



Centre for Arctic Gas Hydrate,
Environment and Climate



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Master of Science in “Environmental Oceanography”

**A REVIEW ON SEDIMENT SAMPLES FROM A
DEEP HYPERSALINE ANOXIC BASIN: TYROS**

Master Thesis

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PROLOGUE AND THANKS

The present dissertation took place in the framework of the postgraduate/master of science course: “Geoscience and Environment” of the Department of Geology, University of Patras and specifically in the field of "Environmental Oceanography".

This work was carried out in the “Department of Marine Geology and Physical Oceanography” (OCEANUS) of the Department of Geology with a research collaboration of the Institute of Oceanography (HCMR) in Greece and the “Centre for Arctic Gas Hydrate (CAGE), Environment and Climate” at UiT, Department of Geosciences, Arctic University of Norway.

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ABSTRACT

The Tyros basin is a presently deep hypersaline anoxic depression in the eastern part of the Mediterranean Sea. Its presence attributes to a combination of submarine dissolution of outcropping or subcropping evaporates (Messinian) which accumulate at the slopes of the basin and at its tectonic subsidence (pull-apart mechanism) that occurs in the western Strabos trench. Therefore, a unique environment is created with its major feature to be a high density stagnant bottom-water column. The core (TYRO5) that was retrieved from that basin had a total length of 285cm and comprises a complex lithostratigraphic sequence due to the strong geodynamic regime of the area. The analysis conducted on sediment samples from the core TYR05 included granulometry, mineralogy, micropaleontology, bulk geochemistry and total CHNS/organic carbon (TOC). All of these took place within the academic year 2018-2019. The grain size distribution along with the planktonic foraminifera presents fluctuations which coincide with changes in the lithology of the core. The mineralogical composition of the sediments confirm the evaporate influence developed on the bottom of the basin, while both geochemistry and total CHNS/TOC verify the present anoxic conditions. The synthesis of all the above analysis suggests that the sediment core consist mostly of sapropel to sapropelic layers and that it has a rather homogeneous character, because of its high re-sedimentation rate. Subsequently, it is indicated that the sapropel units refer to an S1 type, but further analyses are needed in order to be safely determine, such as radiocarbon dating C^{14} and stable isotopes of O, C.

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1. INTRODUCTION OF BRINE LAKES

Over the last 30 years, a new salt-accumulating subaqueous brine-lake style, tied to the dissolution of shallow sub-seafloor salt has been documented on the deep seafloor below a normal and well oxygenated water column (Fig.1), (Oliveri et al 2013). These are the so called deep hypersaline anoxic lakes or brine basin deposits. Presently they can be mostly found on the Gulf of Mexico (Orca basin), the Mediterranean Sea (Tyros, Bannock, Urania, Atalante etc.) and the Red Sea. A typical water column of a brine lake is characterized by an extended separation of the brine mass from the upper normal seawater. This stratification is due to a lack of water circulation, which is controlled by extreme conditions of elevated salinity, anoxia, relatively high hydrostatic pressure and temperatures in the bottom waters (Warren 2018).

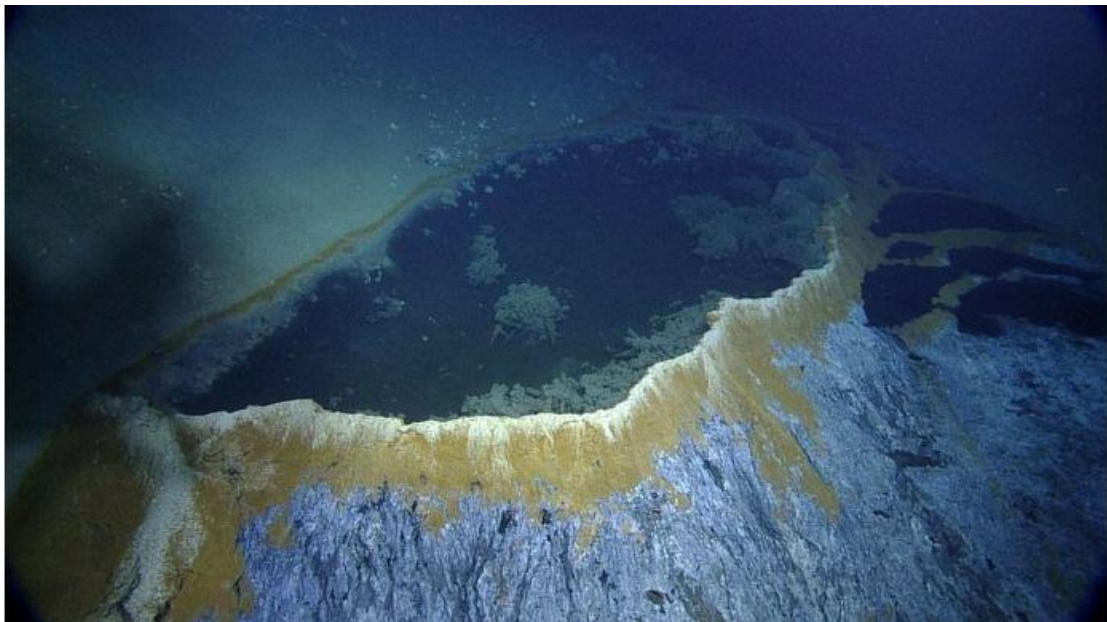


Figure 1: A typical realistic depiction of a brine lake.

Brine lakes tend to form in depressions, where dense anoxic conditions and presently or past tectonically active environments prevail on the seafloor. The ponded bottom brines create a distinctive interface with the overlying seawater, while the sediments are transported by occasional slump events or turbiditic depositions (Warren 2018, Henneke et al 1996). Finally, another feature that all the brine lakes appear to have, which is decisive for its forming progression, is the subsidence or dissolution of evaporitic deposits (Fig. 2), (De Lange et al 1990).

More specifically from a hydrological perspective the brine lake is a depression of hypersaline water, which is more saline than the overlying seawater. Their deep-sea formation (>3km) means that they are high-pressure regions (> 35 MPa), with total darkness, anoxicity and extreme saltinity (>250-350‰). Concentrations of sulfides, manganese and ammonium are typically high, but at levels that vary across different basins. The high density of the brine prevents it from mixing with the overlying oxidic seawater, and so it acts like a sieve, allowing only the passage of particles (Van der Weijden et al 1990). Hence, the water column is always density-stratified with permanently structured depth profiles typified by a halocline interface (suboxic) separating the brine layer below (anoxic) and the normal seawater (oxic) water column above. The thickness of the halocline can vary from basin to basin and it has a range of one meter to a few meters.

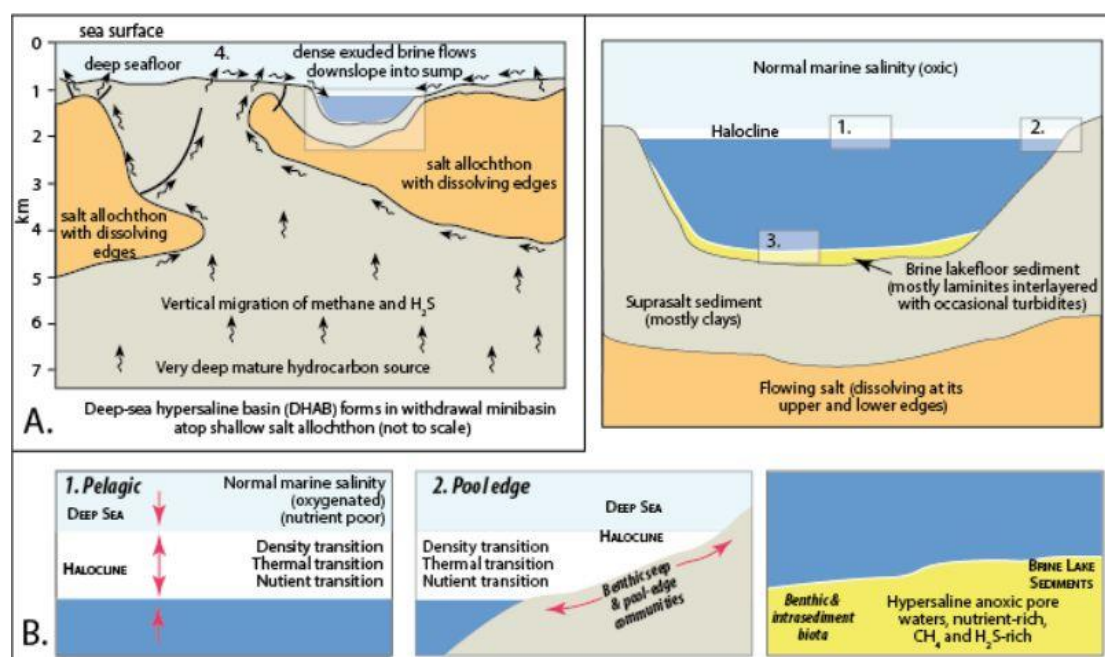


Figure 2: The formation of a brine basin (A) as well as the typical features appearing from the upper interface to the bottom seafloor sediments (B). (Warren 2018)

Therefore, because they do not contain dissolved oxygen (O₂) the only organisms that live there are anaerobes, which run their metabolism without it (Fig. 3) (Shokes et al 1977). Some of them rely on molecules such as nitrate for respiration, and some get their carbon from gases like carbon dioxide (CO₂) and methane (CH₄) instead of eating other organisms or particles of organic matter.

The area where the halocline touches the sides of the basin floor is called “bathtub ring” because it is like the ring of soap scum and dirt that forms on a bathtub when the water is drained out. The sediment in this narrow "scum" zone has a little bit of oxygen and less salt than sediments inside the anoxic basin (Warren 2018).

Temperature wise the profile of a brine lakes water column is distinct and it is always characterized by an increase as you move downwards (Fig. 3) (Shokes et al 1977). Across some haloclines the temperature contrast is only a degree or two, in others (e.g. Red Sea brine lakes), the temperature contrast is tens of degrees.

