TOC and CaCO3 content in Oligocene shelf deposits on Lemnos Island and their relation with depositional conditions

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TOC AND CaCO₃ CONTENT IN OLIGOCENE SHELF DEPOSITS ON LEMNOS ISLAND AND THEIR RELATION WITH DEPOSITIONAL CONDITIONS

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Abstract

A series of seventy seven samples from outcrops of mudstones were analyzed in order to evaluate their total organic carbon (TOC) and calcium carbonate (CaCO₃) concentrations. Results showed that TOC ranges between 0% to 1.15% (with a mean value of 0.34%) introducing that Oligocene shelf deposits on Lemnos island have fair to good conditions to be potential source rocks. Analysis of CaCO₃ presented a range between 1.37% to 42.52% (with a mean value of 16.95%). The comparison of TOC and CaCO₃ suggests that the two parameters are either inversely or positively related. The inversely related contents, high TOC and low CaCO₃, may indicate anoxic conditions, whereas low TOC and high CaCO₃ occur in oxic conditions due to the decomposition of TOC. The CO₂ produced by decomposition of organic carbon and production of organic acids reduces the pH in pore water enough to dissolve any CaCO₃ that reaches the sediment water interface. On the other hand, a positive relation, with both high TOC-CaCO₃ contents, could be related with oxic conditions and high sedimentation rate or incidents of abrupt death and bury of great amounts of benthic organisms (TOC) increasing the maintenance of organic material in the sediment.

Key words: Lemnos island, source rock, CaCO₃, TOC.

Περίληψη

Αναλύθηκαν εβδομήντα εφτά δείγματα από επιφανειακές εμφανίσεις ιλυολίθων με σκοπό να προσδιορίσουν η ποσότητα του συνολικού οργανικού ανθράκα (TOC) και του ανθρακικού ασβεστίου (CaCO₃) του συνολικού οργανικού υλικού κυμαίνεται από 0% έως 1.15% (με μέση τιμή 0.34%) δείχνοντας ότι οι αποθέσεις υφαλοκρηπίδας ηλικίας Ολιγοκαίνου, στο νησί της Λήμνου έχουν μέτριες έως καλές δυνατότητες να είναι μητρικά πετρώματα. Το ποσοστό του ανθρακικού ασβεστίου κυμαίνεται από 1.37% έως 42.52%, με μέση τιμή 16.95%. Η σύγκριση των αποτελεσμάτων μεταξύ TOC και CaCO₃ προτείνει ότι οι δύο παράμετροί έχουν είτε αρνητική ή θετική συσχέτιση. Η αρνητική συσχέτιση των ποσοστών, TOC υψηλό και CaCO₃ χαμηλό, μπορεί να συσχετιστεί με ανοξικές συνθήκες, ενώ TOC χαμηλό και CaCO₃ υψηλό, εξ’ αυτών της αποκολλώσεως του TOC σε οξικές συνθήκες. Το CO₂ που παράγεται από την αποσύνθεση του οργανικού υλικού και η παραγωγή οργανικών οξέων μείω-

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νον το pH του νερού των πόρων τόσο ώστε να επιτρέπει η διάλυση όσου CaCO3 φτάνει στην διεπιφάνεια ιζήματος- νερού. Από την άλλη μεριά, η θετική συσχέτιση, με υψηλά και τα δύο TOC και CaCO3, μπορεί να συσχετιστεί με οξικές συνθήκες και μεγάλο ποσοστό θάνατο και παρά μεγάλος ποσοστός επισπεύδων βενθικών οργανισμών αυξάνοντας έτσι τη διατήρηση του οργανικού υλικού στο Ίζημα.

Λέξεις κλειδιά: Λήμνος, μητρικό πέτρωμα, ανθρακικό ασβέστιο, οργανικός άνθρακας.

1. Introduction

Continental shelves constitute one of the preferential zones for the productivity of biomass, which is converted into hydrocarbons (Biju-Duval, 2002). A typical source rock consists of fine sediments that release enough hydrocarbons so as to form a remarkable concentration of oil or natural gas (Brooks et. al., 1987). Source rock prediction requires an understanding of the structural and stratigraphic evolution of the sedimentary layers inside a basin. Characterizing the organic matter from sedimentary rocks is now widely recognized as a critical step in the evaluation of the hydrocarbon potential (Lafrague et. al., 1998).

