyrolysis yield and the amount of CO_2/g rock yield (S3) during kerogen's thermal breakdown. Furthermore, some more parameters are measured. The amount of oxygen relative to the organic carbon of the sample or Oxygen Index (OI) or in other words the relative oxygen richness, the amount of hydrogen relative to the organic carbon amount present in the sample or Hydrogen Index (HI) or in simple words the hydrogen richness and the maturity of a homogenous source (PI).

HI and OI determine the type of kerogen, that the hydrocarbon, would be and the maturation level of the samples. Moreover, the generation potential of HC is related to S2. The higher the value of s2, the higher the generation potential it is. As far as the maturation level (based on Tmax) the range is: immature (organic matter) when Tmax < 430°C, mature (organic matter) at Tmax=435-450°C, over mature zone when Tmax > 450°C.

The principal guidelines (Tissot and Welte (1984), Peters (1986), Burwood et al. (1995) and Dymann et al. (1996)) that we complied with, for the evaluation of the RE experimental data, are the same that previous researchers like Tserolas et al (2017) have followed.

What is more, kerogen classification diagrams were constructed from data obtained from the above-mentioned geochemical analysis (from RE 6) from all 3 sections.

2.2.2 Results

2.2.2.1 Kalyves Section

Our geochemical results show strong variations in the TOC content throughout the whole section. High values of TOC are recorded within the diatomaceous levels, ranging up to 3.33%. A clear negative trend of the values is recognized from the bottom (Profile 1 and 1a, minimum value of 2.2%) to the top of the synthetic section (maximum value of 0.27% in Profile 3). This refers to the samples, that have been taken by the Diatomites.

Similar results are observed through the samples of sands-silts. In the basal part, TOC values range up to 3.37% (Profile 1), while at the top part maximum value is 0.31% (Profile 3). All values are presented in the next table (Table 1) and Figure 40. Furthermore, all other parameters that have been measured through RE 6 are visible on the table 1.

Sample	S1 (mg/g)	S2 (mg/g)	Tmax(°C)	S3 (mg/g)	TOC(%)	HI	OI
smpl_1	0,4	11,51	414	3,77	3,37	342	112
smpl_1B	0,28	9,41	413	3,52	3,27	288	108
smpl_2	0,02	0,51	425	2,11	0,73	70	289
smpl_3	0,06	1,84	425	3,15	1,24	148	254
smpl_4	0,33	10,27	418	4,14	3,33	308	124
smpl_5	0,27	8,56	418	3,84	3,05	281	126
ex_2	0,31	8,84	418	3,51	3,02	293	116
smpl_6	0,27	6,35	420	3,13	2,29	277	137

smpl_7	0,27	6,52	417	2,91	2,45	266	119
smpl_8	0,46	8,4	412	3,48	2,77	303	126
smpl_9	0,25	6,02	421	2,94	2,19	275	134
smpl_10	0,04	1,61	415	1,62	0,77	209	210
smpl_11	0,07	2,62	424	2,47	1,28	205	193
smpl_12	0,17	5,02	418	4,62	2,14	235	216
smpl_13	0,09	2,24	416	2,17	1,23	182	176
smpl_14	0,04	0,51	428	1,59	0,47	109	338
smpl_15	0,05	0,88	423	1,84	0,71	124	259
smpl_16	0,38	9,25	419	3,36	3,29	281	102
smpl_17	0,08	0,38	416	4,65	0,88	43	528
smpl_18	0,02	0,15	409	4,37	0,57	26	767
smpl_19	0,04	0,12	410	3,91	0,44	27	889
smpl_20	0,02	0,17	368	0,96	0,27	63	356
smpl_21	0,02	0,28	400	1,73	0,57	49	304
smpl_22	0,02	0,34	536	1,29	0,41	83	315
smpl_23	0	0,06	496	0,46	0,04	150	1150
smpl_24	0,01	0,13	432	1	0,27	48	370
smpl_25	0,01	0,12	395	1,28	0,31	39	413
smpl_26	0	0,06	535	1,32	0,31	19	426

Table 1. Measured Parameters by RE 6 pyrolysis for synthetic section in Kalyves Basin

The results demonstrate high productivity in the diatomaceous facies prevail at the basal part and fair productivity as we proceed to middle and upper part of the section.

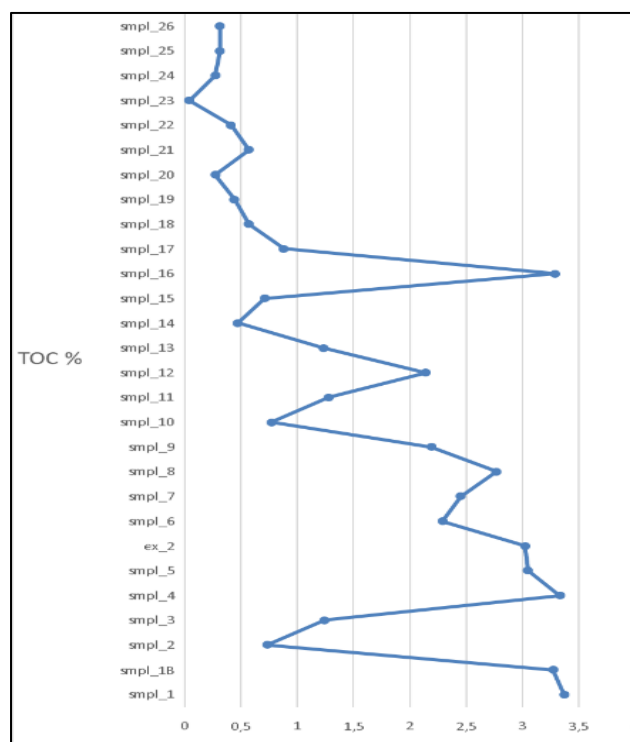


Figure 40. TOC values of synthetic section in Kalyves Basin

2.2.2.2 Kalydhonia Section

In contrast to Kalyves' samples, here in Kalydhonia's Basin samples TOC values are very low, not exceeding 0,5% ,with immature or overmature samples based on the Tmax's values. In the next table (Table 2) and Figure 41, TOC and other Parameters of pyrolysis are given.