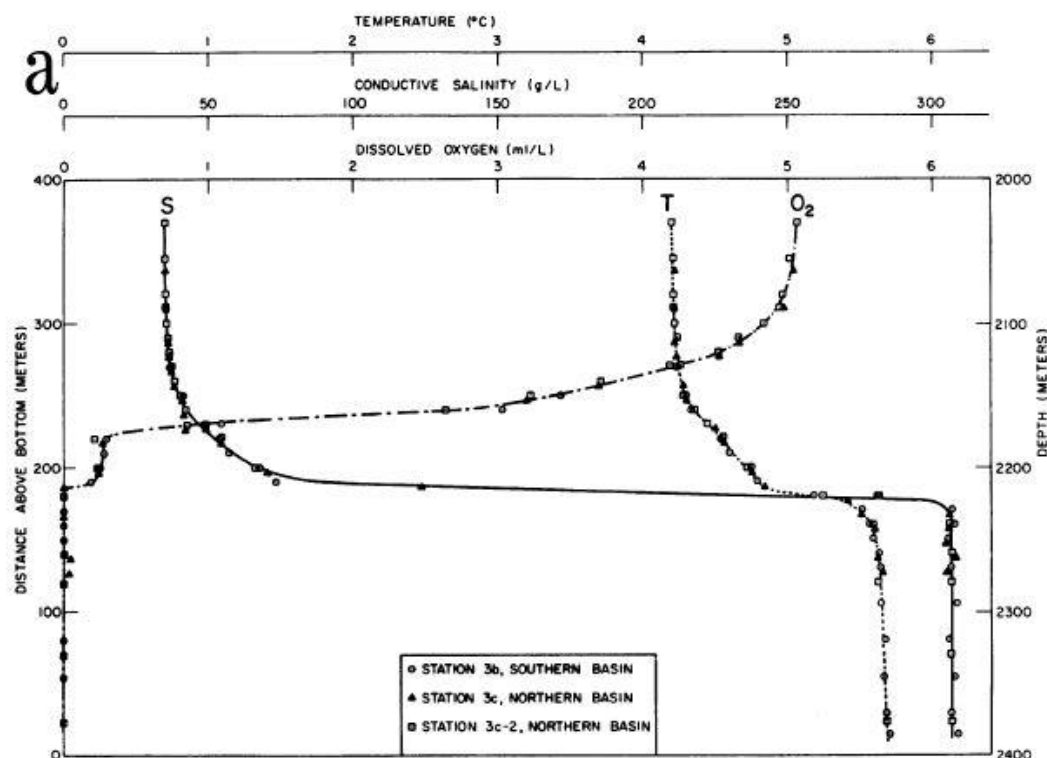


Figure 3: The abrupt change of the temperature, salinity and dissolved oxygen as you move downwards to the brine lake of the Orca basin in Mexico in the last 200m above the seafloor, which indicates the interface between the hypersaline water and the normal seawater. (Shokes et al 1977)

Brine lakes typically need a long-term salt source. That’s why they are found in halokinetic seafloor provinces where salt has flowed into a sufficiently shallow sub-seafloor position to be dissolved (salt karst). Often there is a faulted margin acting as a preferential brine conduit and seep zone supplying the nearby salt-withdrawal depression (Fig. 2). Hence, the interaction between two processes (tectonic deformation of sediments and dissolution of evaporates) is the key to understanding the geological evolution of deep-sea anoxic brine pools (Camerlenghi 1990). More information will be reported in the following chapters.

1.1 Life in the deep anoxic hypersaline basins

With no light, no oxygen, very high salt concentrations, and very high pressure, brine lakes seem like they should be “dead zones.” On the contrary scientists have found that hundreds of different species of bacteria, archaea, and protists live there.

The halocline has the greatest number of individuals and species, but the super-salty, totally anoxic basin also has thriving populations of microbes. So far, scientists have mainly looked for microbes living in the water. The sediments, especially the “bathtub ring”, probably harbor even more different species.

Many protists are able to survive the harsh conditions an anoxic environment by associating with bacteria that either cling to the outside of the protist or actually live inside the protist. The protists, in turn, may help the bacteria by shielding them from predators or by moving them to prime locations. This kind of symbiosis, in which both partners benefit, is called "mutualism" i.e. a close association between different organisms where both partners benefit (Fig. 4).

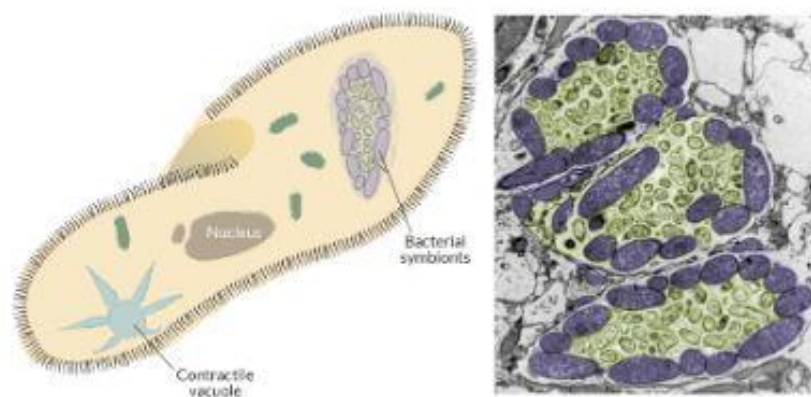


Figure 4: At left, a diagram of a ciliate that hosts different kinds of bacteria in its cell (left). Colorized electron micrograph showing compartments inside a ciliate where different kinds of bacteria live (right). (Dive & Discovery, DHABs (n.d.), retrieved May 3, 2019 from <https://divediscover.whoi.edu>)

Finally, many brine lakes contain toxic chemicals such as sulfides or methane, which are produced by geothermal activity or by microbes living in the basins. For example, bacteria that obtain their energy for living by using sulfates instead of oxygen (as an electron acceptor) create sulfide as a by-product. Sulfide is toxic for many forms of life, including most bacteria, though some bacteria and archaea have evolved to be

able to use these substances in their metabolism (Dive & Discovery, DHABs (n.d.), retrieved May 3, 2019 from <https://divediscover.who.edu>).

1.2 Other Aspects

Some brine lakes contain salt domes, which may contribute to the formation of the basins. In some other cases methane and other gases collect in reservoirs beneath the seafloor and can percolate upward, pushing up domes of sediment at the seafloor that are called mud volcanoes (Fig. 5). This can be observed in a few cases around Mediterranean, as show in the Fig. below (Charlou et al 2003).

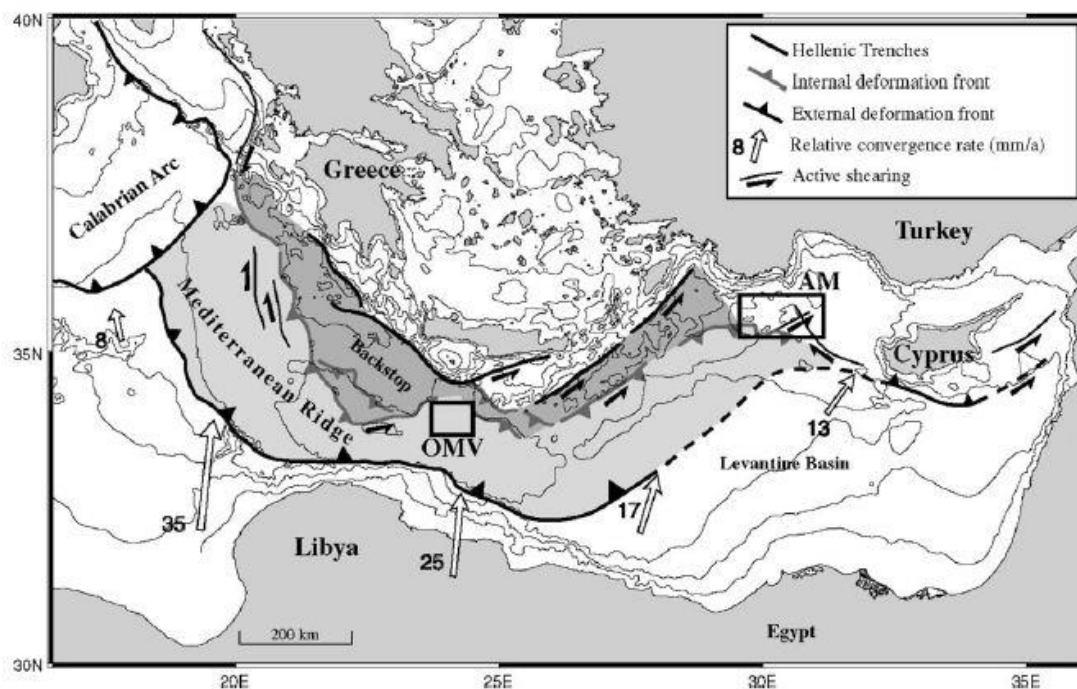


Figure 5: The Olimpi Mud Volcano field (OMV) and Anaximander Mountains (AM) (in boxes) in their general eastern Mediterranean context. (Charlou et al 2003)

1.3 Mediterranean Ridge Accretionary Wedge

Brine lakes in the Mediterranean Sea are mostly located at its eastern part with depths of 3000-4000 m. In the last few decades a number of brine basin areas have been discovered, such as L'Atalante, Urania, Discovery, Bannock, Tyro, Thetis, Medee etc. and Kryos basins (Fig. 6).

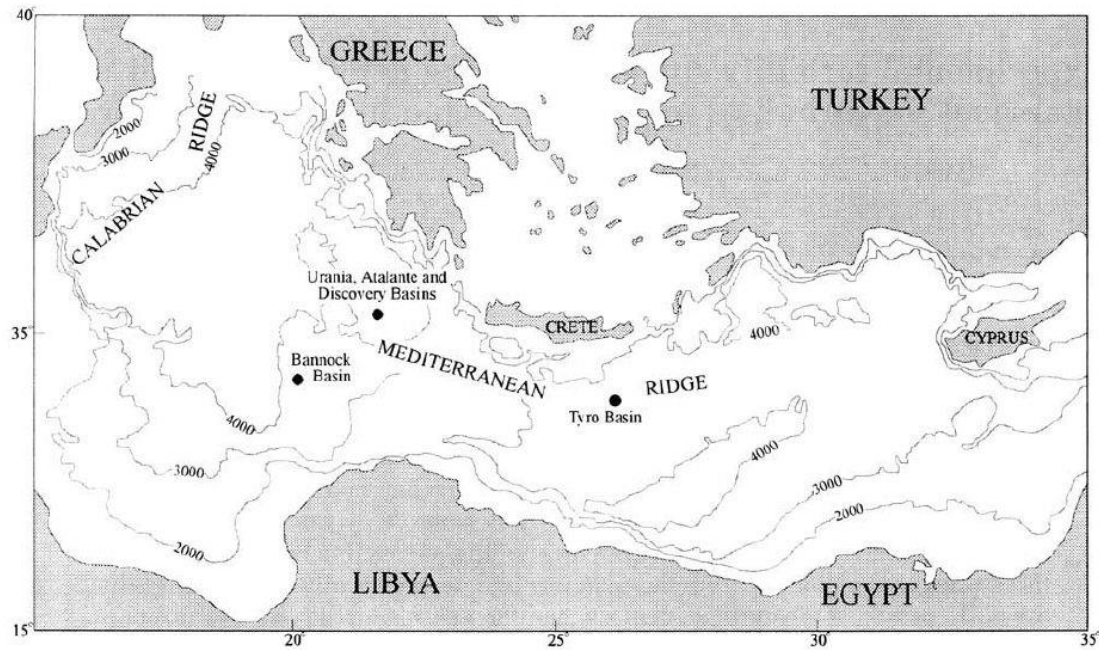


Figure 6: Some brine basins of the eastern Mediterranean including Tyros basin, which is the subject of the master thesis. (Rimoldi et al 1996)

These hypersaline anoxic seafloor depressions where formed during an exceptional event in the Messinian age of the Miocene Epoch (~ 5.8 - 5.2 Ma B.P.), when the Mediterranean Sea interrupted its marine communication with the Atlantic Ocean (Camerlenghi 1990). Then the completely or partially desiccated Mediterranean Sea flooded again with the opening of the Strait of Gibraltar and the Messinian evaporitic and clastic deposits were slowly covered by Plio-Quaternary pelagic/hemipelagic muds and terrigenous sediments (Abranites et al 2010, Nesteroff 1973). This hypothesis was not acknowledged until the discovery of giant evaporitic deposits in the deepest basins of the Mediterranean due dissolution which ultimately vented onto the seafloor and created those brine haloes (Abranites et al 2010).

