Depositional environments and hydrocarbon potential of the Miocene deposits of Zakynthos Island

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http://dx.doi.org/10.12681/bgsg.11094

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To cite this article:
DEPOSITIONAL ENVIRONMENTS AND HYDROCARBON POTENTIAL OF THE MIocene DEPOSITS OF ZAKYNTHOS ISLAND

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Abstract
Structure, sedimentary features, and biostratigraphy were taken into account to provide additional knowledge into the depositional conditions that influenced the sedimentary sequence along the southern coast of Zakynthos. This succession is exposed from Keri village to Ag. Sostis peninsula and appears to have been influenced by intense tectonic activity. The active tectonics resulted in the formation of at least four coarsening upward cycles. The co-occurrence of Bouma sequence subdivisions and slump horizons within the studied sediments suggest a deep-sea depositional environment. Grain size analysis indicates a regional swallowing upward trend. TOC and CaCO3 contents are presented with both positive and negative correlations while the TOC values indicate that the study area contain samples with source rock potential.

Key words: Sedimentology, source rocks, Bouma sequence, grain-size analysis.

Περίληψη
Λαμβάνοντας υπόψη τις ιζηματογενείς δομές, τα τεκτονικά χαρακτηριστικά και την βιοστρωματογραφία, μπορούμε να αντλήσουμε γνώσεις για τις συνήθεις απόθεση που επηρέασαν την ιζηματογενή ακολουθία κατά μήκος της νότιας ακτής της Ζάκυνθου. Η ιζηματογενής ακολουθία από το χωριό Κερί μέχρι τη χερσόνησο του Άγιου Σώστη φαίνεται να έχει επηρεαστεί από έναν τεκτονικό δραστηριότητα, παράγοντα που δημιούργησαν τέσσερις κύκλους με αυξανόμενο κοκκομετρικό μέγεθος προς τα πάνω. Η κοκκομετρική ανάλυση έδειξε μια σταδιακή πλήρωση του κάθε κύκλου ιζηματογενούς, αλλά και την απόθεση της περιοχής. Επιπροσθέτως, η παρουσία των αναιμίαλματος της ακολουθίας Bouma και των ολίσθησης εντός των ακολουθίας ιζηματογενούς προτείνει ότι η παρουσία των ολίσθησης υπόδεικνυει μια διάδοση απόθεσης. Η κοκκομετρική ανάλυση έδειξε μια σταδιακή πλήρωση τον κάθε κύκλου ιζηματογενεύνσης, αλλά και την εξέλιξη της περιοχής. Επιπροσθέτως, η απόθεση της περιοχής Bouma και την CaCO3, είδε ότι είχε επηρεαστεί μια σχέση του περιβάλλον τους με την απόθεση. Οι τιμές TOC δείχνουν ότι η περιοχή είναι μετασχηματισμένη διάφορα με διαφορετικές γένεσης αμυδρηνοπρότερων, ενώ οι τιμές TOC δείχνουν ότι η περιοχή είναι μετασχηματισμένη διάφορα με διαφορετικές γένεσης αμυδρηνοπρότερων. Ακολούθως, οι τιμές TOC δείχνουν ότι η περιοχή είναι μετασχηματισμένη διάφορα με διαφορετικές γένεσης αμυδρηνοπρότερων. Τα τιμές TOC δείχνουν ότι η περιοχή είναι μετασχηματισμένη διάφορα με διαφορετικές γένεσης αμυδρηνοπρότερων.

Λέξεις κλειδιά: Ζάκυνθος, ιζηματογενείς, δομές, τεκτονικά χαρακτηριστικά, βιοστρωματογραφία.
1. Introduction

Marine depositional environments with low depositional rate are typified by increasing carbonate content towards the coarse fractions (Saadellah & Kukal, 1969). The organic material is intimately related to sedimentary environments (Folk, 1968). The accumulation of organic matter requires: (1) high organic productivity, (2) high subsidence rates and (3) anoxic conditions. Such conditions occur either because of overproduction and deposition of organic material, or because of limited water circulations resulting in non-oxygen recycle.