Sample	S1 (mg/g)	S2 (mg/g)	Tmax(°C)	S3 (mg/g)	TOC(%)	HI	OI
KLD_0	0	0,09	422	0,63	0,36	25	175
KLD_1	0	0,07	427	0,63	0,37	19	170
KLD_2	0	0,08	427	0,72	0,41	20	176
KLD_3	0	0,11	424	0,58	0,42	26	138
KLD_4	0	0,1	426	0,48	0,44	23	109
KLD_5	0	0,03	426	1,1	0,3	10	367
KLD_6	0	0,05	426	0,59	0,27	19	219
KLD_7	0,02	0,06	549	1,97	0,5	12	394
KLD_8	0	0,04	431	1,21	0,4	10	302

Table 2. Measured Parameters by RE 6 pyrolysis for section in Kalydhonia Basin

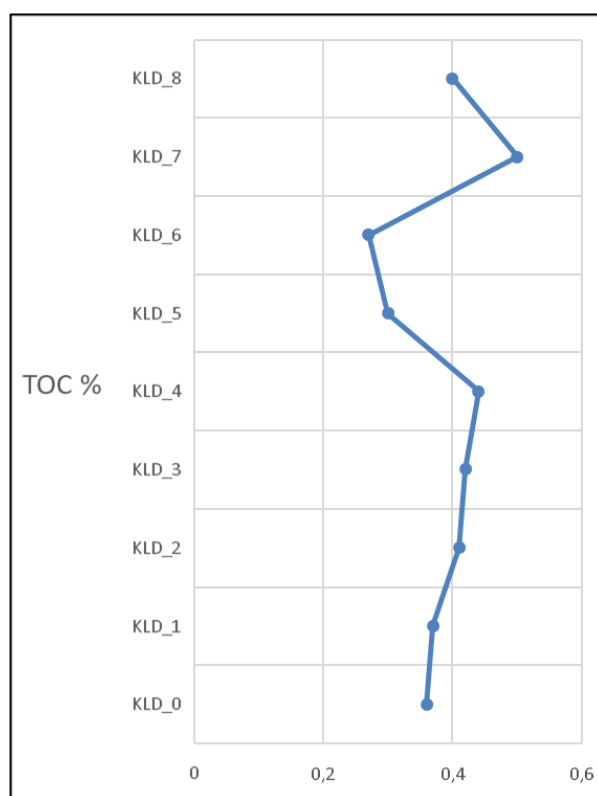


Figure 41. TOC values of Kalydhonia section

2.2.2.3 Afrata Section

Similar results with those of Kalydhonia section were analysed from the Afrata section. The samples, again, are found to be either immature or overmature based on their Tmax values. TOC values are not exceeding 0.46 %. The latter are shown in the next table 3 and Figure 42.

Sample	S1 (mg/g)	S2 (mg/g)	Tmax(°C)	S3 (mg/g)	TOC(%)	HI	OI
AFR_1	0	0,06	514	0,66	0,37	16	178
AFR_2	0	0,14	425	0,7	0,46	30	152
AFR_3	0,01	0,14	429	0,99	0,43	33	230
AFR_4	0	0,07	435	0,92	0,36	19	256
AFR_6	0,01	0,08	544	0,86	0,37	22	232
AFR_5	0	0,07	433	0,68	0,3	23	227
AFR_7	0	0,02	519	1,36	0,14	14	971

Table 3. Measured Parameters by RE 6 pyrolysis for section in Afrata Basin

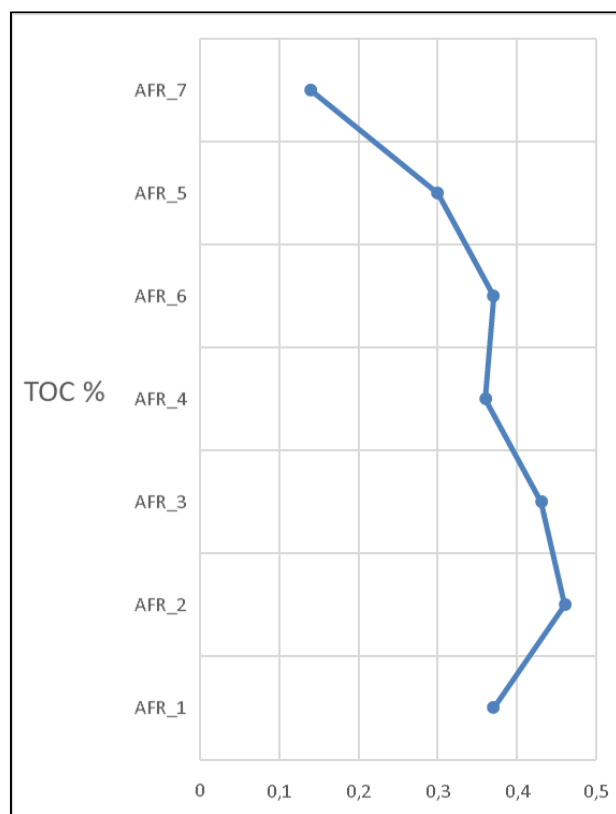


Figure 42. TOC values along the Afrata section

In the next table (Table 4), the results of the extra samples, that were taken near Kalyves section, are shown. TOC values are low with Tmax's exceed or haven't reached the maturity window.

