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CARBONATE AND ORGANIC CARBON CONTENT IN THE RECENT SEDIMENTS OF ELEFSIS BAY AS INDICATORS FOR THE PALEOENVIROMENTAL EVOLUTION OF THE SYSTEM

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Abstract

During the Holocene period Elefsis bay acted as a semi-enclosed system obstructing water circulation. In some areas, sampling has revealed the problems of anoxia that prevails in the bay, which has been worse during the summer months. Analyses undertaken in a core from the bay of Elefsis showed notable changes in carbonate and organic material, which prove the paleo-environmental evolution of the bay. Such changes of carbonate are due to the different deposition of calcium carbonate from biogenic source (probably and from inorganic source). The variation of organic carbon is still a factor of limited water circulation in the bay.
***Key words**: coastal paleolakes, authigenic carbonate minerals, Elefsis Bay/Greece.*

Περίληψη

Κατά τη διάρκεια του Ολοκαίνου έως σήμερα ο κόλπος της Ελευσίνας λειτουργεί ως ένα ημίκλειστο σύστημα με δυσκολία στην ανανέωση νερού. Σε πολλές περιπτώσεις, δειγματοληψίες αποκάλυψαν το πρόβλημα της ανοξίας που επικρατεί στον κόλπο, το οποίο και επιδεινώνεται τους καλοκαιρινούς μήνες. Αναλύσεις που έγιναν σε πυρήνα από τον κόλπο της Ελευσίνας έδειξαν αξιοσημείωτες μεταβολές σε ανθρακικά και οργανικό υλικό, με βάση τα οποία έγινε η αξιολόγηση και η μελέτη της παλαιο-περιβαντολογικής εξέλιξης του κόλπου. Οι μεταβολές αυτές των ανθρακικών οφείλονται στην διαφορετική απόθεση ανθρακικού ασβεστίου βιογενούς προελεύσεως, (πιθανότατα και από ανόργανη απόθεση). Η διακύμανση του οργανικού άνθρακα είναι ακόμα ένας μάρτυρας της περιορισμένης κυκλοφορίας των υδάτων μέσα στον κόλπο.
***Λέξεις κλειδιά:** παράκτιες παλαιολίμνες, αυθιγενή ανθρακικά ορυκτά, κόλπος Ελευσίνας.*

1. Introduction

Elefsis Bay is a geomorphological embayment between Attica and Salamis Island in northern Saronikos Gulf (Greece) (figure 1). It communicates through shallow straits, in west and east, with the open Saronikos Gulf. The straits show nowadays a depth of 8 m at the western and 12 m at eastern and the deepest part of the bay shows a depth of 35 m.

The description of the sediment units of one core (S-2 PERSEUS - Saronikos) from the deepest part of the bay, as well as sediment analyses from the core, -carbonate content and carbonate mineral differentiation, organic carbon and nitrogen content,- lead to important indicators for the paleoenvironmental evolution of the Elefsis aquatic system. This paleoenvironmental evolution of the Elefsis Bay is the aim of this work.

2. Description of the Area

Elefsis Bay is the result of neotectonic processes leading to the fragmentation of the broader area. Two main faulting systems dominate in the area, the WNW-ESE system and the SW-NE system (Lekkas, 2001). These two systems regulate the geomorphological diversity of the extended area and consequently the configuration of the bay. The area is characterized by a small drainage basin, mainly extended in the northern part of Elefsis Bay (figure 2). Ephemeral tributaries with low fresh water input drain into the bay. They contribute also to the sedimentation processes of the bay with terrigenous sediment particles supply.