In contrast, erosion results to the oxidation of the organic material of the rock and to the dissolution and precipitation of minerals in both sandstones and limestones. The dissolution of calcium carbonate (CaCO$_3$) is affected by the temperature, pressure and the partial pressure of carbon dioxide (CO$_2$). The dissolution of calcium carbonate (CaCO$_3$) is controlled by the dissolution of carbon dioxide (CO$_2$). In particular, the more carbon dioxide (CO$_2$) dissolved in water, the more the calcium carbonate (CaCO$_3$) will be dissolved. The CO$_2$ is dissolved rapidly at high pressures and low temperatures and thus, the CaCO$_3$ is dissolved more in the deep ocean waters of the, compared to shallow, surface water. The saturation of CaCO3 is also related to the pH. The higher the pH of the water is, the greater is the concentration of CO$_2$. Since more CO$_2$ is incorporated to the deep ocean waters because of the respiration of organisms, the more easily the water erodes the calcareous shells. The organic matter and amount of oxygen are also affected by the level of sea level (Reolid et al. (2010)).

The decomposition of marine sediments from the oxygen and the oxidation of organic material, results in the release of CO$_2$ into the water. Such process reduces the pH of the water and leads to a subsaturation of the CaCO$_3$. Through this procedure, the CaCO$_3$ may be subjected to post-consequential dissolution (Martin & Sayles, 2004). The dissolution of CaCO$_3$ by organisms can be independent of the saturation of water environments (Milliman et al., 1999). On the other hand, CaCO$_3$ in pelagic sediments is controlled by several factors described by (Khim et al., 2011). The extent of carbon provided in the seabed at a constant volume of dilution factor (productivity), variations in the content of carbon in carbon feed rate constant (factor of dissolution), change in the proportions of calcareous/silicate particles in the flow and dilution of non biogenic material such as wind and volcanic suspensions are the principles factors that affect the CaCO$_3$ content.

When there is an inverse correlation between CaCO$_3$ and Corg in sediments, then the CO$_2$ that is produced by the decomposition of Corg in the subsurface layer of water (where we have no circulations and O$_2$ recycling) and sediments, resulted in a decrease in the pH of water, thus expediting the dissolution of CaCO$_3$ produced in the surface layer of water. This happens when the sediment’s Corg percentage is above 12% or there are seasonal anoxic bottoms (Dean, 1999, 2002). On the other hand, when there is a positive correlation between the two percentages, occurs due to removal of CO$_2$. At high temperatures, where the solubility of CaCO$_3$ and the pH in the surface layer of water is reduced, thus accelerating the production of CaCO$_3$ (Hodell et al., 1998). The interruption of this relation in stratigraphic column shows that the CaCO$_3$ in sediments is mainly controlled by dissolution of the subsurface layer of water and sediment due to the decomposition of organic material.

For this purpose, five sections have been selected from Keri to Kalamaki area, where fifty samples have been selected in order to determine grain-size; total organic carbon (wt. % ToC) and CaCO$_3$ contents (Figure 1).

2. Geological Setting

The study area is situated at the western part of Greece. Western Greece represents the southern edge of the Dinarides-Albanides-Hellenides active margin and has been the focus of oil/gas exploration over the last decade (e.g. Zelilidis et al., 2003; Karakitsios and Rigakis, 2007; Maravelis et al., 2012). It has been influenced by both a compressional and an extensional tectonic
regime, because of the motion of the Adriatic and the Apulia plates. Zakynthos Island is part of the parautochthonus Apulian lithospheric plate of Hellenic mountain belt and contains rocks of two different geotectonic zones, the western Pre-Apulian zone and the eastern Ionian zone (Underhill, 1985).

The region under study was influenced by the Ionian thrust during the early Pliocene (Zelilidis et al., 1998). As a result, the area was fragmented and separated into two discrete sedimentary basins, the westward Alikanas foreland basin and the eastward Gerakas piggy-back basin (Zelilidis et al., 1998). The Foreland basin hosts the oldest rocks seen in the area (Kontopoulos et al., 1997). The study area was served as a continental shelf during Tortonian and thus, mudstones that contain rare sandstone beds were accumulated (Keri area, Figure 1). The upward coarsening upward trend suggests a progressive regional swallowing upward. A large-scale NNW directed normal fault brings in contact the Tortonian shelf with the underlying Late-Cretaceous limestones (Figure 1). Messinian evaporites have been also identified (Agios Sostis area, Figure 1). Such salts evolve into a depositional sequence that contains evaporitic beds of turbiditic origin and further upslope, early Pliocene deep-sea sands. The sedimentation develops with the deposition of shelf deposits with hummocky cross-stratification. This depositional environment is represented by “trubi” marly limestone.