Sample	S1 (mg/g)	S2 (mg/g)	Tmax(°C)	S3 (mg/g)	TOC(%)	HI	OI
ex_1	0	0	497	0,29	0,01	0	2900
Sl_1	0	0,03	555	0,61	0,49	6	124
Sl_2	0	0,06	559	1,46	0,72	8	203
Sl_3	0,01	0,11	423	0,8	0,42	26	190
Sl_4	0,01	0,06	427	0,83	0,38	16	218

Table 4. Measured Parameters by RE 6 pyrolysis for extra samples

2.3. Type of Kerogen and abundance of samples

An important factor about samples that may consider to have hydrocarbon genesis potential is their type of Kerogen. Though that we can have a general idea of what type of hydrocarbon has been produced (gas and/or oil) and the type of material that contributed to its creation. In our project, after taking the results of Rock Eval 6 pyrolysis , we introduced the values of the pyrolysis into p:IGI-3software (Integrated Geochemical Interpretation). Several diagrams were plotted for each section, showing the Type of kerogen of the samples , the prone type and maturity of the samples, the source rock quality and the hydrocarbon generation potential. In the next figure (Figure 43), we show the locations of the collected samples of all sections and their type of Kerogen.

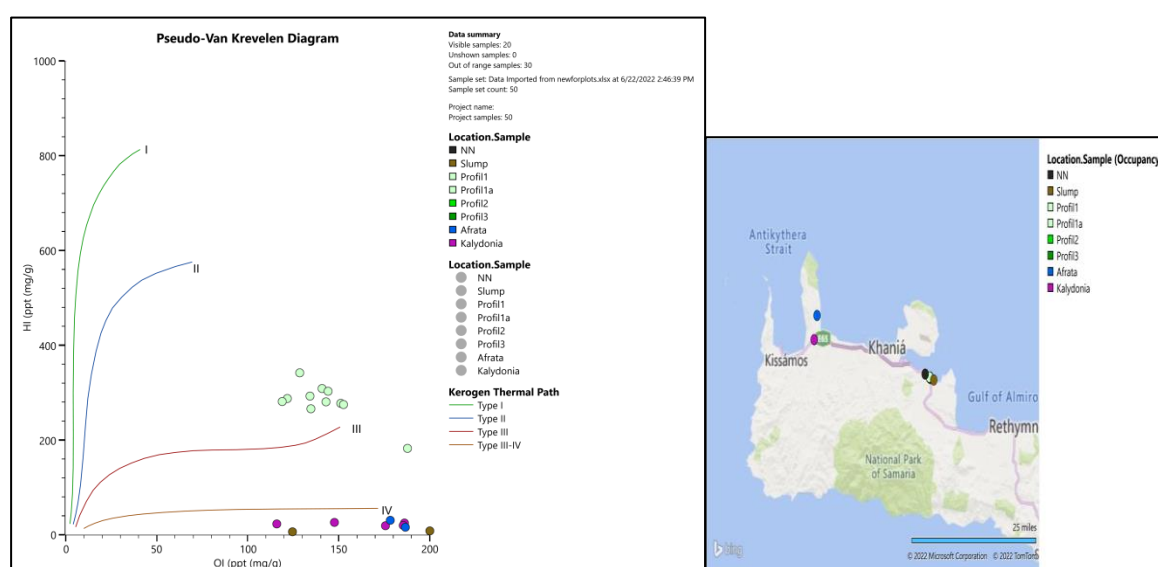


Figure 43. Pseudo Van Krevelen Diagram for all sections/samples together

A first observation is the difference of Type of Kerogen in Kalyves section in comparison with the other two sections. Samples of Profiles 1 and 1a are between Type III-III (closer to III), while samples of Khalydonia and Afrata sections are Type IV.

Kalyves Section

As we pinpointed before, most of the samples of the whole section are of Type II-III (but mainly type III) (Figure 44). Similar results have also been proved by Aoyagi K. and Omokawa M.

(1992), who studied Late Miocene to Pliocene Diatomites in Japan. Additionally, the Tmax vs HI diagram (Figure 45) reveals that the samples haven't reached maturity window yet, not exceeding 430°C. However, it is depicted that a gas to oil-gas prone source rock exists, which potentially can produce both gas and oil.