The amount of organic matter in rocks is usually measured as the total organic carbon content (TOC) and expressed as a percentage of the dry rock. At this study sequence stratigraphy has been combined with total organic carbon (TOC) analysis to develop a model of TOC accumulation in marine source rocks. Various factors play a role in the preservation of organic matter, notably the oxygen content of the water column and sediment (oxic versus anoxic), primary productivity of new organic matter by plants, water circulation, and sedimentation rate (Demaison and Moore, 1980; Emerson, 1985). Anoxic conditions are critical to the preservation of organic matter in sediments. Source rock prediction is therefore concerned primarily with the predicting where and when in the geological past anoxic conditions are likely to have existed. Anoxic conditions develop where oxygen demand exceeds oxygen supply. Oxygen demand is high in areas of high organic productivity (Allen and Allen, 2005).

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 and Moody, 1979, Tissot and Welte, 1984).

In present study a series of seventy seven samples were chosen from outcrops of shelf deposits in order to measure the TOC and CaCO3 content and after correlation to introduce the factors that influence the above relation and their influence on depositional environments.

2. Geological Setting

The Thrace Basin has been considered as a fore arc basin of the ‘contracted’ type (Görür and Okay, 1996; Maravelis and Zellidis, 2010a) and is the largest and thickest Tertiary sedimentary basin of the eastern Balkan region (Turgut et al., 1991; Turgut and Eseller, 2000). It is exposed on Hellenic, Turkish, and Bulgarian territory and comprises an important hydrocarbon province (e.g. Turgut and Eseller, 2000; Siyako and Huvaz, 2007; Maravelis and Zellidis, 2010b; Maravelis and Zellidis, 2012). A large accretionary prism in the Central Aegean region bounds the basin on the seaward side, and the landward flank was bound by an active volcanic arc, the Rhodope Zone. Most of the basin strata are Lower Eocene to Upper Oligocene and form thick sedimentary successions (up to 9000 m) made of deep-sea fan deposits (Turgut et al., 1991; Turgut and Eseller, 2000). Sedimentation along the basin margin was dominated by deposition of carbonates during the Eocene and by deltaic bodies, prograding towards the basin center, in the Oligocene (Sümengen and Terlemez, 1991; Turgut et al., 1991).

The Greek part of the Thrace Basin in Lemnos Island and Rhodope was mainly influenced by two major sediment inputs (Maravelis and Zellidis, 2010b, 2013). The southern part (Lemnos) was significantly affected by the accretionary prism and associated ophiolitic units (Maravelis and Zellidis,
2010a, 2012) while the northern part (Greek Rhodope) reflects a Circum-Rhodope Belt influence (Maravelis and Zelilidis, 2010b). On Lemnos, the source area contributed significant a volume of ultramafic, gabbro, basalt, chert, and possibly some volcaniclastic detritus of variable grain size into the forearc basin and was probably located south-southwest of Lemnos (Maravelis and Zelilidis, 2010a). The source area was probably rugged and rapidly eroded, causing the ophiolitic bedrock to be deeply incised, enabling a significant amount of coarse-grained material from the uplifting source area to be transported to the Lemnos area (Maravelis and Zelilidis, 2010b, 2013).

This material was deposited in submarine fans in the Lemnos area, which, as a result of tectonic activity, are overlain by shelf deposits (Maravelis et al., 2007). The submarine fan is a sand-rich system, which comprises a basin-floor fan overlain by a slope fan, suggesting submarine fan progradation. Both basin-floor and slope fans are characterized by monotonous alternations of sandstone and mudstone beds (Maravelis et al., 2007).

The shelf environment at Lemnos consists of sandstones interbedded with very thin mudstone beds. Many types of sandstone appear featureless, although others show grooves and tool marks. Internal structures are dominated by a prominent parallel lamination. The sandstone beds show, generally a single set of ripple cross-laminae at the top. Mudstones commonly contain a high proportion of coal debris. Upwards, this unit grades from a sand dominant to an almost completely mud-dominant sequence that consists of massive, homogeneous green or green-grey mudstones (Maravelis et al. 2007).

**Figure 1** - Simplified sketch map and plate tectonic configuration of the Eastern Mediterranean and adjacent region and schematic diagram illustrating the north-east Aegean Sea tectonic setting (Modified from Maravelis & Zelilidis, 2010a).