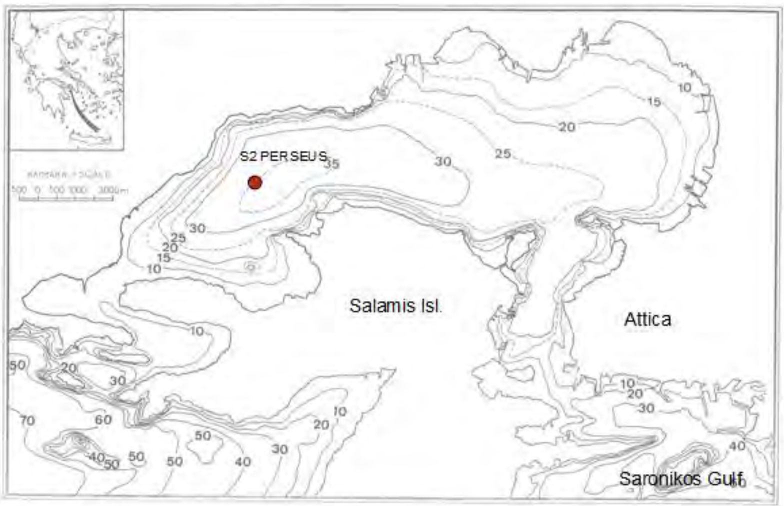


Figure 1 - Bathymetric map of Elefsis Bay (map produced by Anagnostou, unpublished data). Red spot shows the coring position of the S2 PERSEUS core.

The bathymetry of the Elefsis Bay shows an eastern part with depths of 10-25 m and a western part with depths of more than 30 m (s. figure 1). Systematic sub-bottom profiling indicates the thickness of the Holocene sediment cover from 3-5 m in the eastern part and 10-15 m in the western part (figure 3).

Sedimentation rate was estimated for the recent sediments in the western part of the bay and shows values of approximately 3 mm/year (Hatzianestis et al., 2004).

The Elefsis ecosystem dynamic is summarized in the work of Pavlidou et al., 2010. The low freshwater input and the limited water mass exchange with the Saronikos system resulted to periodical anoxic events (s. Pavlidou, et al., 2010).

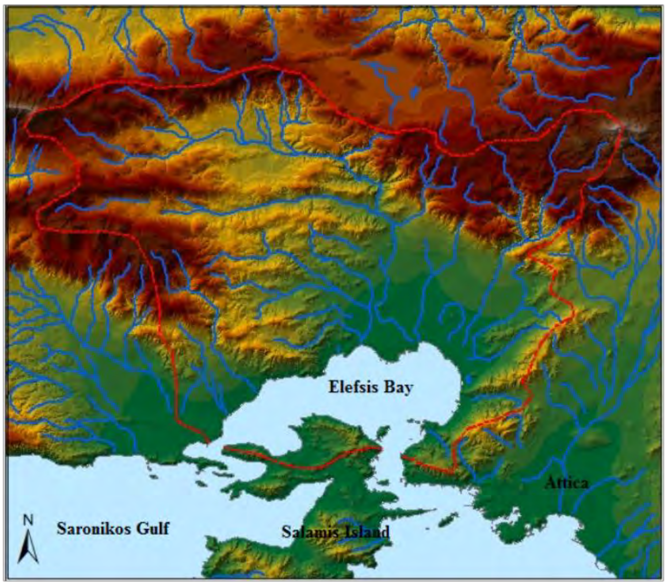


Figure 2 - The drainage area of the Elefsis Bay (red line).

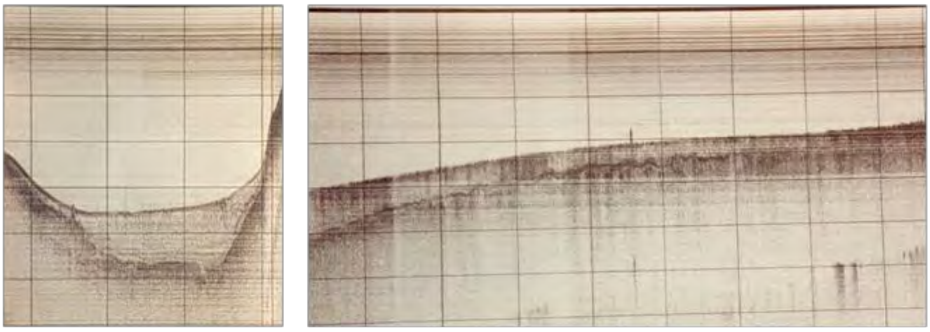


Figure 3 - Sub-bottom profiles of the Elefsis Bay. They show clear the Holocene marine sediment cover and the pre-depositional unconformity, Left: The Holocene sediments in the western part of Elefsis Bay with a thickness of 8-13 m. Right: A 3–5 m thickness of the Holocene sediment cover in the eastern part of the bay.