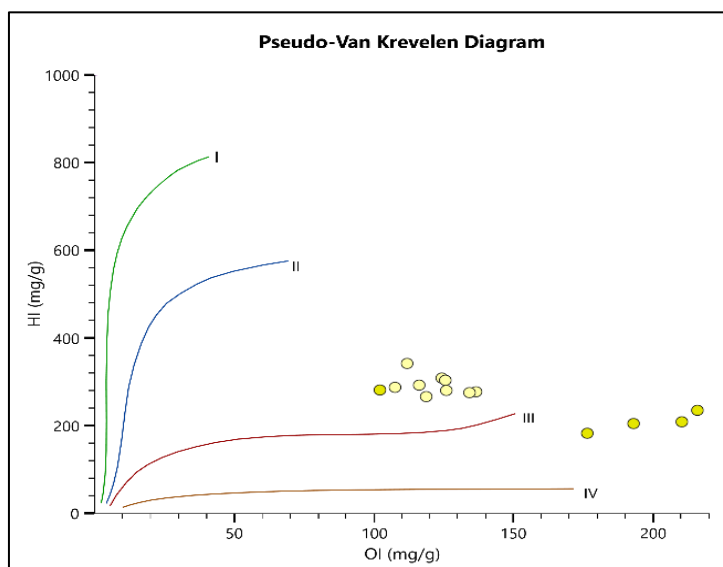


Figure 44. Most of the samples are of Type III kerogen

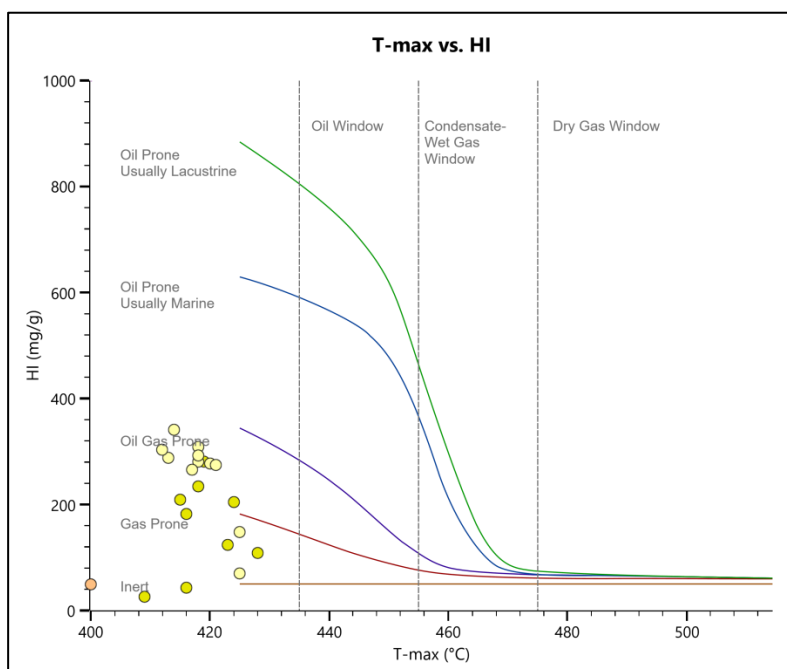


Figure 45. The gas to oil-gas prone source rock is clear in the diagram

Source Rock quality

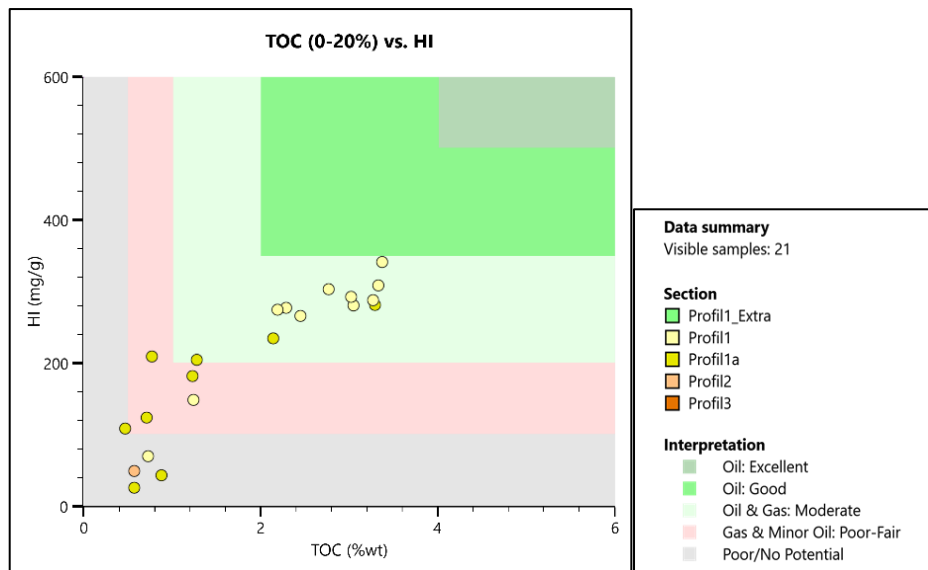


Figure 46. TOC VS HI diagram for quality of source rock

Although, we have an immature source rock, the upper figure (Figure 46) indicates that its quality reaches up to good levels with most of the samples in the moderate level of Oil and Gas. At the same time, it is noticeable, in the TOC vs S2 diagram (Figure 47 below), that most of the samples have a good to excellent hydrocarbon potential (a lot of them exceed 2%).

HC generation potential

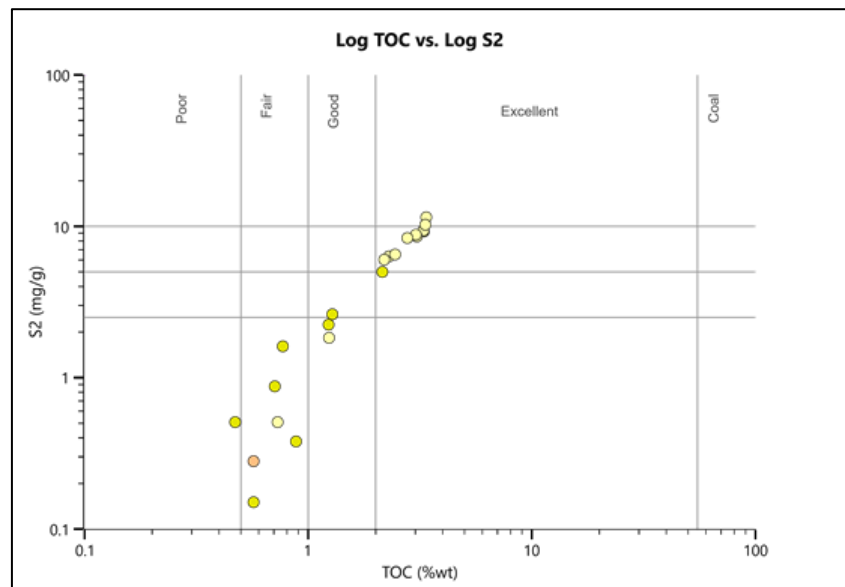


Figure 47. HC generation reaches up to excellent potential

Kalydhonia Section

Unfortunately, results in Kalydhonia section are not the same with those of Kalyves. Here, samples lead to a type IV kerogen (Figure 48). Furthermore, this source rocks appear to be inert according to the Tmax vs HI diagram (Figure 49).