Almost all brine lakes, which occur either in a classic marine deep anoxic seafloor site or a continental site, require karstification of a subsurface halokinetic salt mass (i.e evaporates) and a topographic depression. So these depressions can be formed via salt withdrawal, via regional tectonism or from a combination of both, creating a more complex setting (Warren 2018).

2. PURPOSE

The Tyros basin, as well as all the anoxic basins in the Mediterranean, comprises an exceptional environment that has attracted for decades the interest of the international scientific community. Though, as a consequence of the location, the depth and the uniqueness itself, not many studies have been conducted in the Tyros brine lake. Hence, this is one of the few studies, which intends to answer the questions that have emerged over the years, while leaving room for future, even more extensive study.

Particularly, this present dissertation aims to study and highlight any processes that took or still take place in the Tyros basin and could have affected the sedimentation regime and its features. Any results will be due to a series of laboratory analyzes on the sediment core collected in the area of interest, such as optical observations, grain size distribution, foraminifera associations and mineralogical/elemental/geochemical compositions.

3. STUDY AREA

The hypersaline anoxic basin that we will study is the Tyros brine lake that was discovered first in 1983, in East Mediterranean, Southeast of Crete, in the western part of Strabos Trench and took its name after the Dutch R/V Tyro (Fig. 7) (Jongsma et al. 1983, Cita 1991). Is one of the smallest (diameter ca. 4 km) brine lake explored in the Mediterranean, with a funnel-shaped depression and a rounded rim. The steep slopes of the basin are approximately 19° , with a vertical relief of 600m and the volume and area to be 2.23km^3 and 20km^2 , respectively (Camerlenghi and Cita, 1986). Close to Tyros two other brines exist, called Kretheus and Poseidon basins, and it is suggested that these two are not anoxic at the present time (Fig. 8) (Cita 1991).

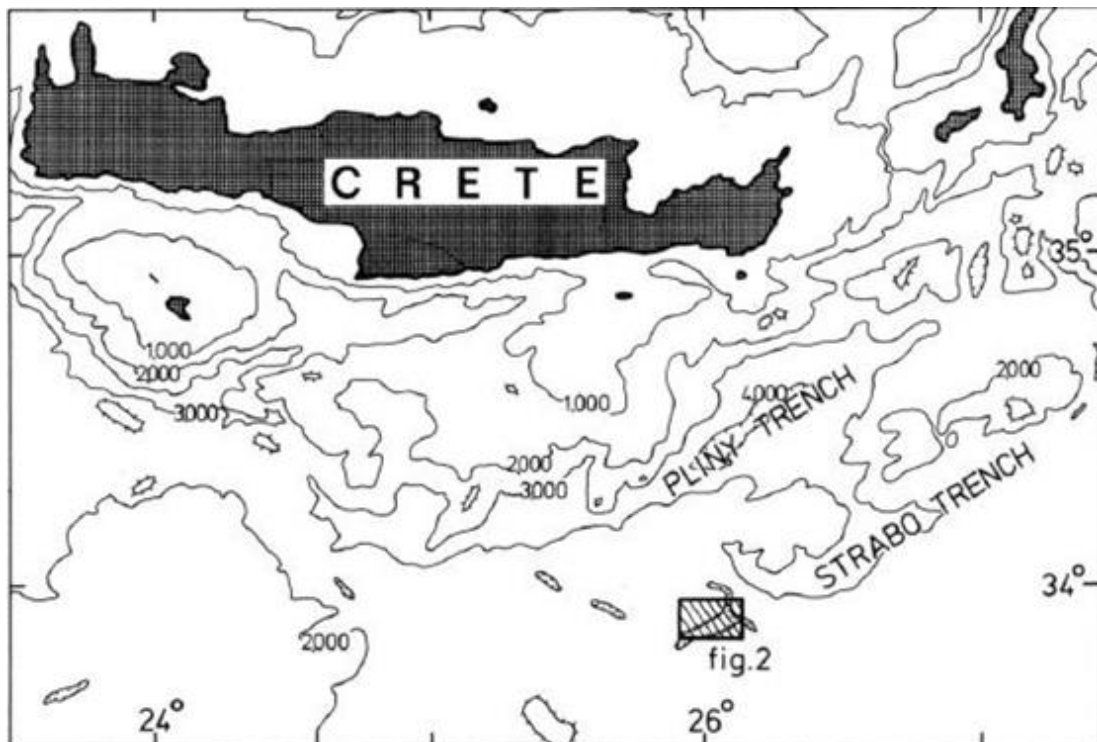


Figure 7 : Bathymetry of the area. Shaded square = Tyros basin. (Jongsma et al. 1983)

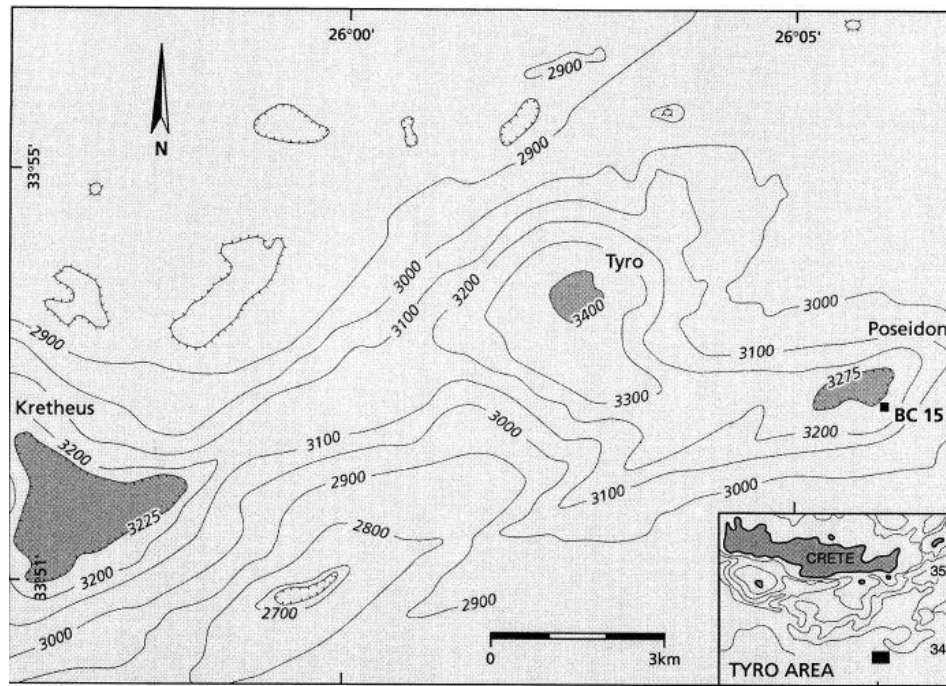


Figure 8 : The Tyros basin area with its "satellite" basin Kretheus and Poseidon. (Rutten et al 1999)

The basin of Tyros is strongly affected by the intense tectonic setting of the Strabos Trench, which is characterized as a left strike-slip motion, in a pull-apart basin (Fig. 9). The Strabos Trench mirrors the boundary between the seismically active Hellenic Trenches and the much less seismically active Eastern Mediterranean Ridge (Jongsma et al 1983). This basin is lying above a sequence of Plio-Quaternary hemipelagic sediments and Messinian evaporites, where the latter causes the formation of the brine lake through their subsurface dissolution (Fig. 10 and 11) (e.g. salt diapirism) (Camerlenghi 1990, De Lange 1990, Camerlenghi and Cita, 1986). Therefore, the Tyros brine lake can be described by a complex system, that both tectonics and salt deposits lead to the formation of the basin.

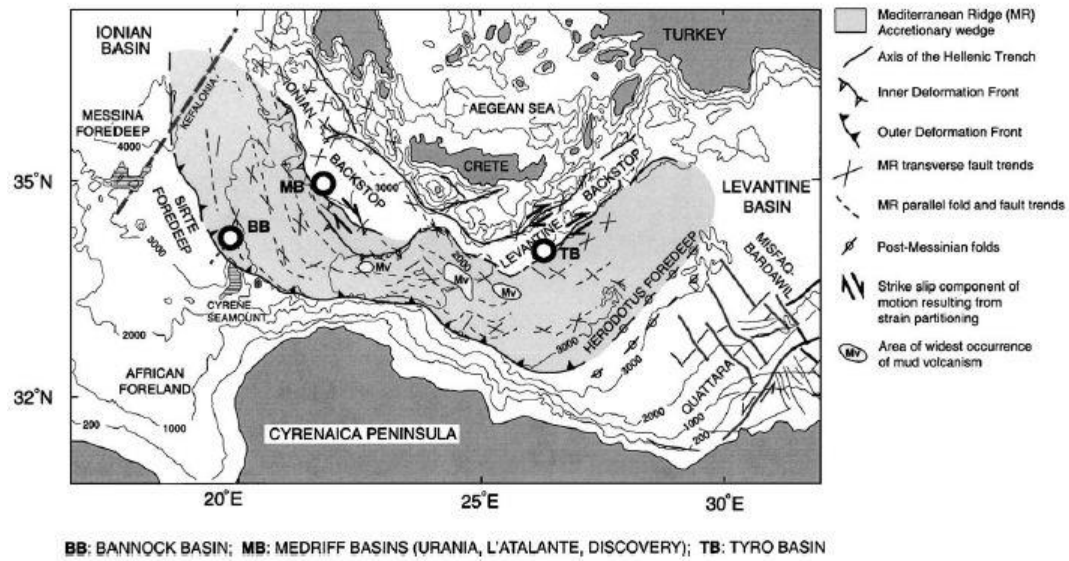


Figure 9 : Structural depiction of the Eastern Mediterranean tectonic system, as well the location of the main hypersaline basins. (by Angelo Camerlenghi). (Cita 2006)

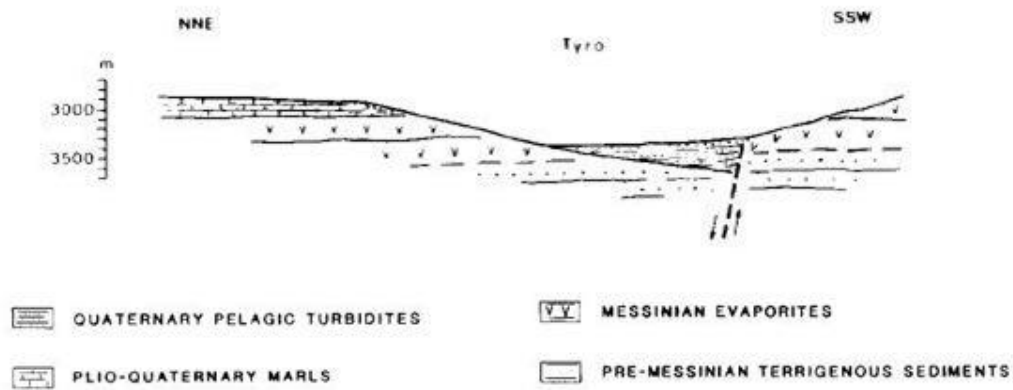


Figure 10 : A geological profile of the Tyros basin. The Messinian evaporites in the slopes of the basin can be confirmed in Fig. 8 as well. The horizontal profile has been stretched, so that the stratigraphy can be illustrated better. (Camerlenghi and Cita 1986)