Figure 1 - Geological map of the study area (IGME, 1980, Zakynthos).

3. Tectonostratigraphy

The activity of the Ionian thrust during the early Pliocene is the most important tectonic event that affected the study area. This orogenic event separated the main basin into two discrete sub-basins, a westward foreland and an eastward piggy-back basin (Zelilidis et al., 1998). The foreland basin is typified by major NNW – SSE anticline, which is crossed-cut by both eastward and westward-directed faults. Vrachionas anticline was developed during the Pliocene as part of the foreland-propagating fold and thrust system within Pre-Apulian zone (Underhill, 1989). The Pre-Apulian zone is characterized by a compression regime, after Miocene time (Sorel, 1976; Underhill, 1989), followed by a Pliocene extension regime (Underhill, 1989). Nowadays, there is a shift in the tectonic regime and the study area is typified by a NNE – SSW directed regime. Finally, palaeomagnetic measurements indicate a late Pleistocene 25° clockwise rotation (Duermeijer et al., 1999).
4. Materials and Methods

A suite of fifty samples were selected from five different sections (Figure 2). The base of the depositional sequence is exposed at section one while, the younger sediments are exposed at sections four and five (Figure 2).

Section one: This section is cited at the southern end of Keri gulf. It is eight meters in total thickness and is composed of at least eight coarsening upward sedimentary cycles. Each cycle is up to 1m in total thickness and is represented by a basal mudstone that evolves upslope into coaly beds. Coals are with 30 cm in total thickness.

Section two: This section corresponds to the laterally equivalent of section one, is located at Keri gulf and is presented with up to 6 meters total thickness. This outcrop consists of a basal gray/brown mudstone up to 25cm thick interbedded with thin-bedded sandstones. There is an upward increase in mudstone-sandstone ratio.

Section three: This section is located northeast of the section two between the Keri gulf and Agios Sostis peninsula. In this area a sedimentary succession with up to 65 meters in total thickness is exposed (Figure 3). This sequence is characterized by a thick slump horizon, placed at the top and with 25 meters in total thickness (figure 4). This slump horizon overlies sandstone beds, one meter thick with no evidence of deformation. The deformation unit underlies undisturbed mudstone strata. Throughout the sedimentary sequence Bouma subdivision are the dominant sedimentary features (Figure 5).

Section four: This section is located west of the section two and southwest of Keri gulf. It is characterized by a thick mudstone bed, up to 25 meters in total thickness, with no evidence of deformation. This mudstone bed overlies sandstone beds, one meter thick, with evidence of mechanical deformation. The deformation unit underlies undisturbed mudstone strata. Throughout the sedimentary sequence Bouma subdivision are the dominant sedimentary features (Figure 5).

Section five: This section is located northwest of the section two and northeast of the section four. It is characterized by a thick mudstone bed, up to 25 meters in total thickness, with no evidence of deformation. This mudstone bed overlies sandstone beds, one meter thick, with evidence of mechanical deformation. The deformation unit underlies undisturbed mudstone strata. Throughout the sedimentary sequence Bouma subdivision are the dominant sedimentary features (Figure 5).

Figure 2 - Map showing the study area and the sections of where the samples were taken. (Photo from Google Earth).