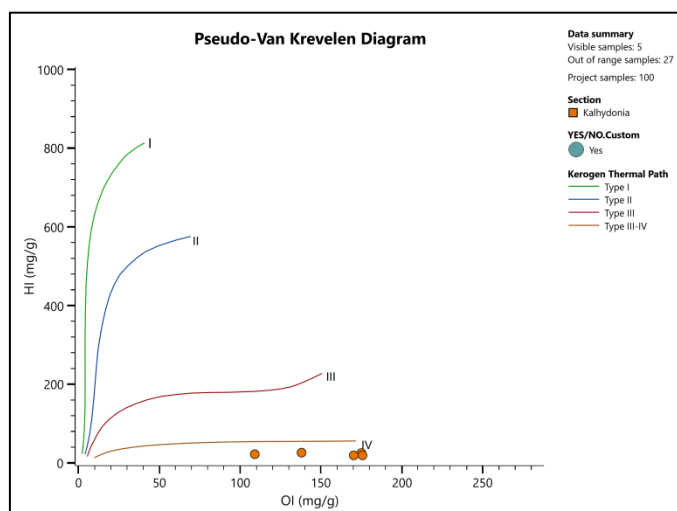


Figure 48. All samples are of Type IV kerogen

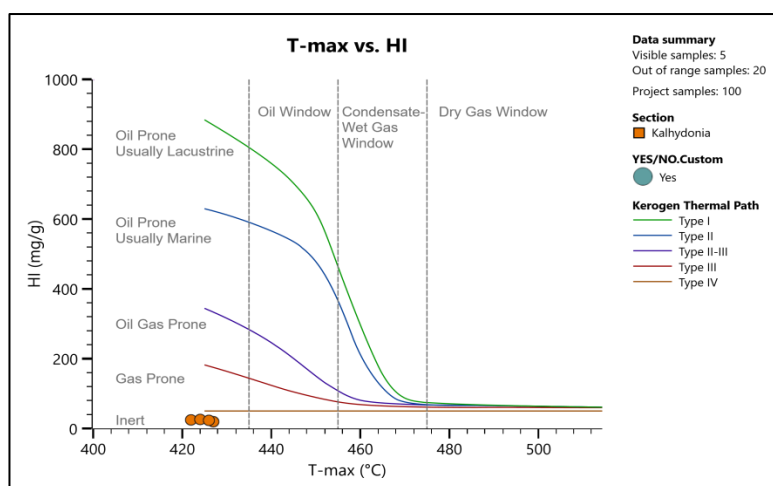


Figure 49. An inert kerogen/source rock is observed

In addition, the quality of the source rock is poor which leads to no production potential (Figure 50). This is also confirmed by the TOC vs S2 diagram (Figure 51), where we observe that all samples give poor hydrocarbon potential.

Source Rock quality

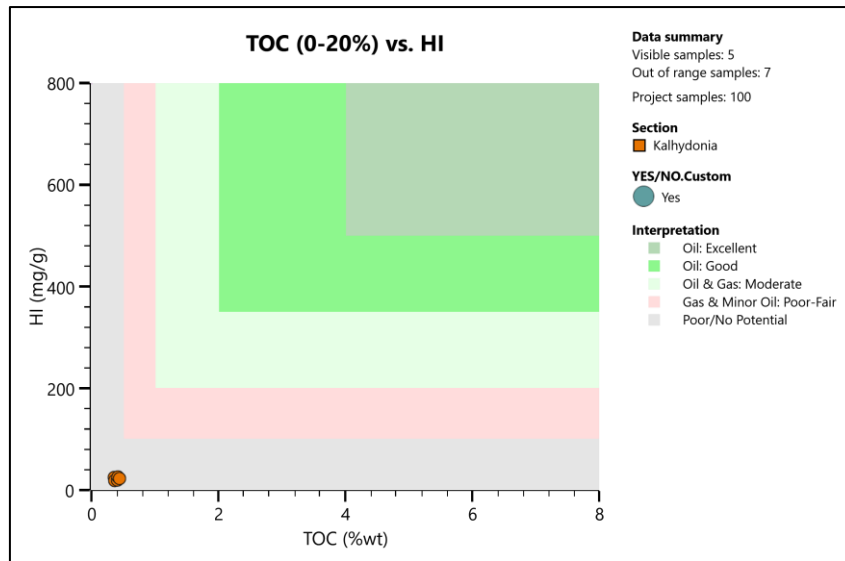


Figure 50. TOC VS HI diagram for quality of source rock

HC generation potential

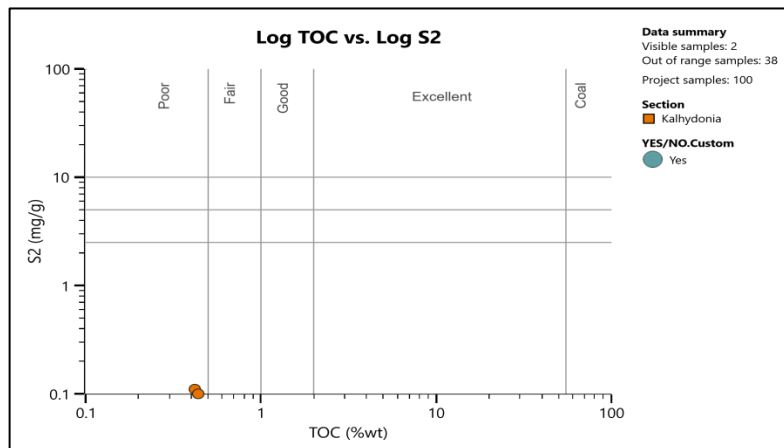


Figure 51. HC generative potential is poor

Afrata Section

Similar results, to those of Kalydhonia section, have been observed in Afrata Section. A type IV kerogen is the outcome of the samples analysis, with again an inert source rock (Figures 52, 53).