3. Methodology

During a research cruise in Elefsis Bay, in February 2012, a sediment core was extracted from the deepest part of Elefsis basin, means of a 5m long gravity core, using R/V Aegaeo of the Hellenic Center of Marine Research (HCMR). Longitudinally splitting of the core, picturing, macroscopic description (the color was determined using the Standard Soil Color Charts) and sub-sampling are carried out in the laboratories of HCMR. The sub-sampling is designed for sedimentological, geochemical and micropaleontological analyses.

For the purposes of this work sediment samples were powdered in a Fritch agate mortal mill for 10 minutes after drying in 60-65 ^{o}C for at least 24 hours.

For the total carbon, organic carbon and organic nitrogen a CHN Analyzer is used. Successful determination of organic carbon relies upon the separation of organic from inorganic carbon. For this reason the sediment samples are separated in two parts, in the one the removal of inorganic forms is achieved by acidification, in the other one the quantity of total carbon and nitrogen is determined. The amount of inorganic carbon is resulted from the difference of the above ones. A small amount is weighted (10-15 mg) in silver weighing pans for organic carbon determination and tin pans for total carbon and nitrogen determination. The sediments which are weighed in tin pans are closed, compacted and formed into a ball in order to be transferred into CHN-analyzer auto sampler. The sediments that are weighed in silver pans are acidified carefully. After the acidification and the drying at 60°C overnight the sediment samples are closed and compacted. Flash EA (1112 Series) CHN-analyzer by Thermo Scientific is used for the determination of carbon and nitrogen (Direction Limits for TC is <5μgC and for TN is <2μgN). Data acquisition, integration and handling are performed by the EAGER 300 software.

From the inorganic carbon the carbonate content of these sediments is calculated. Carbonate mineral proportions were semi quantitative determined by X-ray diffraction (XRD) using a Rigaku D/MAX B X-ray diffractometer fitted with a CuKα_1 radiation tube, goniometer and a graphite monochromator. Instrument settings were standardized usually at 40 kV and 20 mA.

Samples for scanning electron microscope (SEM) study were carbon –coated in Baltec sputter coater.

4. Results

Macroscopic description of the sediment core: The sediment core was extracted from the deepest part of the Elefsis basin in a depth of 35 m [Gravity core S2-Perseus Saronikos (figure1). The length of the sediment core is 342 cm. The macroscopic description shows a differentiation of the sediment depositions in five main units (A, B, C, D, E). In Table I the description of the core is presented. The dominated sediment type is mud. The sand content, the biogenous debris and the color differentiate the sediment depositions. Remarkable is the fine layer D (298–300 cm), which shows a dark color and coarser sand particles, gradated in coarser grains at the basis of the fine layer going progressively to finer grains upwards.

Table 1 - Description of core S-2.

Extraction of the **GRAVITY CORE S-2 PERSEUS SARONIKOS** [09 February 2012] Position: 38° 00.50 E, 23° 27.48,00 N, Depth 35 m			
Opening and descriptions day Thursday 08 March 2012			
Main Units		**Finer description**	
A 000-192 cm	**light olive gray - olive gray mud + biogenous debris**	**00-03 cm 03-92 cm 92-192**	**black mud light olive-gray mud with shell fragments olive-gray mud with shell fragments (192 sharp color boundary)**
B 192-231 cm	**gray clay**		**gray clay**
C 231-298 cm	**alteration of mud and sandy mud layers, color differentiation from pelow yellow, light gray, gray**	**231-234 cm 234-236,5 cm 236,5-241 cm 241-249 cm 249-251 cm 251-257,5 cm 257,5-262 cm 262-282 cm 282-288 cm 288-298 cm**	**pelow yellowish mud gray mud with biogenous fragments gray mud with biogenous fragments pelow yellowish grey clay gray mud light gray mud gray mud olive gray mud (two fine layers, thickness ~1 cm in 276-277 cm and 281-282 cm) olive gray mud brownish gray mud**
D 298-300 cm	**black sandy mud (organic)**		**[sharp color boundary, transgression?]**
E 300-342 cm	**Gray sandy mud (biogenous debris)**		