During the Miocene, Lemnos was the site of volcanic activity resulting in accumulation of magmatic rocks (Pe-Piper and Piper, 2001). Both plutonic and volcanic rocks accumulated, principally trachyan-desites and dacites, and cover a large part of the studied area. These rocks have been interpreted as belonging to the high-K province along the Aegean–Anatolian boundary (Pe-Piper et al., 2009). In particular, they belong to the northern, ‘shoshonitic province’ that includes the islands of Samothrace,
Lemnos and Lesvos (Pe-Piper et al., 2009). These high-K rocks, mostly of intermediate composition, indicate ensuing calc-alkaline orogenic volcanism, emitted from large volcanic centers. Upwelling of asthenospheric mantle has been invoked to account for their genesis (Pe-Piper et al., 2009). The end of the Miocene is characterized by the deposition of conglomerates, marls and calcareous sandstones. Local Pleistocene porous calcareous and locally oolitic limestones and Holocene alluvial, coastal deposits and dunes are sparse.

3. Stratigraphy

Studied shelf deposits, up to 84m thick, consist of four sedimentary cycles of repetition character, start with mud and terminate upwards with an increasing grain size either of sand with mud or only of sand (Figure 2).

![Stratigraphic column of sediments samples of the study area.](image)

The fact that the cycles are completed with sand indicates that the processes of sand transport and deposit were of a higher energy than those of mud transport and deposit. More specifically, the first sedimentary cycle is 36.5m thick, and consists of 6 mudstone layers (33m thick) and a layer
of sandstone which overlies the mudstones about 3.5 meters thick. The second sedimentary cycle is composed of a mudstone layer (7m thick) and a sandstone layer (6m thick) and has an overall thickness of 13 meters. The third sedimentary cycle includes 4 layers of mudstones (15m thick) and a thick sandstone layer with a total thickness of about 17.5 meters. The last sedimentary cycle, up to 17m thick, is formed by a mudstone layer (10m thick) and a layer of sandstone (7m thick).

4. Methodology and Results

4.1. Materials and Methods

The TOC % concentrations were evaluated with the use of the titration method by Gaudette et al. 1974. 10 ml of potassium dichromate (K2Cr2O7) were added and mixed thoroughly. Then 20 ml of concentrated sulfuric acid (H2SO4, 96%) were added and the mixture was stirred with a gentle shake for one minute. This is done carefully to achieve full contact (reaction) of the precipitate with the reagent while avoiding residue on the walls of the bottle and not in contact with the reagents. After 30 minutes, the solution was diluted with 200 ml distilled water and afterwards 10 ml of phosphoric acid (H3PO4, 85%) 0,2 gr of sodium fluoride (NaF) and 15 drops of indicator difenylaminis were added. The solution was back-titrated with a solution of ferrous ammonium sulfate regularity 0,5 N (FeSO4 (NH4)2 (SO4) 6H2O). The color develops from dull green-brown to green by adding approximately 10 ml of the ferric solution. The color continues to change with the addition of 10 to 20 drops of the ferric solution until very bright green. The same procedure is followed in a blank sample (a sample containing no precipitate) per ten samples.

For the determination of calcium carbonate (CaCO3) % concentration of the samples, the method for cleaving the CaCO3 with CH3COOH (acetic acid) is used as described by Varnavas, 1979. This method relies on the full decomposition of calcium carbonate (CaCO3) with acetic acid (CH3COOH), to form a soluble salt of calcium acetate ((CH3COO)2Ca) and escape the produced carbon dioxide (CO2).

4.2. TOC Results

Organic carbon content (Figure 3) of the Lemnos studied sediments exhibits variable contents ranging from 0 to 1.15% with an average value of 0.34% and these values prove that the studied rocks have from poor to good source rock potential. Generally, TOC value is characterized by an intense fluctuation throughout the stratigraphic column. At the first sedimentary cycle (samples D1-D37), a sudden negative shift in the TOC rations occurs over the samples D1 and D35 with 0% TOC. At the second sedimentary cycle (samples D38-D47), TOC values reach a peak at D40-1.03%. At the third sedimentary cycle (samples D48-D69) TOC values reach a peak at D67-1.15% and D68-0.98% while D51, D53, D54, D55, D57, D58, D59, D66, D69 contain 0% TOC. At the fourth sedimentary cycle (samples D70-D77) and at the top layer of the stratigraphic column D70, D71, D73, D75, D76 contain 0% TOC. The average TOC content presents a general decreasing trend through each sedimentary cycle (Figure 3).

Figure 3 - TOC percentages in sediments of study area.

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4.3. CaCO3 Results

Variation of CaCO$_3$ throughout the stratigraphic column is presented in Figure 4 with CaCO$_3$ variable content ranging from 1.37 to 42.52% with an average value of 16.95%.