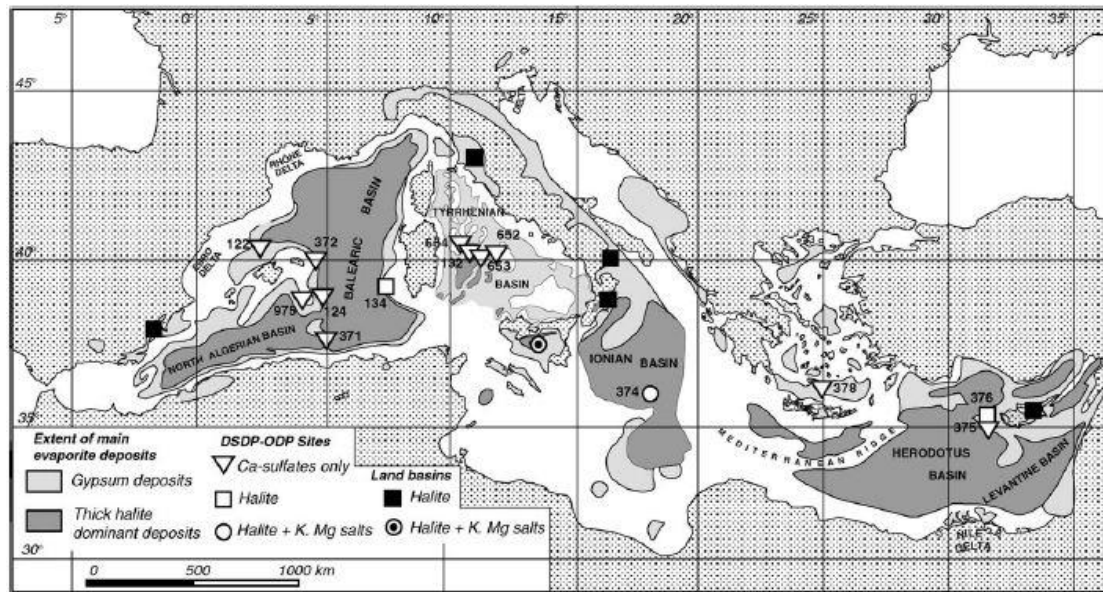


Figure 11 : The above map shows the distribution of the Messinian evaporites beneath the seafloor of the Mediterranean Sea. (Rouchy and Caruso 2006)

The depth of the basin is 3450 m and in the last 100m there is a ~1m thick interface (halocline), which divides the normal water with the hypersaline (ten Haven *et al.* 1987). Regarding the salinity and the temperature, moving below the interface there is a significant increase ($\times 10$ normal seawater and 1.5°C), whereas the dissolved oxygen drops to zero, showing a stable physical configuration with no water circulation (Fig. 12) (De Lange *et al.*, 1990, Cita 1991). The density of the brine lake reaches up to 1.199g/cm^3 and has a chloride concentration of 5.7mol/l as a result of the dissolution of tectonically exposed Messinian evaporitic salt deposits (ten Haven *et al.* 1985).

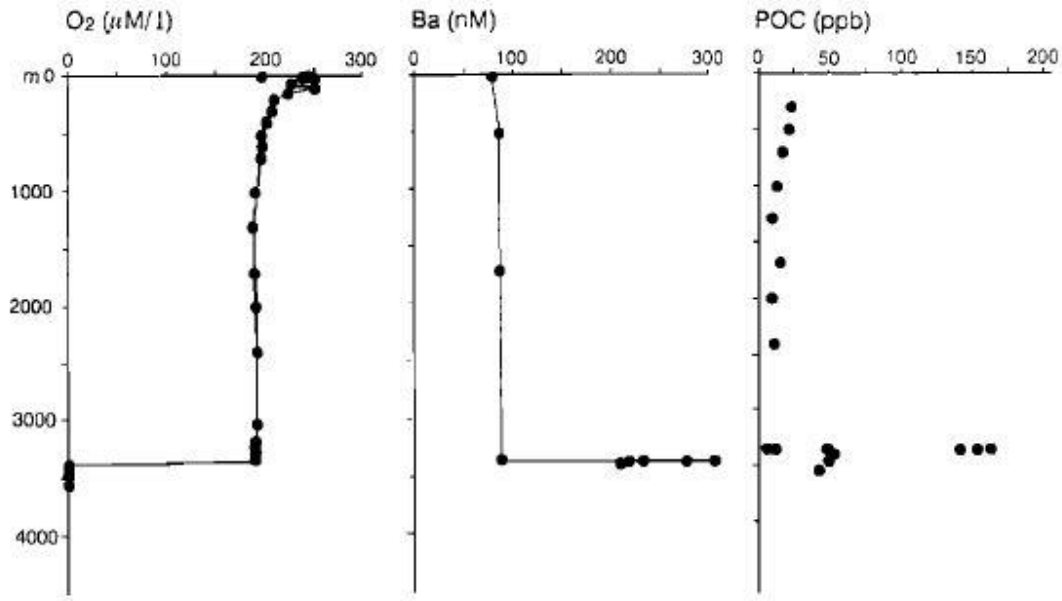


Figure 12 : The diagrams of oxygen, including Ba and POC (particulate organic carbon), show the abrupt change in the water column transitioning from the normal seawater to hypersaline water of the Tyros basin. (Cita 1991)

The dissolution of the Messinian evaporates that outcrops the seafloor of the basin, as its referred before, is actually the main reason that the Tyros basin, as well as other hypersaline basins, has been formed (Geraga et al. 2016). Though, due to the fact that different conditions occur in each basin, there are also a few variances between them, such as the example of the Bannock basin in relation to the Tyros basin (Fig. 13). The first one is enriched in K, Mg, SO_4 through a late-stage evaporitic salt deposit and presents a double-brine structure, while the latter is characterized by a relatively high Na content, low Br/C1 ratio, originated from an earlier-stage (halite) evaporate and presents a homogeneous brine composition (De Lange et al. 1990).

Brine	Na	Cl	Mg	K	Ca	Sr	SO ₄	Li	H ₃ BO ₃	Br	F ^a ($\mu\text{mol l}^{-1}$)	Ba ^b ($\mu\text{mol l}^{-1}$)
Tyro	5300	5350	71.1	19.2	35.4	0.329	52.7	0.075	1.00	1.28	45.3	579
Bannock I	4160	5333	613.3	124.8	21.8	0.214	103.8	0.26	4.27	8.45	107	290
Bannock II	4200	5378	643.9	126.5	16.3	0.168	135.2	0.28	4.49	9.02	143	157
Ostro	4150	5300	594	118	22.5	0.211	100	0.26	4.10	8.80	101	–
Scirocco	4100	5250	570	119	26.3	0.270	72	0.26	4.02	8.8	90	–
Orca ^a	4720	5000	51.2	19.1	32.3	–	47.1	–	–	1.2	–	–
Red Sea ^b	4850	5260	40.0	66.5	141	0.65	10	0.046	0.87	1.9	3.2	7800
Avg. seawater ^c	480	560	54.5	10.4	10.5	0.092	28.9	0.026	0.43	0.86	70	(100)
Evaporite brine ^d	4480	5080	519	101	5.5	–	180	0.26	4.3	7.9	–	–

Brine	$\delta^{34}\text{S}^e$	Density (kg m ⁻³ , at 20°C)	T (°C)	Mn ($\mu\text{mol l}^{-1}$)	Fe ($\mu\text{mol l}^{-1}$)	Si ($\mu\text{mol l}^{-1}$)	HPO ₄ ³⁻ ($\mu\text{mol l}^{-1}$)	NH ₄ ⁺ ($\mu\text{mol l}^{-1}$)	HS ⁻	T.alk. ^f	pH (NBS)
Tyro	26.0	1.209	14.17	4.8	<1	266	19.1	1.3	2.1	4.45	6.75
Bannock I	20.6	1.210	14.25	(5)	<1	195	(16)	3.35	2.0	4.20	6.55
Bannock II	20.9	1.213	15.12	3.9	<1	264	17.2	3.30	2.9	4.10	6.50
Ostro	–	1.207	14.2	4.8	–	–	–	3.30	1.8	4.00	6.55
Scirocco	–	1.204	14.2	–	–	–	–	3.25	0.6	3.3	6.6
Orca ^a	–	1.185	5.66	265	30	278	82	0.50	<0.002	(5)	(7)
Red Sea ^b	20.3	1.196	>45	1770	1760	1100	–	–	<0.002	(3.3)	(5.5)
Av. seawater ^c	20.5	1.027	–	0.001	0.001	(1)	(0.1)	0	0	2.2	8.1
Evaporite brine ^d	–	1.21	–	–	–	–	–	–	–	–	–

^aWiesenburg et al. (1985), LaRock et al. (1979), Addy and Behrens (1980), Sackett et al. (1979).

^bBrewer and Spencer (1969), Hartmann (1969), Trüper (1969).

^cTen-fold evaporated seawater brine, after McCaffrey et al. (1987).

^dAverage seawater composition, after Bruland (1983).

^e $\delta^{34}\text{S}$ relative to Canyon Diablo.

^fTotal titration alkalinity in mequiv l⁻¹.

Figure 13: A typical chemical composition of the eastern Mediterranean basins, the Mexico basin (Orca), the Red Sea basin, along with average seawater and an evaporated-seawater brine. This can help with the comparison between them and the better understanding of their differences. (De Lange et al 1990)

More specific, seismic profiles of previous studies that took place in the area of the Tyros basin, revealed some very important observations. The presence of a horizontal mid-water sound reflector has been spotted at approximately 100m above the seafloor of the basin, which is evidence of the halocline between the normal seawater and the hypersaline, and thus evidence of the stratification of the water column (Fig. 14) (Jongsma et al 1983). In addition to this, another reflector has been identified in the Tyros basin (M' reflector), associated with Messinian evaporates, suggesting that they are most likely outcropping from the edges of the basin (Troelstra et al 1987, Osmario Leite and Jean Mascler 1982, Ryan et al 1966).