The lithological characteristic of the core and the color differentiation along the core are figured in the figure 4. Color photos of the core attach also the lithological description. At the right side of the lithology column the subsampling places of the core are signalized. The exact sample of sampling is seeing in table 2. Two macroscopic marks allow a differentiation of three stratigraphic sections (figure 6). Starting from the bottom the third stratigraphic section extends from 300 to 342 cm (description unit E). The fine sand horizon (298-300 cm) forms the boundary to the next stratigraphic section. These fine horizons signalize probably a transgression layer. Color differentiation is used to separate the next stratigraphic section upwards. The intermediate second stratigraphic section extends from 192 to 300 cm (description units B, C, D) and it is characterized by mud sediment type and lighter colors. The sharp color line at 192 cm forms the boundary of this stratigraphic section to the next one, to the more recent one. The younger stratigraphic section is characterized by dark colored mud and extends from the surface to 192 cm in the core.

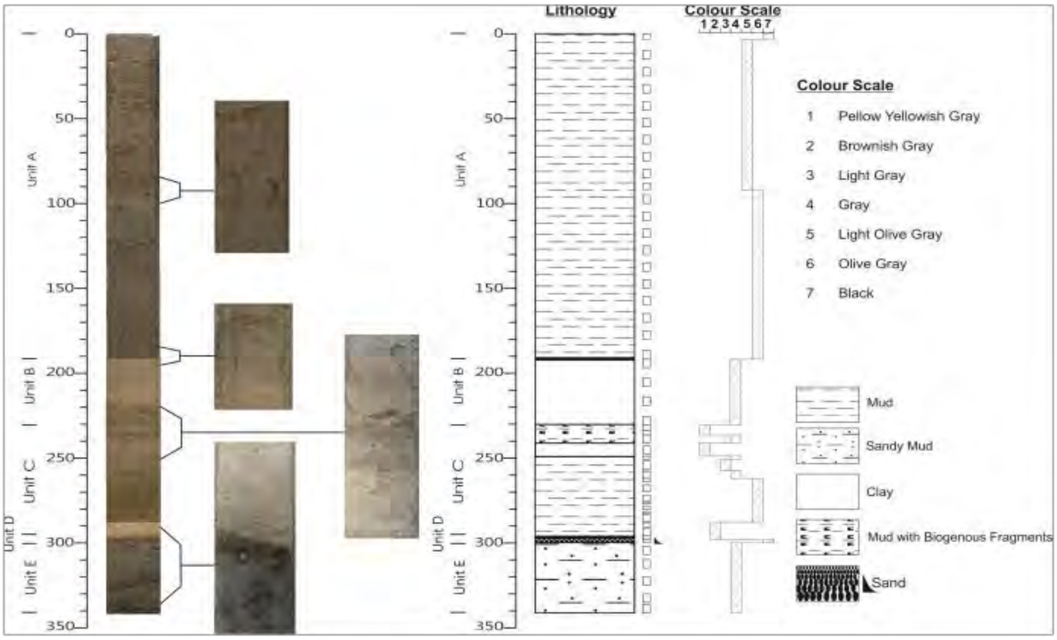


Figure 4 - Macroscopic description of the core S2 Perseus - Saronikos. The left part of the figure is covered by a synthesis of photos showing the whole core as well as by photos showing some important details of the core. The right part of the figure shows the sediment characteristics of the core and its color variation.

<u>Carbonate, organic carbon and nitrogen content distribution:</u> Using CHN-Analyzer in 46 samples the carbonate, organic carbon and nitrogen contents are measured. In the Table 2 the results of the measurements are given. The carbonate content values show a fluctuation from 36,87 - 85,82%, the organic carbon content from 0,257 to 2,676%, with an average value of 1,249%, and the total nitrogen from 0,017 to 0,160%, with an average value of 0,84%. In the Table 2 are also the values of the calculated C/N ratios included.

The vertical distribution of the carbonate content as well as of the organic carbon and nitrogen content are showed in figure 5. Looking at the vertical distribution of the carbonates we can differentiate the deepest stratigraphic section with relative low carbonate values (35,84-51,93%), the intermediate stratigraphic section with higher carbonate values (59,14-85,82%) and the younger stratigraphic section with relative lower carbonate values (36,87-59,35%). We can also recognize the same trends if we look at the organic carbon and the total nitrogen distribution.