![Figure 4 - Calcium carbonate percentages in sediments of study area.](http://epublishing.ekt.gr)

At the first sedimentary cycle, (samples D1-D37) max values of CaCO$_3$ occur at D17-27.67% and at D32-24.74% while minimum values occur at samples D21-9.24% and D31-9.82%. At the second sedimentary cycle (samples D38-D47), the elevated values are punctuated by major peaks at D39-34.85% and D41-29.58% while its minimum values correspond to samples D38-1.37% and D42-8.23%. At the third sedimentary cycle (samples D48-D69), occur major peaks at D48-33.13%, D50-38.3% while minimum values occur at D66-9.98% and D59-10.9%. At the fourth sedimentary cycle (samples D70-D77) CaCO$_3$ reaches a peak of 42.52% at D74 and D77-25.71% as well as minimum values at D76-9.42% and at D72-9.74%. The average CaCO$_3$ content presents a general increasing trend through each sedimentary cycle (Figure 4).

In the study area the results of the study of calcareous nannofossils (biostratigraphy) showed that during the lower Oligocene the cold paleoclimatic conditions led to changes in palaeoenvironment and biotic conditions at the open seas (Maravelis and Zellidisis, 2012). For example, calcareous nanofossils *Braarudosphaera bigelowii* and *Micrantholithus spp.* which were recognized at the study area indicate changes in climate at Eocene / Oligocene. These species are typical of eutrophic waters with low oxygen and salinity (Peleo-Alampay et al., 1999) and indicate the input of terrestrial material (Švábenická, 1999).

4.4. Correlation Between TOC and CaCO$_3$

TOC and CaCO$_3$ values can be compared to one another for each sample separately observing Figure 5. The mean values for each sedimentary cycle are presented in Table 1.

At the first sedimentary cycle, TOC and CaCO$_3$ values are increased at Sample D17 with values of 0.49% and 27.67%, respectively. At sample D26 organic matter increases while CaCO$_3$ decreases with values of 0.70% and 14.84%, respectively. At sample D32 TOC with a value of 0.51% decreases and CaCO$_3$ increases to 24.74% increases. At sample D34 both percentages increase with TOC-0.84% and CaCO$_3$-16.61%.

Specifically, the mudstones of the first sedimentary cycle have an average of 0.38% of TOC and 15.5% of CaCO$_3$ while the upper layer of sandstone/mudstone has an average of 0.46% TOC and 15.97% CaCO$_3$. At the second sedimentary cycle, at sample D39 a decrease of organic material (0.53%) and an increase of CaCO$_3$ (34.85%) are observed. An increase in organic matter (1.03%) and a decrease of CaCO$_3$ (12.76%) is observed at sample D40. Specifically, the mudstone layer of the second sedimentary cycle has an average of 0.56% TOC and 17.6% CaCO$_3$ while the upper layer of sandstone is described by 0.37% TOC and 17.77% CaCO$_3$. At the third sedimentary cycle at sample D50 organic matter decreases (0.21%) and CaCO$_3$ increases (38.3%) while at sample D67 both TOC and CaCO$_3$ are increased with values of 1.15%, 17.42%, respectively. At the third sedimentary cycle the four layers of mudstone have a TOC average of 0.38%, 15.5%, 0.46%, 0.51% and CaCO$_3$ average of 15.97%, 15.5%, 15.97%, 17.6%, respectively.
0.23% and a CaCO3 average of 18.99% while the sandstone layer of this cycle has percentages of 0.54% and 14.55%, respectively. At the fourth sedimentary cycle, the sample D74 has values that increase at 0.06%, for TOC and at 42.52% for CaCO3. Also, the mudstone layer of the fourth sedimentary cycle is characterized by TOC of 0.06% and CaCO3 of 16% while the layer of sandstone/mudstone has an average of 0.04% TOC and 21.71% CaCO3.

<table>
<thead>
<tr>
<th>CYCLE</th>
<th>no. S</th>
<th>CaCO3 avg</th>
<th>TOC avg</th>
</tr>
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<tbody>
<tr>
<td>1st</td>
<td>37</td>
<td>15.57</td>
<td>0.39</td>
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<tr>
<td>2nd</td>
<td>8</td>
<td>17.67</td>
<td>0.48</td>
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<tr>
<td>3rd</td>
<td>22</td>
<td>17.97</td>
<td>0.30</td>
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<tr>
<td>4th</td>
<td>8</td>
<td>19.57</td>
<td>0.04</td>
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</table>

Nearly 3m with dark mudstone where samples D48-49 were taken from, contain an average of 31.21% CaCO3 and 0.57 TOC % while the overlying white mudstone of 4m (D50-D55) contain an average 17.96% of CaCO3 and 0.1 TOC. The anoxic conditions predominated during deposition of the sediments of the dark mudstone while these conditions changed in an environment with higher oxygen (white mudstone).