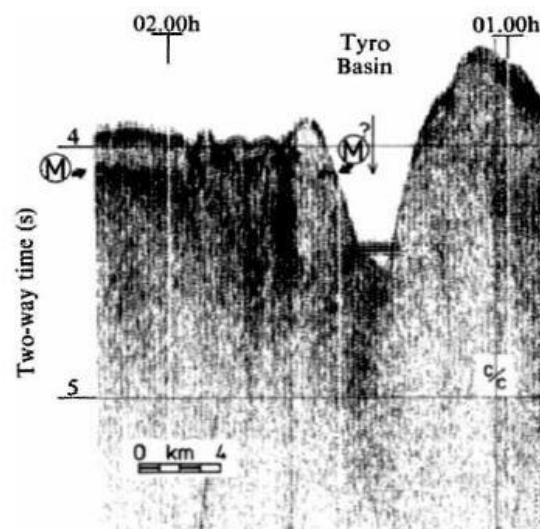


Figure 14: A seismic reflection profile of the Tyros basin, which shows a midwater horizontal sound reflector at a depth of 4.37s two-way time (ca. 100 m above the seafloor). The 'M' symbol is a reflector due to the Messinian evaporates and is mainly exposed to the slopes of the basin. (Johgsma et al 983)

Regarding all the previous characteristics, there is a conclusion that stable anoxic conditions (stagnant water) prevail in the Tyros basin, which favours the accumulation as well as the preservation of organic-rich sediments, i.e. sapropels. Sapropels occur mostly throughout the eastern Mediterranean during some periods in the past, at depths over 2000m and their organic carbon content exceeds 2% (Fig. 15) (De Lange et al 1990, De Lange et al 1983, Ganssen & Troelstra 1987). They are often well laminated, relatively dark brownish to black color, where the amount of pyrite, S and Ba is notably above average whereas the contribution of the benthic foraminifera is nearly or completely absent. All the above can be indicators of low bottom water oxygen conditions (Rohling 1994). However, partially because of erosional processes or bioturbation, many cores do not contain the complete sapropel record (Ganssen & Troelstra, 1987). Also, an interesting observation that needs to be verified is the thick deposits that were found in previous studies in the same area, and were interpreted as turbidites (sediment gravity flow deposits) (Rimoldi et al 1996).

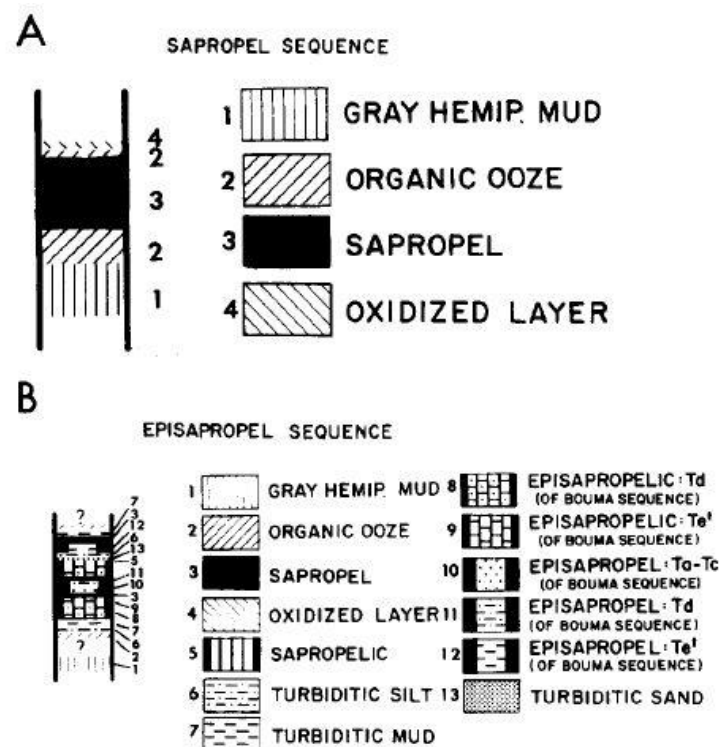


Figure 15: An Easter Mediterranean sapropel sequence from the base up, as it proposed by Stanley 2006. Episapropel is a term (suggested by Anastasakis and Stanley 1984) for an expanded sapropel, in which intergraded layers are due to gravity flow and/or current transport, and mainly occurs in high sedimentation areas.

4. MATERIALS AND METHODS

4.1 Sampling site

Hence, in this master thesis we will look into the Tyros basin, from a sedimentary point of view. The main piece of the research is a ~3m core (“TYR05”) and it was collected by R/V Aegaeo, in the framework of HCMR Research Projects. The sampling site is defined by the following coordinates: 33° 52.245' N, 26° 9.423' E and a water depth of 2.953 m. The core was initially described in detail based on the variation of color and sedimentary structures (Geraga et al 2016). Generally, sediment cores from the Tyro basin are rarely reported, so this is one of the few “deep dives” into the history of that area.

4.2 Laboratory methods of analysis

Following the thorough photography archive of the TYRO5 core by HCMR, a dense sampling (per 3 cm) was performed and all the samples were sent to the Department of Geology in Patras, Greece. A series of in-depth laboratory analyzes were conducted to study the sedimentation environment of the brine lake. The core was collected at a depth of about 3000 m and has a total length of 2.85 m.

The core was initially opened and split into two diametrically opposed segments. The first half is used for the current analyzes and the second is being stored for possible future use.

4.2.1 Macroscopic description

The examined core half was measured smoothed with a special spatula to clarify all the optical characteristics that can be recorded such as particle size variation, possible structures and inclusions, inter-lattice contacts, texture and color (using the Munsell Soil color chart of the Minolta type, Fig. 16). Based on these characteristics a few different lithological units were determined and a first sketch of the core was draw.



Figure 16: The Munsell Soil color chart

4.2.2 Methodology of granulometry

Granulometry analysis is perhaps considered the most basic laboratory analysis in core sediment as it gives a true picture of the energy of sedimentation processes, the sedimentation environment and the behavior of the transport medium and deposition. All the results were carried out with the help of the Gradistat software.

The results can help with the determination of the different lithological units within the core. The Wentworth-Krumbein-Udden scale (Fig. 17) was used to identify the lithological character of the samples in combination with the classification triangles according to Folk, (1974). The philosophy of this particular sorting method is based on the determination of the percentage frequency of each class size in each sample.

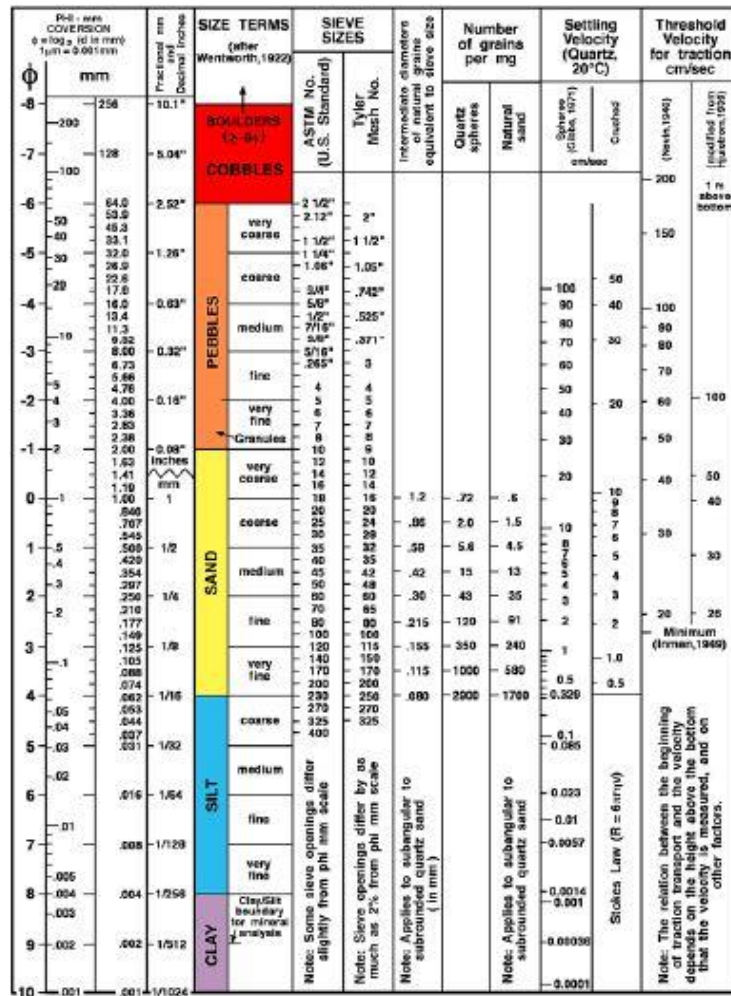


Figure 27: The Wentworth-Krumbein-Udden scale.

A dense granulometric analysis was performed in 92 samples, so that we can cover the whole spectrum of the sedimentary history on the research basin. The analysis was carried out using the Malvern Mastersizer 2000 Hydro apparatus, based on laser diffraction (Fig. 18). This method is best suited:

- for the detailed comparison of samples of the same origin
- for the granulometric size study
- for the changes in agglomeration

The Malvern Mastersizer 2000 Hydron particle size analyzer is mainly used for the distribution of the particle size of the sediment with a size range of 0.02 - 2000 μm . Its function is based on the principle of laser diffraction and on the theory of Mia to determine the percentage (%) of the grain volume in each of the granulometric classes.



Figure 18: The Malvern Mastersizer 2000 Hydron particle size device that was used for the purpose of this study.

Mie theory is a solution to Maxwell's equations (which are a series of four fundamental equations that control the behavior of electric and magnetic fields). The Mie theory is based on the assumptions that

1. The particle is supposed to be spherical. This is important because few particles are really spherical. Light scattering is sensitive to particle volume. For this reason, particle diameters are calculated by measuring the volume of the particle, assumed to be equivalent to a sphere of corresponding volume.
2. The suspension is diluted. The particle concentration is considered to be so low that radiation scattering is measured directly by the detector and that there is no scatter from other particles before it reaches the detector.

The technique of laser diffraction is based on the fact that particles passing through a laser beam will scatter the light at an angle that is directly related to its magnitude. The size range during measurement is directly related to the scattering angle spectrum. As the particle size decreases, the scattering angle increases logarithmically. The intensity of scattering depends on the particle size and decreases, in a good approach, with respect to the cross-sectional particles. Large particles, therefore, scatter light at small angles with high intensity, while small particles scatter at broader angles but with low intensity.

Each sample was placed in a small beaker with deionized water and left for about one minute in an ultrasound device with water to dissolve any aggregates. Then each sample was placed in a beaker of the Mastersizer 2000 Hydroscopic analyzer with 700-800ml deionized water. When the device starts, the water clarity is measured. If the measurement is within the allowable limits then the sample is inserted and it works for 30 seconds using ultrasound because without it the average size is overestimated. The final result is the percentage of shading / turbidity, which is automatically recorded in a program connected to Mastersizer.

As it is suggested by Folk & Ward (1957), the data obtained from the granulometric analyzer was the particle size fraction in μm and the respective percentage by volume (%w/v) of the fractions (sand, clay, clay). The lithological characterization of the samples was then made using the triangular classification chart (Fig. 19) (Folk 1974).