Table 2 - Results of the measurements of carbonate, organic C and total nitrogen content.

Sample (Elefsis S2)	Carbonate content %	Organic carbon %	Total N %	C/N ratio	Sample (Elefsis S2)	Carbonate content %	Organic carbon %	Total N %	C/N ratio
0-3	36,87	1,870	0,160	11.672	226-231	64,15	1,695	0,127	13.315
10-15	42,00	1,006	0,089	11.318	231-234	75,24	1,481	0,110	13.413
20-25	47,47	0,795	0,070	11.290	234-236	73,28	1,690	0,130	12.967
30-35	43,12	0,781	0,072	10.787	236-241	76,46	1,475	0,101	14.552
40-45	42,71	0,785	0,071	11.042	243-248	78,29	1,69	0,091	18.486
50-55	41,82	0,729	0,065	11.148	249-251	78,16	1,784	0,112	15.995
60-65	40,37	0,706	0,064	11.083	252-257	81,79	2,190	0,129	17.029
70-75	40,55	0,738	0,066	11.218	258-262	82,30	2,351	0,132	17.754
80-85	39,59	0,716	0,063	11.409	262-264	82,66	2,053	0,110	18.631
88-92	43,13	0,705	0,060	11.702	266-270	82,05	2,242	0,121	18.491
95-100	46,42	0,724	0,059	12.196	272-275	81,28	2,677	0,124	21.509
105-110	50,25	0,733	0,061	12.020	276-277	81,59	2,045	0,109	18.764
115-120	49,45	0,756	0,062	12.156	278-280	83,71	2,033	0,098	20.699
125-130	45,71	0,761	0,062	12.182	283-287	83,92	2,136	0,102	20.899
135-140	47,45	0,860	0,066	13.121	288-290	85,39	1,624	0,087	18.636
145-150	48,23	0,860	0,069	12.385	291-295	83,19	2,211	0,121	18.198
155-160	57,16	0,838	0,067	12.477	296-298	85,82	1,783	0,101	17.709
165-170	59,04	0,792	0,061	12.951	298-300	59,14	1,777	0,091	19.447
175-180	58,54	0,863	0,066	13.074	302-307	37,35	0,601	0,042	14.184
187-192	59,35	0,816	0,063	13.021	310-315	35,84	0,354	0,033	10.582
192-197	62,52	1,072	0,077	13.907	320-325	44,74	0,289	0,025	11.681
203-208	64,14	1,416	0,102	13.843	330-335	46,33	0,263	0,023	11.682
214-219	66,36	1,408	0,110	12.849	337-342	51,93	0,257	0,017	15.543

Remarkable are the relative high values of organic matter, 1,072-2,677%, and total nitrogen 0,087 – 0,132%, in the intermediate stratigraphic section indicating more or less anoxic conditions at least in the water/sediment boundary layer. The higher values of the surface sediments correspond to the hypoxia/anoxia conditions of today in the Elefsis Bay. From the carbon and nitrogen data the C/N ratio was calculated, which is an indicator of the predominant source of organic matter in aquatic systems (s. Table 2) (Mayer, 1994; Lamb et al., 2006). The C/N ratios of phytoplankton degradation are in general close to 6,7, while the C/N ratios of vascular plants, where the N is depleted, exceed to 12. Higher C/N ratios indicate that terrestrial material can be the important source for organic matter. During sediment diagenesis the C/N ratio can be altered by the selective degradation of the organic matter (Mayer et. al 1994). Typically the C/N ratio degreases overtime due to release of CO_2 and CH_4.

In the study area relative high C/N values was calculated, indicating differential decomposition rates for carbon and nitrogen rich compounds, showing more to proteinaceous organic matter decomposition. The average C/N value in the sediments of the study core is 14,327 and the values fluctuate from 10,582 to 21,509. The values in the samples of the 1st stratigraphic section fluctuate from 10,787 to 13,074, which indicate an environment with vascular plants. In the 2nd stratigraphic section the values range from 12,967 to 21,509 indicating the dominance of a terrestrial source of the organic matter. In the 3rd stratigraphic section values from 10,582 to 15,543 indicate the influence of vascular plants in the aquatic environment. The diagram of the figure 5 shows good correlation for the lower C/N values of the 1st and 3rd stratigraphic unit and a scattering of the values of the 2nd stratigraphic unit.