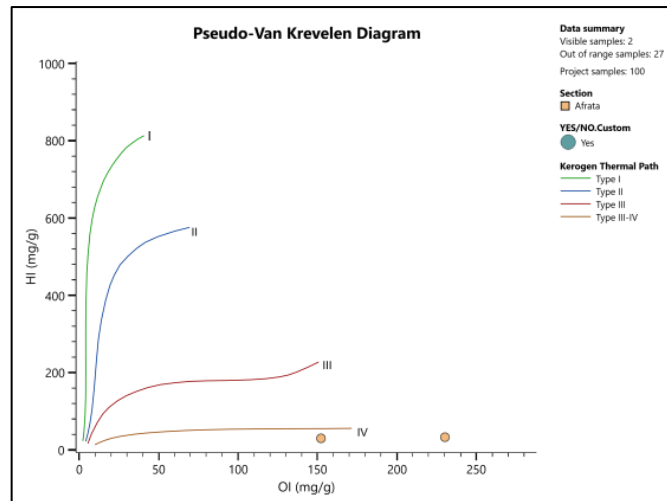


Figure 52. All samples are of Type IV kerogen

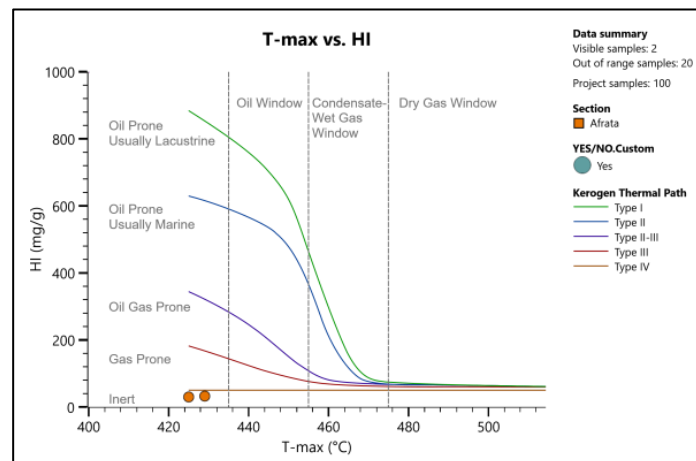


Figure 53. An inert kerogen/source rock is observed

To add up, the quality of the source rock is poor, which leads to no production potential (Figure 54), something that can be noticed by the TOC vs S₂ diagram (Figure 55) too. The results provide that the hydrocarbon potential in this outcrop is again poor.