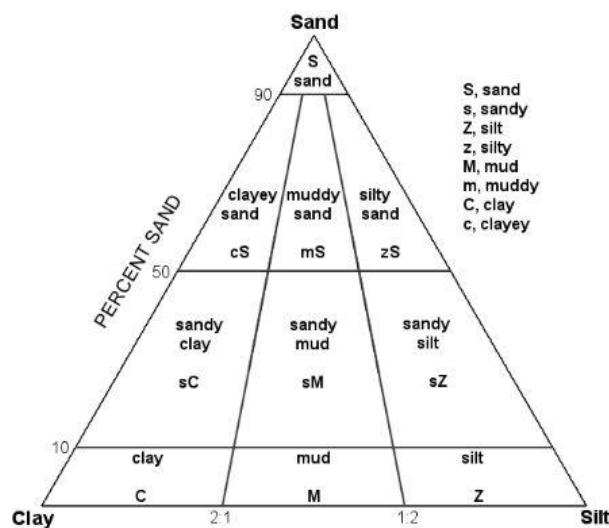


Figure 19: The triangular diagram classification system for fine grain sediments, that was used in each sample after the Mastersizer results. (Folk 1974)

Finally, the statistical parameters (average size - M_z , constant deviation - σ_i , skew - S_{ki} , curve - KG) of each sample were calculated according to the mathematical method (method of the moments) and subsequently the sediments were defined with classification nomenclatures (Table 1), (Folk & Ward 1957).

- ✓ Mean Size: Inman proposed the formula $(\Phi_{16} + \Phi_{84} / 2)$ for the arithmetic mean, but it is not effective in asymmetric curves. The graphical mean (MZ) by Folk & Ward ($MZ = (\Phi_{16} + \phi_{50} + \phi_{84} / 3)$) gives a more faithful overall picture of the distribution with respect to the median and is based on three points.

- ✓ Standard deviation (sorting): Expression of the uniformity or sorting of sediments.
- ✓ Asymmetry, skewness: When the values of a variable are not equal to the point of the maximum frequency (prevailing value or type=Mode) and on one side of the maximum frequency point (Mode) there is always a larger number of frequencies in relation with the other side, then the curve is asymmetric.
- ✓ Kurtosis: It measures the ratio between the dispersion of values at the extremes and at the central part of the distribution, ie it reflects the concentration of the variable values around the middle and the edges ("tails") of the distribution.

Statistical Parameters	Values	Classification
Standard Deviation (σ)	<0,35	Very well graded
	0,35-0,50	Well graded
	0,50-0,71	Medium well graded
	0,71-1,00	Medium graded
	1,00-2,00	Poor graded
	2,00-4,00	Very poor graded
	>4,00	Extremely poor graded
Skewness (S_{ki})	{1,00}-{0,30}	Very positive skew
	{0,30}-{0,10}	Positive skew
	{0,10}-{0,10}	Normal skew
	{-0,10}-{0,30}	Negative skew
	{-0,30}-{1,00}	Very negative skew
Kurtosis (K_G)	<0,67	Very platykurtic
	0,67-0,90	Platykurtic
	0,90-1,11	Mesokurtic
	1,11-1,50	Leptokurtic
	1,50-3,00	Very leptokurtic
	>3,00	Extremely leptokurtic

Table 1: The classification of sediments according to the values of their statistical parameters. as purposed by Folk & Ward (1957).

The study of the statistical parameters aims at the following:

- a) To compare samples from similar sedimentation environments or similar stratigraphic units.
- b) To interpret the means of transport and deposition (wind, river, turbidites, etc.).
- c) To clarify the procedures for the final deposition (suspended, dragged, bouncing, etc.).

- d) To understand the deposition environment because each setting appears to be characterized by specific ranges of values in the statistical parameters of its sediments.

4.2.3 Methodology of XRD

Forty samples were taken from each lithological unit identified in the core archive (TYRO5) to be mineralogical analyzed by means of X-ray powder diffraction (XRPD) analysis.

The identification of the minerals and the semi-quantitative participation in each sample was performed in a Bruker D8 Advance X-Ray diffractometer, with Ni filtered $\text{CuK}\alpha$ radiation, operating at 40kV/40mA, in the Laboratory of Mineral and Rock Research of the Department of Geology at the University of Patras (Fig. 20). The interpretation of the acquired diffractograms and mineral identification was performed using DIFFRACplus EVA software (Bruker-AXS, Madison, WI, USA) based on the International Centre for Diffraction Data Powder Diffraction File (2006).

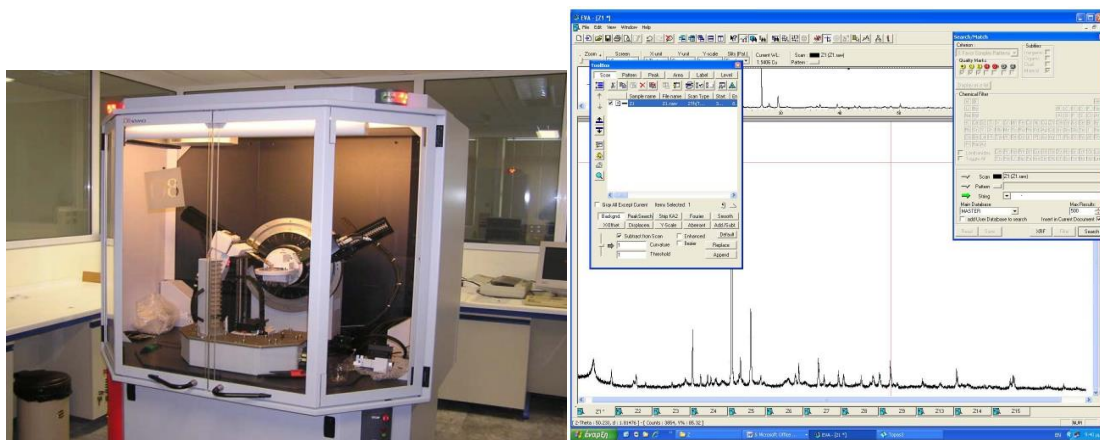


Figure 20: Left= Bruker D8 Advance X-Ray diffractometer, Right=The Eva software that was used for the identification of the minerals.

The procedure was carried out as follows:

1. Initially, the samples were dried in a special laboratory oven (110 ° C for one day).
2. Then they were pulverized and placed in a suitable holder with diameter 25mm and depth 3mm for insertion into the diffractometer (Fig. 21A, B, C). *The operation of the device is based on the correlation of the X-ray incidence angle to the crystal lattice of the minerals with the Bragg set values*

representing each mineral, with a scanning time step of $2\theta = 0.015^\circ$ (scanning step) and step time $t = 0.1$ s (step interval) in a range of $2-70^\circ$.

3. Mineralogy was completed by processing the resulting digital data, ie, the identification and interpretation of the radiograph peaks produced by each sample (Eva software).
4. Finally, a semi-quantitative analysis of the identified minerals was based on the calibration of the following table 5 based on the height of the reflections (Table 2). *All minerals identified by X-ray diffraction analysis are reported as major (>30%), moderate (20-30%), minor (10-20%), few (3-10%) and trace (<3%) amounts.*

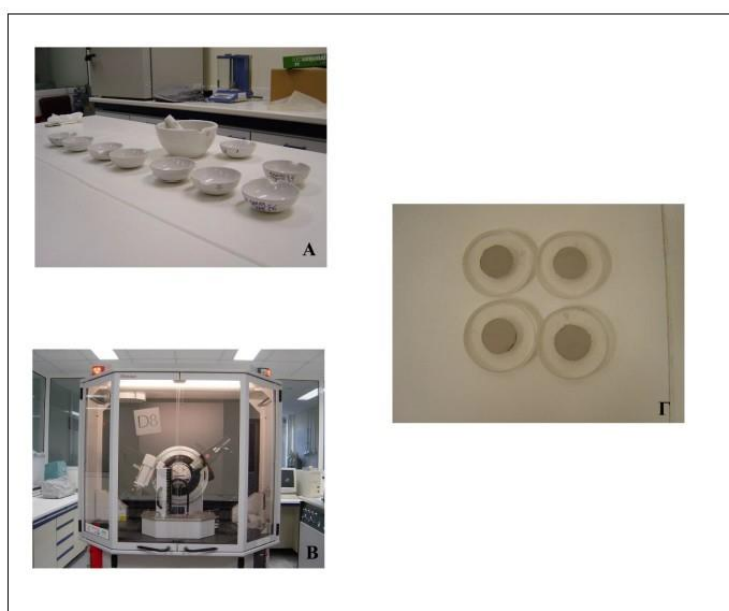


Figure 31: A) The pulverized samples, B) Bruker D8 Advance X-Ray diffractometer, Γ) special samples (holders).

Table 2: A semi-quantitative interpretation and classification of the minerals in each sample based on the height of their reflections.

-	0	not detected
tr	0,5	traces
+ / tr	1	traces to few
+	1,5	few
+ / ++	2	few to common
++	3	common
+++	4,5	frequent
++++	7	dominant

4.2.4 Methodology of foraminifera

Forty samples were selected from this core for foram analysis (Fig. 22). Each sample covered approximately a 2 cm thick interval in the core. The samples were treated with H_2O_2 , washed and sieved over mesh widths of $63\mu m$ and $125\mu m$. The dry and weighed samples were split into separate aliquots containing about 300 planktonic foraminiferal specimens. At least 300 different planktonic specimens were identified and counted in each sample. Each taxon is expressed as a percentage of the total assemblage. The numbers of planktonic and benthic foraminifera specimens per weight of dry sediment ($>150\mu m$ and $>63\mu m$, respectively) were estimated as indexes of planktonic (PFPI) and benthic productivity (BFPI), respectively. Hierarchical cluster analysis (R-mode) was performed on the planktonic foraminifera species which were sufficiently abundant in the examined species. The tree diagram was constructed using the Ward's method based on Squared Euclidian distance on SPSS software.



Figure 22: The process that was conducted in all samples in order to be ready for the observation and identification of the foraminifera through the microscope. Up left: A descent amount of sediment was taken from each sample. Up right: It was placed for a few minutes in the ultrasound device. Down left: It was sieved for a $+4\phi$ diameter. Down right: Then it was left overnight in the lab oven at around $55^{\circ}C$.

4.2.5 Methodology of organic/inorganic C and total C, H, N, S

Elemental Carbon and Nitrogen Assays were performed using the Carlo Erba Elemental Analyzer EA1108 analyzer at the Laboratory of Instrumental Analysis of the School of Sciences of the University of Patras, Greece. The determination of total organic carbon (Toc), inorganic carbon (Ic) and total percentages of H, N, S was conducted in 40 samples, which were collected throughout the whole core length.