Figure 3 - Panoramic view of Section three.
Section four: This section represents the upper parts of the studied stratigraphy (Kontopoulos et al., 1997). In the current research samples were collected at the base of the section. The upper parts of both sections four and five are represented by carbonates. The “Trubi” marly limestones are considered as the typical early Pliocene sedimentary facies of the Mediterranean. Such facies are overlain the turbiditic sequence, which contains sandstone and re-sedimented evaporitic turbidites (Kontopoulos et al., 1997). Both the upper part of the studied section four (overlying the stratigraphic column of this work), and the upper part of the Kalamaki cross-section (Section five) consist of the typical for the Mediterranean environment during the Early Pliocene, "trubi" marly limestone (Figures 6 and 7), formed over Pliocene turbiditic sequence, with sandstone and re-sedimented evaporitic clast turbidites (Kontopoulos et al., 1997).
According to the above description a synthetic stratigraphic column was produced (Figure 8). From the whole sequence a detailed calcareous nannofossil biostratigraphy showed that the age of section one and two sediments is Tortonian, and only from slumps we found many resedimented mostly Oligocene and Aquitanian to Burdigalian sediments (Figure 8). Samples of section three and section five (e.g. samples 30, 45, 52) display rare to common small *Gephyrocapsa* spp. coccoliths (2.5-3.0 μm), within a rich but re-deposited from Eocene, Late Oligocene, Aquitanian-Burdigalian, Messinian, assemblage. *Gephyrocapsa* spp. presence along with the absence of *Discocystis* species (*D. tamalis, D. pentaradiatus, D. surculus*); only *Discocystis* cf. *brouweri* has been documented, enables tentative age assignment in Early Pliocene (subbottom of *Gephyrocapsa* spp. at 4.33 Ma, Lourens et al., 2004). Sample 36 from section three yields nannofossil flora (*Reticulofenestra pseudoumbilicus, Pseudoemiliania lacunosa, small* *Gephyrocapsa* spp.) of Early Pliocene (NN14-15 biozone).

As depicted on Figure 8, a synthetic stratigraphic column was constructed based on sedimentologic evidence. The detailed calcareous nannofossil biostratigraphy indicates a Late Miocene (Tortonian) age for the sections one and two. Samples from the slump horizon determined as Oligocene-early Miocene in age (Figure 8). Sections three and five (e.g. samples 30, 45, 52) display rare to common small *Gephyrocapsa* spp. coccoliths (2.5-3.0 μm), within a rich but re-deposited fossils from Eocene, Late Oligocene, Miocene (Aquitanian-Burdigalian, Messinian) sedimentary sequence. The occurrence of *Gephyrocapsa* spp. in association with the absence of *Discocystis* species (only *Discocystis* cf. *brouweri* has been documented), suggests an Early Pliocene age (subbottom of *Gephyrocapsa* spp. at 4.33 Ma, Lourens et al., 2004). Sample 36 from section three yields nannofossil flora (*Reticulofenestra pseudoumbilicus, Pseudoemiliania lacunosa, small* *Gephyrocapsa* spp.) of Early Pliocene (NN14-15 biozone).

One cycle of section four at Agios Sostis and fourteen cycles of section five in Kalamaki display the influence of the Ionian thrust during the depositional evolution. The section five is intimately related to the activity of the Ionian thrust because of its proximity to the thrust front whereas; the remotely positioned section four is little influenced by the thrust activity.

5. Methodology - Materials and Methods

Sieve analysis for sediments sandstone (>63mm) and pipette analysis for mudstones (<63mm) were used in order to determine grain size and their parameters. The determination of organic carbon content was based on the method of titration (Gaudette et al., 1974). The content of calcium carbonate was measured with the complete dissolution of calcium carbonate (CaCO$_3$) with acetic acid (CH$_3$COOH) (Varnavas, 1979).

6. Results

The grain size analysis aims to determine the lithology and grain size parameters in order to describe the particle size distribution of sediments. The data exported from the grain size analysis were used for the construction of cumulative grading curve and the determination of the lithologic character of the sediments. The statistical parameters were calculated based on the Folk & Ward (1957) method.

The grain size analysis suggests that silt is the main lithology with minor presence of clay. Coarser material is totally absent. As portrayed on Figure 9, the depositional depth of the studied samples is variable. In Figure 11, it is depicted that the selected samples display a random scatter in terms of the stagnant water.