Important information can be retrieve from the fluctuation values of organic carbon and nitrogen as well as C/N ratio in the 2nd stratigraphic unit, indicating alteration of the aquatic condition, probably different fresh water flushing in the semi-closed system.

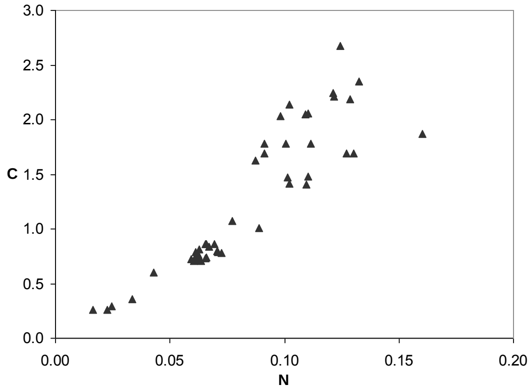


Figure 5 - Correlation of Carbon and Nitrogen contents of the sediment samples of core S-2 Perseus.

Carbonate mineral definition: X-ray diffraction patterns of the sediments, focussed in the carbonate minerals, revealed the presence of calcite, Mg-calcite, aragonite and dolomite. Representative difractogramms are presented in figure 7. Semi quantitative analyses of the difractogrammes, based on the peak intensity of the carbonate minerals, allow us to figure the distribution of the carbonate minerals along the core-profile (Fig 6). The most important fact of the vertical distribution of the carbonate minerals is the domination of the aragonite in the intermediate stratigraphic section.

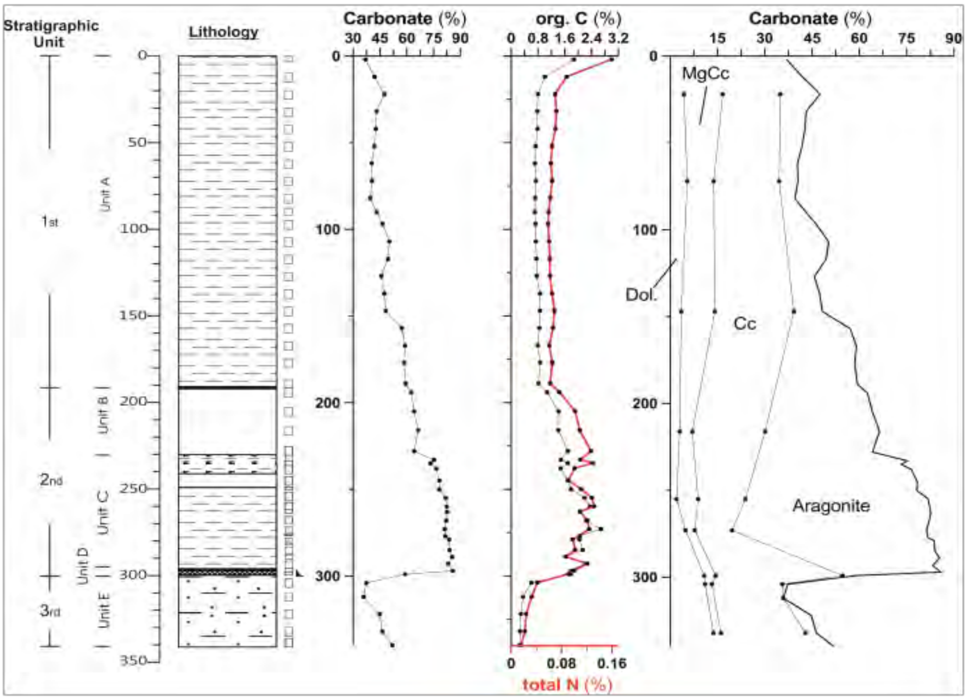
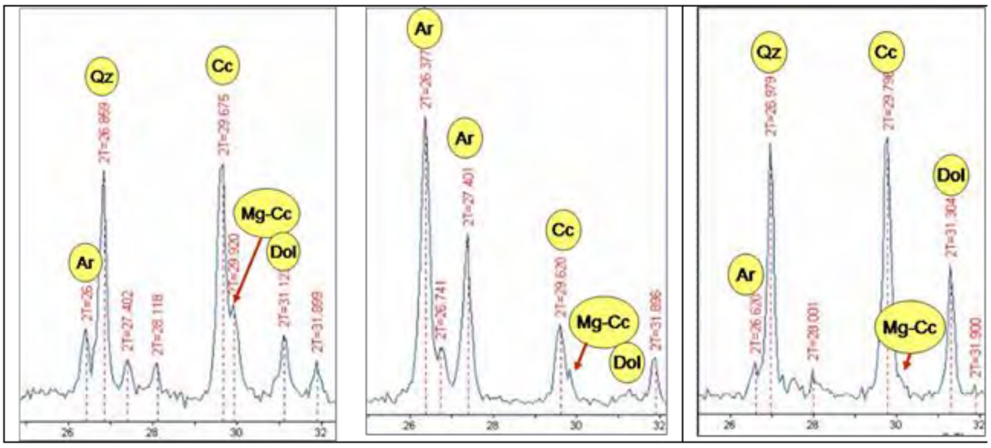