The preparation of the samples for the calculation of total percentages of C, H, N, S had the following steps:

- a. Each sample was dried at 50°C for 24 hours.*
- b. Pulverized in the mill grinder.*
- c. The final powder weighted (at least 0,22g).*
- d. Then it was stored into a small container in a desiccator until ready to be analyzed.*

The preparation for the calculation of total organic C had a different procedure:

- a. Again each sample was dried at 50°C for 24 hours.*
- b. Pulverized in the mill grinder.*
- c. Then they were placed in individual beakers and weighted with it (Wi).*
- d. A solute of distilled water (500ml) and hydrogen chloride (50ml) was created.*
- e. In each beaker/sample an amount of 10ml from the solute was poured in using a 10ml pipette (Fig. 23).*
- f. Next they were placed in a heating plate of approximately 90°C for 1, 5 hour until it was solidified (Fig. 23).*
- g. Once solidified, they were left to dry in the laboratory oven for almost 16 hours at 70°C and after that the temperature raised at 105°C for 2 more hours.*
- h. Each sample was weighted again with the beaker (Wf).*
- i. Lastly, they were placed into a small container, which was immediately transferred to the laboratory for the analysis (preventing humidity).*

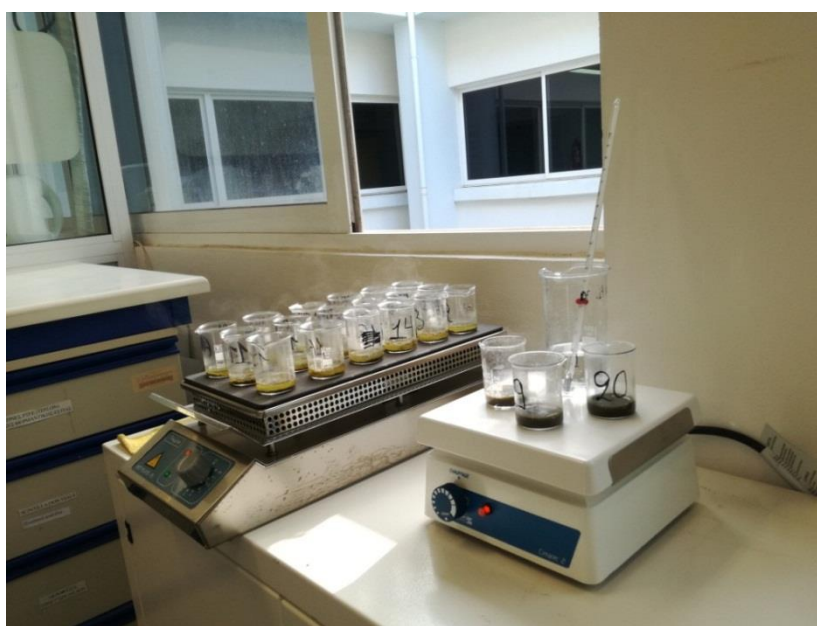


Figure 23: The procedure of the preparation of the samples for the organic carbon analyses. Left= the step were 10ml of the solute (10/1, distilled water/hydrogen chloride) are inserted into the sample, Right=the heating plates were the samples are left to solidify.

The function of the elemental analyzer is based on the full and instantaneous oxidation of the sample by combustion whereby all organic and inorganic substances are transformed into combustion products. With temperatures $> 1000^{\circ}\text{C}$ in the presence of pure oxygen, the organic and inorganic parts of the sample are converted to gaseous phases (CO_2 , SO_2 , N_2 , H_2O), which are transferred to a chromatographic column with the help of the noble gas (He), where they are separated and quantitated with the help of the Thermal Conductivity Detector (TCD).



Figure 44: The silver capsule where the samples are placed and measured by the elemental analyzer.

The percentages of C and N are automatically calculated by the system (calibrated) and data is given in electronic form as well as the chromatogram. Calibration of the system is performed with weighed amounts of 0.5 mg, 1.0 mg, 2.0 mg, 4.0 mg and 10 mg acetanilide. A calibration curve is thus plotted.

Besides the calibration, a blank correction is made, where a blank silver capsule is inserted and sealed into the tin capsule without, however, containing a sample (Fig. 24). Blank samples provide values for corrections of the % content of the samples and patterns due to background values of the instrument. The C and N concentrations in the samples are calculated automatically by the system using the equation:

$$C_i (\%) = 100 \times A_i / mw$$

Where:

- C_i : the content of the analyzer in the sample
- A_i : the area (corrected by the blank) of the analyzer peak in the sample (impact)
- m : the slope of the straight calibration (impacts / gr)
- w : the mass of the sample (gr)

4.2.6 Methodology of bulk geochemistry

The method that was used for the geochemical analysis is Four Acid Digestion with ICP-MS Finish at the ALS Geochemistry, in Ireland. Four acid (or multi-acid) digestion uses a combination of HCl (hydrochloric acid), HNO₃ (nitric acid), HF (hydrofluoric acid) and HClO₄ (perchloric acid), which is a very effective dissolution procedure for multi-element analysis at trace levels of detection in the majority of the geological materials such as rock types, soils, and sediments (Table 3). Because hydrofluoric acid dissolves silicate minerals, these digestions are often referred to as 'near-total digestions'.

Nitric acid and perchloric acid are added to the sample pulp, and then they proceed to oxidise the samples, changing the oxidation stages of some semi volatiles elements and reducing loss in later stages of the dissolution process. Hydrofluoric acids is then added to the samples to dissolve the silicate lattice, allowing for release of the major rock forming elements such as Ca, K, Mg and Na. Although these elements may be underreported at high levels, below concentrations of a couple of percent results are robust, repeatable and accurate. The solution is then heated and digested, where it evaporates down to incipient dryness, again reducing the loss of semi volatile elements at this stage of the process. Finally, Hydrochloric acid is added and the sample can be sent to the analytical instruments with the spectroscopy process.

ANALYTES & RANGES (ppm)							
Ag	0.01-100	Cu	0.2-10,000	Na	0.01%-10%	Sr	0.2-10,000
Al	0.01%-50%	Fe	0.01%-50%	Nb	0.1-500	Ta	0.05-100
As	0.2-10,000	Ga	0.05-10,000	Ni	0.2-10,000	Te	0.05-500
Ba	10-10,000	Ge	0.05-500	P	10-10,000	Th	0.01-10,000
Be	0.05-1,000	Hf	0.1-500	Pb	0.5-10,000	Ti	0.005%-10%
Bi	0.01-10,000	In	0.005-500	Rb	0.1-10,000	Tl	0.02-10,000
Ca	0.01%-50%	K	0.01%-10%	Re	0.002-50	U	0.1-10,000
Cd	0.02-1,000	La	0.5-10,000	S	0.01%-10%	V	1-10,000
Ce	0.01-500	Li	0.2-10,000	Sb	0.05-10,000	W	0.1-10,000
Co	0.1-10,000	Mg	0.01%-50%	Sc	0.1-10,000	Y	0.1-500
Cr	1-10,000	Mn	5-100,000	Se	1-1,000	Zn	2-10,000
Cs	0.05-500	Mo	0.05-10,000	Sn	0.2-500	Zr	0.5-500
Dy	0.05-1,000	Gd	0.05-1,000	Nd	0.1-1,000	Tb	0.01-1,000
Er	0.03-1,000	Ho	0.01-1,000	Pr	0.03-1,000	Tm	0.01-1,000
Eu	0.03-1,000	Lu	0.01-1,000	Sm	0.03-1,000	Yb	0.03-1,000

Table 3: All the elements that can be analyzed with the Four Acid Digestion method.

A more detailed ICP-MS technique was developed in the early 1980s and today is one of the most popular analytical techniques with applications in geology, environmental studies and medicine. The technique uses high temperature plasma to produce positively charged ions or ionic fragments of molecules which are then separated and quantitated by recording the relative intensity of the ionic current corresponding to each mass to mass (m/z) ratio in a mass spectrometer.

Like AES, atomic mass spectrometry is a multi-element analytical technique that provides additional information on the isotopic specimens of sample data. Typically it is applied for the analysis of solutions with the possibility of insertion and solid samples using laser ablation (Rose et al., 1979).

The ICP-MS technique (Fig. 25) is performed in the following steps:

- Insertion of the liquid or solid sample into the plasma system and ionization, through a stream of argon gas for transport.
- Separation of the ions produced on the basis of the mass / charge ratio on a mass spectrometer.
- Measuring the relative intensity corresponding to each m/z ratio in an electronic multiplier / detector.

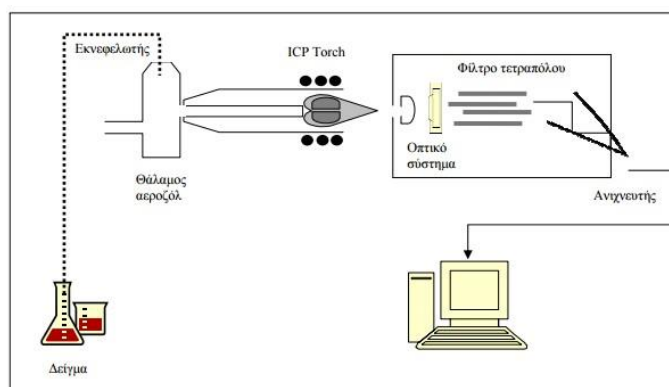


Figure 55: ICP-MS instrument

The sample insertion system includes the nebulizer and the spray chamber. The nebulizer converts the liquid sample into an aerosol by mixing it with argon gas in the spray chamber. The aerosol produced is then passed to the plasma temperature of 5000-10000K where it evaporates, vaporizes and is ionized. The resulting ions are transferred to the mass spectrometer via a transfer system consisting of an interface region and an ionic ion system. The medial surface extracts the ions from the plasma and passes the ion beam into the mass spectrometer chamber by means of an absorbent pump. The ionic optical system focuses and directs the ionic beam electrophoretic ions on the spectrometer, where they are separated according to the m/z ratio (Vutchkov, 2005).

The ICP-MS technique continuously records the relative intensity of the ionic current corresponding to the m/z ratio for each cell. The resulting peak spectra allow identification of the chemical elements contained in the sample, while the signal intensity is used for quantification. Semi-quantitative analysis of the sample is also possible, which can be applied for the rapid testing of unknown samples (Vutchkov, 2005).

Concentration quantification is based on internal or external calibration using analytical standards. The internal calibration method is usually used to correct the systematic errors of the instrument, the external calibration is based on the recording of the range of analytes of known concentration, which cover the range of concentrations of the samples to be analyzed, while inoculating the samples with a known amount of analyzer minimizes the errors due to uterine material (Rose et al., 1979).

5. RESULTS

5.1 Macroscopic description

The TYRO5 core is 285 cm long and consists mostly of mud. The macroscopic description showed that the core represents a rather complex sediment deposition at the core location. Ten lithological units (IX) have been observed and are described in (Fig. 26) 1. Noticeable are the laminas of light color which were often observed between 52 cm and 128 cm, within the units III and IV. Furthermore, the unit V (128 - 142.5 cm) is characterized by an alternation between light gray and reddish black mud. The same pattern continues within the unit VI (142.5-202 cm) but there the light gray layers are replaced by greenish to olive colored muddy layers (observed at 191-207 cm: VI a, 163.5-172 cm: VI b and 152-157 cm: VI c).