Source Rock quality

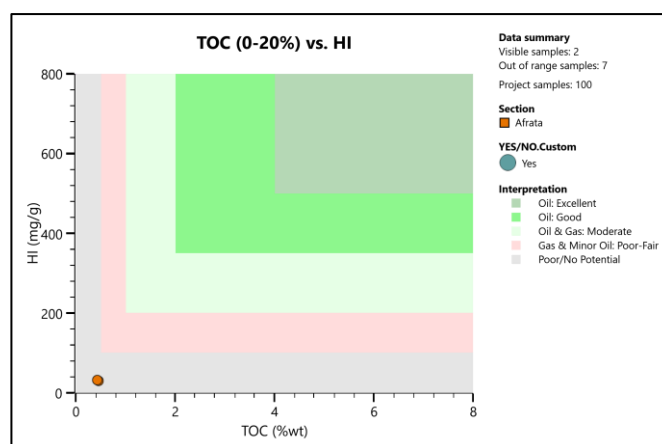


Figure 54. TOC VS HI diagram for quality of source rock

HC generation potential

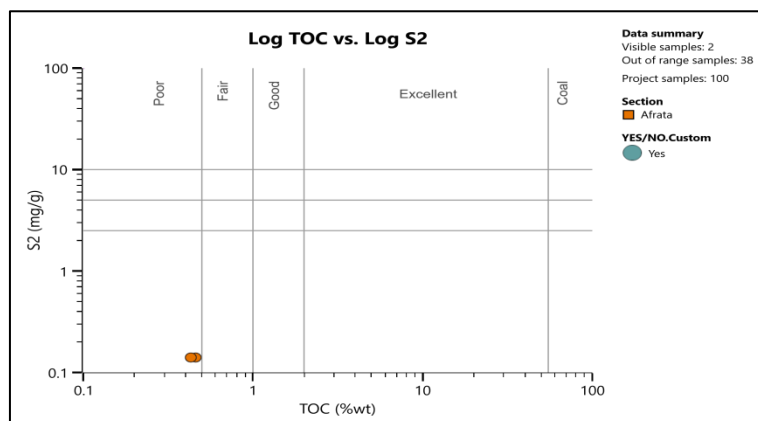


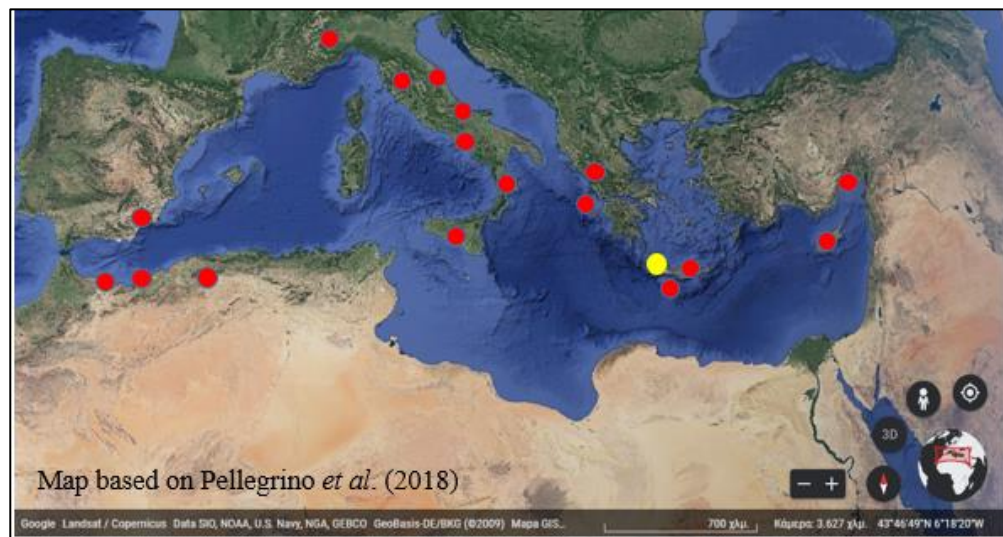
Figure 55. HC generative potential is poor

CHAPTER 3

3.1 Conclusions/ Discussion

Based on the above-mentioned geochemical analysis and all observations, clear outcomes have been made.

- First, we update the recorded Mediterranean distribution (map below based on Pellegrino et al. 2018) with a new Diatomitic evidence –occurrence of Late Miocene pre evaporitic age of the deposits, the 3rd one of this age on Crete. Four stratigraphic levels of diatomites are well documented along this synthetic section.



Map: Distribution of lower Messinian marine bio siliceous deposits in the Mediterranean (modified)

- The stratigraphic analysis in the Kalyves synthetic section, supports the establishment of System Tracts, with a Transgressive System Tract illustrated by fining upward sequences, followed by a final coarsening upwards sequence suggesting a Highstand System Tract reaching up to the final Regressive System Tract.
- This deposition of the diatomites is most likely correlated to an early Messinian upwelling system prior to the MSC onset, which was undergoing major changes and strongly affected by the climate variability. Four small to medium scale sea-level variations are recorded within the described beds and layers.
- The whole record of the outcrop contributes to the general palaeogeographic setting of Crete.

As for the geochemical analysis:

- The results of this study reveal the potential of Hydrocarbon genesis in the Neogene Basins of NW Crete.
- Results are different in each case (studied section). TOC values reach up to very good levels in the Kalyves sections, while in Afrata and Kalydhonia are fair.
- Moreover, a clear trend of very good to poor hydrocarbon generation potential is observed in the diatomites from the bottom to the top of the synthetic outcrop, in agreement with the stratigraphic interpretation.
- A kerogen type of II-III, leaning towards type III is documented by the analyzed set of samples of Kalyves section. A kerogen type IV is reported for both sets of samples of Kalydhonia and Afrata sections.
- In addition to the measured TOC values, a gas/ oil-gas prone source rock with fair to excellent hydrocarbon potential is pinpointed for the samples of Kalyves. On the other hand, inert source rock emerges from the analysis of the samples of the other two sections with poor- to no hydrocarbon potential.
- Moreover, the quality of the source rock, for Kalyves sections, lies around intermediate to good levels.
- Concisely, this study supports the extent of Messinian diatomites in North-Western Crete and their potential as source rock for hydrocarbon generation.
- In combination with the results of the other two sections, it is demonstrated and highlighted the significance for the offshore hydrocarbon exploration in the Eastern Mediterranean, and especially in offshore Crete.
- Last but not least, this is a good interval, becoming a trigger point for further investigation for potential hydrocarbon source rocks in Crete.

REFERENCES

- Aoyagi, K. and Omokawa, M. (1993). Diagenesis of Neogene diatoms and their importance as a source of petroleum in Japan. *The Island Arc* 2, 273-279.
- Aoyagi, K. and Omokawa, M. (1992). Neogene diatoms as the important source of petroleum in Japan. *J. Pet. Sci. Eng.* 7, 247-262.
- Bellas, S., Frydas, D. and Keupp, H. (2007). Late miocene calcareous nannofossil stratigraphy and bioevents correlation: Kalidonia case section (NW crete, greece), *Bulletin of the Geological Society of Greece* vol. XXXX, 2007 Proceedings of the 11th International Congress, Athens, May, 2007.
- Bonneau, M., (1972a). La nappe métamorphique de l'Asteroussia, lambeau d'affinités pélagoniennes charrié jusque sur la zone de Tripolitza de la Crète moyenne (Grèce). *Comptes Rendus de l'Académie des Sciences D* (275), 2303–2306.
- Brachert, T.C., Bornemann, A., Reuter, M., Galer, S.J., Grimm, K.I., Fassoulas, C. (2015). Upwelling history of the Mediterranean Sea revealed by stunted growth in the planktic foraminifera *Orbulina universa* (early Messinian, Crete, Greece). *Int. J. Earth Sci. (Geol. Rundsch)*, 104: 263-276.
- Burwood R., De Witte, SM., Mycke B, Paulet J. (1995). Petroleum geochemical characterization of the lower Congo Coastal Basin Bucomazi formation. In: Katz BJ (ed) *Petroleum source rocks*. Springer-Verlag, Berlin, pp 235–263 .
- Douwe J. J. van Hinsbergenn and Johan E. Meulenkampn, (2006). Neogene supradetachment basin development on Crete (Greece) during exhumation of the South Aegean core complex. *Basin Research* (2006) 18, 103–124.
- Dymann, TS., Palacas, J.G., Tysdal, R.G., Perry, W.J.Jr., Pawlewicz, MJ. (1996) Source rock potential of middle cretaceous rocks in southwestern Montana. *AAPG Bull* 80(8):1177–1183.
- Freudenthal, T. (1969). Stratigraphy of Neogene deposits in the Khania Province, Crete, with special reference to Foraminifera of the Family Planorbulinidae and the Genus *Heterostegina*. *Utrecht Micropaleontological Bulletins* 1, 1-208.
- Frydas, D. (1996). Silicoflagellate Stratigraphy for Neogene to Quaternary marine sediments in Greece. *Newsl. Stratigr.* 33(2), 99-116.
- Frydas, D. (2004). Calcareous and siliceous phytoplankton stratigraphy of Neogene marine sediments in central Crete (Greece). *Revue de micropaléontologie* 47, 87–102.
- Frydas, D. (2006). Siliceous phytoplankton assemblages and biostratigraphy of the pre-evaporite Messinian diatomites on Gavdos Island, Greece. *Revue de micropaléontologie*, 49: 86–96.
- Frydas, D., Keupp, H. & Bellas, S. (2008). Stratigraphical investigations based on calcareous and siliceous phytoplankton assemblages from the Upper Cenozoic deposits of Messara Basin, Crete, Greece. *Z. dt. Ges. Geowiss.* 159/3, 415-437.
- Frydas, D. & Keupp, H. (1996). Biostratigraphical results in Neogene deposits of NW Crete, Greece, based on calcareous nannofossils. - *Berliner geowiss. Abh.*, E 18: 169-189; Berlin.
- Keupp, H. & Bellas, S.M. in collab. with Frydas, D. & Bartholdy. J. (2000). Neogene development of the sedimentary basins of NW Crete island, Chania Prefecture, South Aegean Arc System (Greece). *Berliner geowissenschaftliche Abhandlungen*, E (34): 3-117.
- Koliopoulos, G. 1. (1952). Contribution to the geology of the isle of Crete (in Greek). Thesis Univ. Athens. Author's edition.