Figure 6 - The vertical distribution of the carbonate, organic carbon, total nitrogen and carbonate minerals [Cc=Calcite, Mg-Cc=Magnesium calcite, Dol=Dolomite] of the S2 Perseus profile.

REM analyses reveal the aragonite crystal needle forms, which certificate the inorganic precipitation of calcium carbonate in elongated aragonitic crystals (length of the crystals 3-8 μm) (figure 8).



70-75 cm	**252-257 cm**	**330-335 cm**

Figure 7 - Representative difractogramms, one from each stratigraphic units, showing the differentiation in the distribution of the carbonate minerals [Qz=Quartz, Ar=Aragonite, Cc=Calcite, Mg-Cc=Magnesium calcite, Dol=Dolomite].

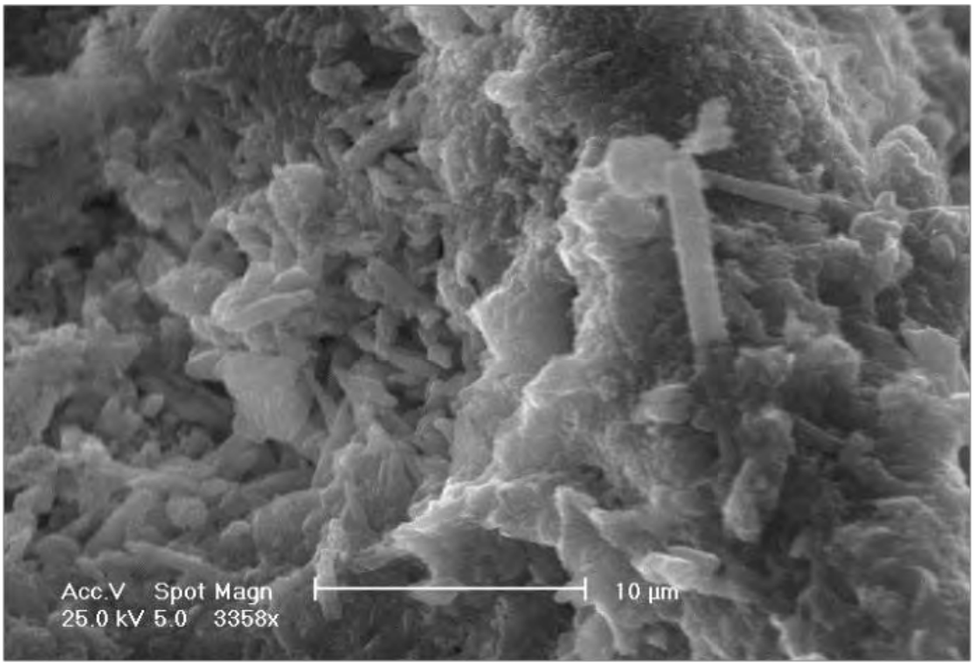


Figure 8 - Aragonite crystal needles certificating inorganic formation of aragonite in the intermediate stratigraphic unit (subsample 252-257 cm).