Generally, the main lithology is siltstone. The analysis of the statistical parameters suggests that studied sediments were mostly deposited in a deep basin depth, but a considerable number of samples were deposited in low depth too. Additional evidence for the deep basin depth is provided by the common presence of Bouma subdivisions in section three.
Figure 8 - Synthetic stratigraphic column of the studied area (age determination was according to Martini, 1971).

Figure 9 - Diagram of Valia and Cameron (1979), showing the depositional depth (Sk1=asymmetry, Mz=mean and σ1= deviation).

Figure 10 - Diagram of Steward (1958) for the determination of the depositional environment.

Figure 11 - Diagram of Passega (1957) for the determination of the depositional environment.
The amount of organic matter in sedimentary rocks is usually measured as the total organic carbon content (TOC) and expressed as a percentage of the dry rock. TOC is not a clear indicator of petroleum potential, as thick, organic-rich potential source rocks cannot become effective source rocks without sufficient burial and thermal maturation (Kenneth et al., 2007).

Organic carbon content of the studied sediments exhibits variable contents, ranging from 0 to 3.19 wt. % (Figure 12).

![Figure 12 - The content of TOC in studied deposits, where the line depict the lower limit of 0.5% that differentiate the potential source rocks with those that have no potential.](image)

Studies of numerous global samples of different ages have led to the conclusion that the minimum TOC value required for the designation as an immature source rock is 0.5 wt. % (Hunt, 1979; Hedberg & Moody, 1979; Tissot & Welte, 1984). Thus, these values suggest that the studied sedimentary sequence contains samples with poor to good source rock potential.

The calcium carbonate of the studied samples ranges between 1.76 to 61.29 (Figure 13).

![Figure 13 - The content of CaCO\textsubscript{3} in studied deposits.](image)

In the study area the content of calcium carbonate is high among the fine material, suggesting high sedimentation rates. The combination of total organic carbon (TOC) content and calcium carbonate contents in sedimentary rocks can be employed to add knowledge into the depositional conditions during sedimentation (Figure 14). There is not a constant trend between these two parameters throughout the studied sedimentary succession. The contents of the total organic carbon and calcium carbonate display both positive and negative correlation. This fact indicates that that the CaCO\textsubscript{3} content is mainly controlled by dissolution in the subsurface layer of water and sediment due to the decomposition of organic material.

The first stratigraphic cycle is typified by a positive correlation between the two parameters. The high percentage of CaCO\textsubscript{3} indicate high sedimentation rates while the variable TOC content can be explained by the existence of seasonal anoxic bottom (no circulation and recycling of O\textsubscript{2}) (Dean, 1999, 2002). Additionally, low organic productivity and high rate of burial of the organic matter resulted in no oxidization. In the other cycles, however, the lower content of CaCO\textsubscript{3} indicates lower sedimentation rates and so the TOC content is not influenced by the depositional environment.

The reduction in the content of CaCO\textsubscript{3} from cycle one to four indicates a gradual swallowing of the basin. Cold climatic conditions are also suggested and are in agreement with the Miocene regional icehouse conditions (Bertolani - Marchetti, 1985). Such conditions may potentially have resulted into an increase in solubility of CaCO\textsubscript{3}. However, the third cycle is characterized by the...
presence of slump horizon and thus, the low rates of CaCO$_3$ cannot be connected to low sedimentation rates. The slumps led to scarification of the subsurface layer and the production of suspensions, which probably concluded to the low content of CaCO$_3$ caused by the dilution due to non-biogenic material (Khim et al., 2011). The high rates of TOC observed in a group of samples of this cycle possible can be related to quick of burial rate, where the organic matter does not have time to be oxidized.

Figure 14 - Correlation of CaCO$_3$ and TOC contents within studied deposits.

7. Conclusions
Grain size analysis suggests a regional upward swallowing upward trend. Sedimentation took place in a deep basin with steep western margins during Tortonian to early Pliocene. The CaCO$_3$ content indicates high deposition rates, while TOC contents indicate potential source rocks for hydrocarbon generation. The comparison of TOC and CaCO$_3$ indicates that these two parameters are presented with both positive and negative correlation. This character is intimately related to the dissolution of the CaCO$_3$ at the subsurface layer of water and sediment because of the decomposition of organic material, in oxic conditions.

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