- Kontakiotis, G., Butiseacă, G.A., Antonarakou, A., Agiadi, K., Zarkogiannis, S.D., Krsnik, E., Besiou, E., Zachariasse, W.J., Lourens, L., Thivaïou, D., Koskeridou, E., Moissette, P., Mulch, A., Karakitsios, V., Vasiliev, I. (2022). Hypersalinity accompanies tectonic restriction in the eastern Mediterranean prior to the Messinian Salinity Crisis. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 592: 110903 (1-14).
- Kontopoulos, N. and Zililidis, A. (1997). Depositional processes in outer arc marginal sub-basins during the Messinian time; Messinian crisis: An example from western Crete Island, Greece. *Geologica Balanica*, 27.1-2, Sofia, August.1997, p. 91-100
- Krijgsman, W. (1999). Chronology, causes and progression of the Messinian salinity crisis, *Nature*, 400, 652-655.
- Maravelis, A., Kontakiotis, G., Bellas, S., Antonarakou, A., Botziolis, C., Janjuhah, H.T., Makri, P., Moissette, P., Cornée, J.J., Pasadakis, N., Manoutsoglou, E., Zililidis, A. and Karakitsios, V. (2022). Organic Geochemical Signatures of the Upper Miocene (Tortonian—Messinian) Sedimentary Succession Onshore Crete Island, Greece: Implications for Hydrocarbon Prospectivity, *J. Mar. Sci. Eng.* 2022, 10, 1323.
- Meulenkamp, J.E. (1979). Field Guide to the Neogene of Crete, Publ. Dept. Geol. Pal. Athens Univ., ser. A, 32, 1-32.
- Pasadakis, N. (2015). Petroleum Geochemistry (Γεωχημεία Πετρελαίου), book of TZIOLAS PUBLICATIONS (2015), p. 130-137.
- Pellegrino, L., Dela Pierre, F., Natalicchio, M., Carnevale, G. (2018). The Messinian diatomite deposition in the Mediterranean region and its relationships to the global silica cycle. *Earth-Science Reviews*, 178: 154-176.
- Peters, K.E. (1986) Guidelines for evaluating petroleum source rock using programmed pyrolysis. *AAPG Bull* 70(3):318–329.
- Silviu O. Martha., Dörr, W., Gerdes, A., Krah, J., Linckens, J., Zulauf, G. (2017). The tectonometamorphic and magmatic evolution of the Uppermost Unit in central Crete (Melambes area): constraints on a Late Cretaceous magmatic arc in the Internal Hellenides (Greece). *Gondwana Research* 48 (2017), 50-71.
- Sonnenfeld, P. (1985). Models of Upper Miocene Evaporitic genesis in the Mediterranean Region. In D.J. Stanley and F.-C. Wezel (eds), *Geological Evolution of the Mediterranean Basin*. 323-346pp, New York Berlin Heidelberg Tokyo, Springer-Verlag.
- Telemenis, D., Makridou, Z., Bellas, S. (2022). New evidence of Diatomitic occurrences in western Crete, Greece; A preliminary stratigraphic and geochemical approach and its implications. *Special Publication BGS (Bulletin of the Geological Society of Greece)* 9, p. 85.
- Thomson, S.N., Stöckhert, B. and Brix M.R. (1999). Miocene high-pressure metamorphic rocks of Crete, Greece: rapid exhumation by buoyant escape. *Geological Society, London, Special Publications* 154:87–107.
- Tissot, B.P., Welte, D.H. (1984). *Petroleum formation and occurrence*, 2nd ed. Springer-Verlag, Berlin.
- Tulan, E., Radl M.S., Sachsenhofer, R.F., Tari, G., Witkowski, J. (2020). Hydrocarbon source rock potential of Miocene diatomaceous sequences in Szurdokpüspöki (Hungary) and Parisdorf/Limberg (Austria). *Austrian Journal of Earth Sciences* 113, 24-42.