5. Discussion

Based on the macroscopic description of the core as well as on the laboratory results of carbonate content, carbonate differention, organic carbon and nitrogen contents we have attempted to unravel the paleoenviromental evolution of the semi-closed Elefsis Bay. We assume that the fine layer at

298-300 cm signifies a transgressive event, which separates the freshwater environment of the preexisting fresh water lake (3rd stratigraphic section) from the lagoonal environment which follows. At this time the Elefsis Bay connected maybe episodically with the marine environment of the open Saronikos Gulf. The lagoonal-marine environment is recorded in the sediment by the inorganic precipitation of aragonite crystals and corresponds to the second stratigraphic section. Remarkable in this section (2nd stratigraphic section) are the relative high values of organic carbon in the sediments, signalizing probably hypoxia/anoxia conditions at least at the water/sediment interface. The fluctuations of the values indicate an unstable system with relative episodic changes in the water column properties (physical, chemical, biological parameters). Results from previous work (Pavlidou et al., 2010), highlighted the fluctuation of the values of organic matter in the core sediments of Elefsis Bay and they are interpreted as anoxia events occurred in Elefsis Bay in the past. These results of the hypoxia/anoxia conditions in the past show us additionally that the occurrence of hypoxia in Elefsis Bay "may not necessarily be attributed to anthropogenic activities but could be naturally driven by oceanographic-climate forcing" (Pavlidou et al. 2010). The abrupt color change at 192cm marks the youngest environmental stage of the ¨normal¨ marine conditions in the Elefsis bay (1st stratigraphic section).

The evolutionary scenario presented is in line with the evolution of the coastline configuration in Greece, which includes several semiclosed gulfs and bays separated from the open sea by shallow sills and which during the LGM where isolated from the open and formed paleolake systems. By rising of the sea level after the glacial retreat (Lambeck & Pucel, 2005) these areas went flooded with marine water and they changed to marine systems. It is remarkable that the transition of the paleolake system to a marine system is characterized by relatively fast inorganic carbonate precipitation. Regularly these deposits are followed by clastic sedimentation. Such carbonate deposits in the Eastern Mediterranean have been described by Lykousis & Anagnostou (1993), Richter et al. (1993) for the Saronikos Gulf (Greece), Lykousis et al. (2007) for Gulf of Corinthos (Greece), Sakellariou et al. (2007) for the north Evoikos Gulf (Greece), Karageorgis et al. (2001) Karageorgis et al. (2013) for Pagasitikos Gulf (Greece), Reicher & Halbach (2007) for the Marmara sea.

The evolutionary dynamic of the Elefsis Bay seems also not to be an isolated event but a part of the general dynamic of the nature. This relative insignificant aquatic subsystem shows rapidly changes from a fresh water system to one saline/ hypersaline and then to a normal marine system.

It is related to the sea level rise.

The inorganic carbonate formation acts mostly as a part of the self-regulation mechanism of the earth system. The formation of the carbonate associations create questions like dolomite vs Aragonite, aragonite vs calcite, etc.

Focusing on the sea level rise we know that the mean sea level during the Last Glacial Maximum (LGM) was approx 120 m lower than at present. The following question remains at this time without answer, "When the sea intruded into the Elefsis Bay". Elefsis bay was isolated with sills at 2,5-3,0 m depth. Farther investigation will probably help us to answer these questions.

A significant unit of the sediments of Elefsis Bay is the unit with the authigenic aragonite formation. It is assumed that in the semi enclosed aquatic system due to high evaporation aragonite is precipitated. The weather conditions, colt and dry, favored the evaporation.

Another condition for the precipitation of aragonite is the ratio Mg/ca which must be >1. The variety of the petrography of the area gave probably as weathering products Mg and Ca.

6. Conclusion – Further Investigation

The macroscopic features of the sediments of one core and the laboratory results of sediment analyses, carbonate content, carbonate mineral specification, organic carbon content, were important indicators to unravel the paleo-enviromental evolution of the semi-enclosed aquatic system of the Elefsis Bay.

The paleolake environment, followed by the saline/hypersaline state and its transit to the normal marine environment is approached in the frame of this work. Supplementary analyses, micropaleontology and radiocarbon dating are planned in order to concretize the paleoenvironmental evolution of the sensitive coastal embayment of the Elefsis Bay.

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