Samples with a synchronous increase of TOC-CaCO3 content occur at samples (D17, D34, D67, D74) and can be interpreted by the abrupt death and bury of a great quantity of both the shells (CaCO3) and the body parts (organic matter) of benthic organisms by successive layers of sediment.

On the contrary, the inverse relation between CaCO3-TOC at samples D26, D32, D39, D40, D50, where increase of TOC is accompanied with decrease of CaCO3 indicates that the CO2 produced by decomposition of that organic carbon and production of organic acids reduces the pH of anoxic pore waters enough to dissolve any CaCO3 that reaches the sediment-water interface (Figure 5).

Table 1 - TOC and CaCO3 percentages in sediments for each sedimentary cycle.

While no general correlation is present throughout the sedimentary cycles (r=0) a general trend of CaCO3 increase and TOC respective decrease can be observed. Furthermore, the correlation between the average % measurements for each sedimentary cycles (Table 1) is strong negative (r=-0.7). The lack of general correlation may indicate different origin for inorganic and organic carbon throughout the sedimentation process.
However, throughout the sedimentation cycles exceptions to this rule occur, where increase of CaCO$_3$ content is synchronous with increase of the TOC content. Specifically, at the closing of each cycle positive correlations occur, while the highest measurements for both parameters co-occur at the closing of the 3$^{rd}$ cycle. The scatter plot of the closing of the 3$^{rd}$ cycle is presented in Figure 7, where the positive correlation is evident ($r=1$). The same pattern applies for the closing of both the 1$^{st}$ and the 4$^{th}$ cycle. For each cycle, the grain size increases as we move upwards which indicates higher energy sedimentation or progradation of the deposition environment, or both. High energy sedimentation can justify the positive correlation, as the organic carbon is buried in a rate that preserves oxidization; both higher energy sedimentation rates and progradation of the depositional environment can be observed through the stratigraphic column, as there is an upward thickening trend and grain size is increasing at the end of each cycle.

Figure 7 - TOC and CaCO$_3$ correlation for the upper part of third sedimentary cycles.

5. Discussion – Conclusions

The study of both TOC and CaCO$_3$ content for Lemnos shelf deposits and the identification of correlations between the two parameters can provide several clues about the depositional environment and conditions and the evaluation of possible source rocks. In general, the results present:

- A poor to good TOC % content (0-1.15%). TOC average % for each cycle decreases upwards. Taking into consideration that a source rock needs to be a fine-grained and rich in organic matter, the mudstone of the second sedimentary cycle with the most elevated percentage of TOC-0.54% may be considered as most suitable source rock in compare to all other sediments of the stratigraphic column. Also, according to the percentages of Peters and Cassa (1994), showing petroleum potential (quantity) of an immature source rock, the mudstone of second sedimentary cycle presents a fair potential to hydrocarbon production.

- A poor CaCO$_3$ content (0.71-45%), not enough to consider the study rocks as calcareous mudstone source rocks. The poor content indicates limited inorganic carbon supply from the terrestrial ultramafic, gabbro, basalt and volcanoclastic detritus.

- CaCO$_3$ and TOC % content does not present a general correlation either positive or inverse, which indicates different source supply of organic and inorganic carbon. However a general inverse trend is observed for each sedimentary cycle and for the most significant measurements, while synchronous changes occur throughout the sequence.

- Detailed analysis has presented positive correlation between the two parameters at the higher energy parts of the sedimentary cycles. The coarse grained sands are of higher energy, and thus higher sedimentation rates; organic content is preserved under successive sediment accumulation in a higher rate than its oxidization. Simultaneous rapid increase in both contents, as is the case in the 3$^{rd}$ sedimentary cycle, can be attributed to abrupt death and bury of benthic organisms, which provide both the organic material (body parts) and the increase of calcium carbonate (shells). Biotic and environmental changes during Oligocene, which are also indicated by the biostratigraphy of the shelf deposits (Maravelis &...
Zelilidis, 2012) could justify such an event, while the rapid sedimentation preserved the geological record. Another fair assumption is that the thickening of the sandstones of the closing of the cycle could indicate elevation of the depositional environment and thus, increased terrigenous supply in both parameters.

6. References


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