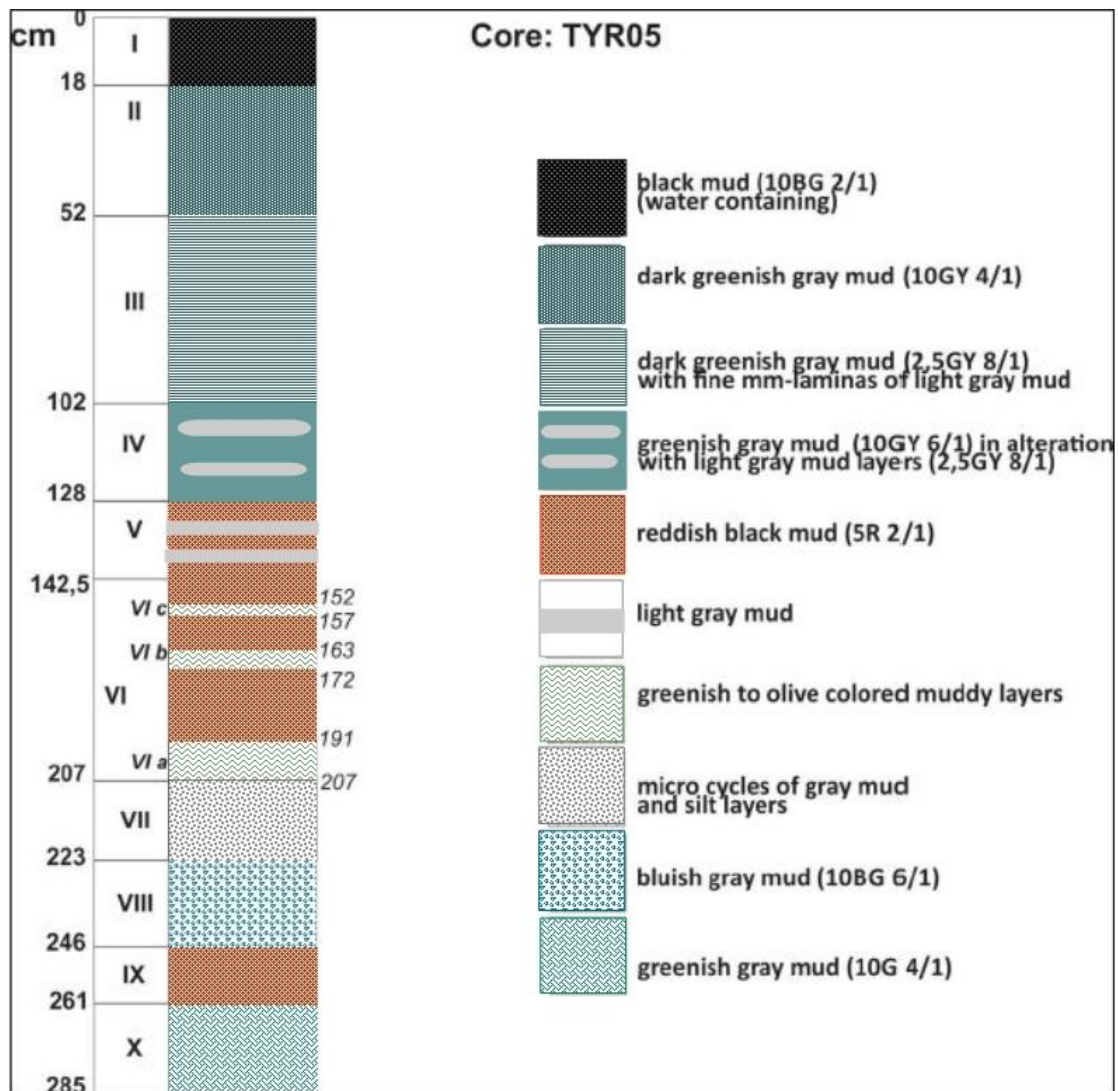


Figure 26: The description of the sediment core TYR05

5.2 Granulometry

Granulometry helped:

1. For the detailed representation of the vertical distribution of the granulometric classes (sand-clay-clay)
2. For the detailed representation of the vertical distribution of the statistical parameters (M_z (mean size) and σ_i (constant deviation))
3. For the recognition of different lithological units (according to Folk, 1974)

The granulometric model of the core shows a hemipelagic sequence of fine-grained sediments (mud-silt) which is occasionally interrupted by sandy sections of 3 to 11 cm.

More specifically, all the samples from the core are comprised mostly by mud, while a small section is dominated by silt/sandy silt (136cm-208cm). The sandy sections are distributed sporadic throughout the whole core with the percentages ranging between 10% - 30%. The mud zones cover the greatest part of the core (0-133cm/210-288cm), where clay and silt obtain similar percentages (40%-50%) and sand does not exceed 8%.

Mean diameter (M_z) values show a rather homogeneous distribution in the intervals 0cm-160cm and 216cm-288cm (ca 7,3 M_z [ϕ]), whilst a transition towards lower values is observed between 160cm-216cm (ca 6,3 M_z [ϕ]). The sorting (σ_i) values show a constant distribution in 0cm-52cm and 216cm-288cm (ca 1,6), though there is a small increase from 52cm to 216cm (ca 2). The variables of skewness (S_{ki}) and kurtosis (K_G) present cohesion throughout the whole core with an average of -0.4004 and 2.9839, respectively (Fig. 27).

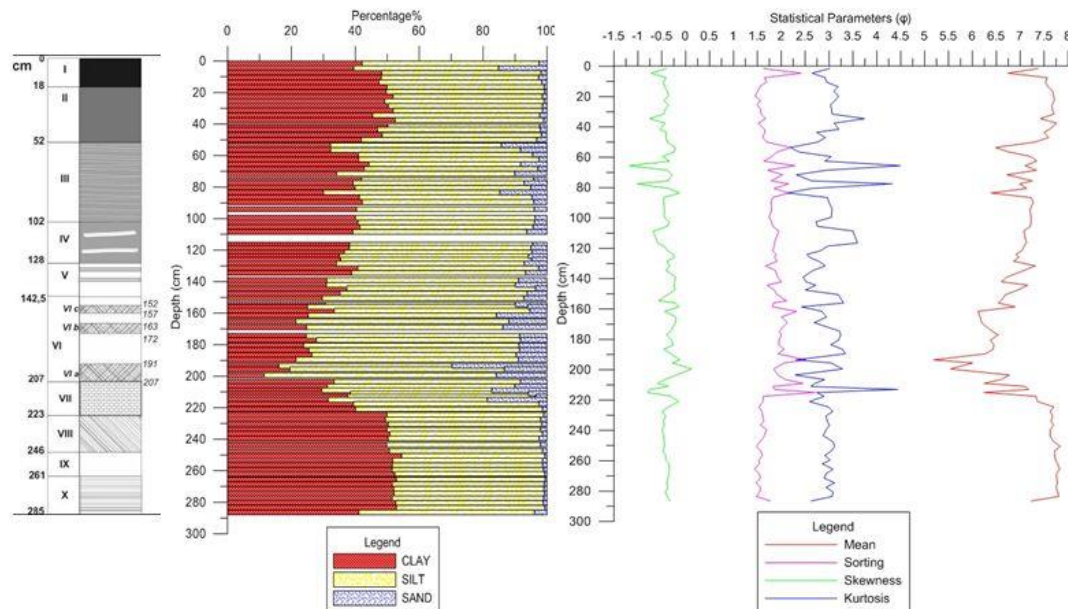


Figure 27: Vertical profiles of the percentages of the grain size distribution as well as their statistical parameters

5.3 XRD

The evaluation of XRD patterns obtained from the analysis of the samples covering the entire core range helped us identify, with the help of the Eva software, their main mineral components (Figs. 28 and 29). All the examined samples appear to have a homogeneous nature regarding the evaporitic minerals such as halite, calcite, gypsum and dolomite, along with quartz which reduces between 127 and 209 cm. Among the detected evaporitic minerals Mg-calcite is absent between 50 and 223 cm, while the aragonite varies between total absence and low content. Clay minerals represented by illite and chlorite as well as feldspars (K-feldspar and plagioclase) show a significant presence in almost every sample. Though the participation of chlorite is rather minor and discontinuous, especially between 58 and 202 cm. Pyrite was also detected at around 50 cm and amidst 136 and 205 cm but in accessory quantities.

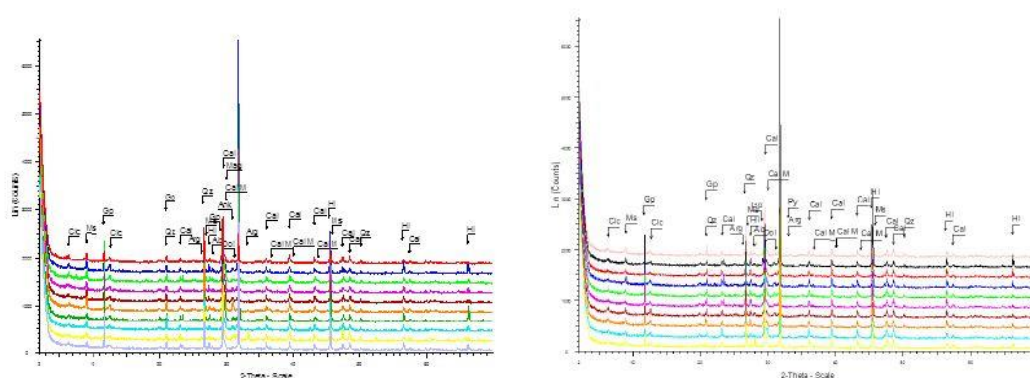


Figure 28: Composite plots of the XRD patterns for samples obtained from 0-64 cm (left) and 70-146 cm (right). Mineral abbreviations: halite (Hl); calcite (Cal); quartz (Qz); gypsum (Gp); illite (I); magnesium calcite (Mag); chlorite (Clc); dolomite (Dol); aragonite (Ar); pyrite (Py); albite (Ab).

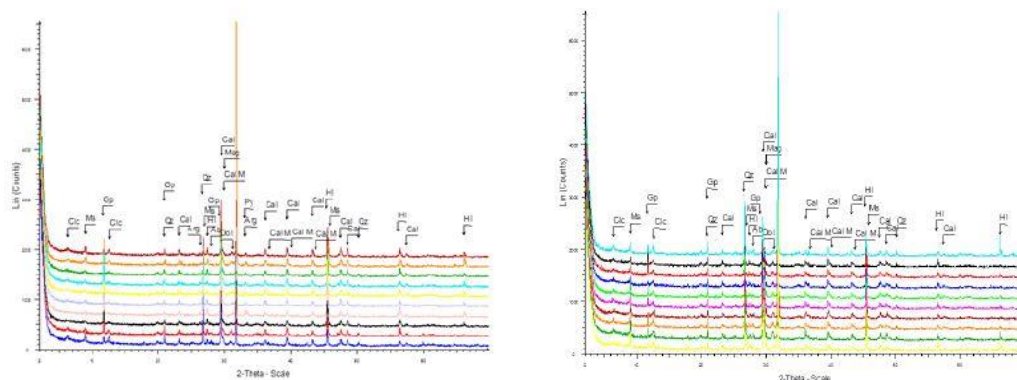


Figure 29: Composite plots of the XRD patterns for samples obtained from 149-216 cm (left) and 219-285 cm (right). Mineral abbreviations: halite (Hl); calcite (Cal); quartz (Qz); gypsum (Gp); illite (I); magnesium calcite (Mag); chlorite (Clc); dolomite (Dol); aragonite (Ar); pyrite (Py); albite (Ab).

5.4 Foraminifera

Planktonic foraminifera are abundant in all the examined samples (Fig. 4). Their presence is lower in the core part between 20 cm and 30 cm. Benthic foraminifera are also present in the same samples (Fig. 30). Their presence is reduced around the 20 cm core part and locally between 120 cm and 200 cm core part. Benthic foraminifera specimen are more rare in the $>125 \mu\text{m}$ sediment fraction than that of the $>63 \mu\text{m}$. All the examined samples contain well preserved and abundant fauna of radiolarian and pteropods.

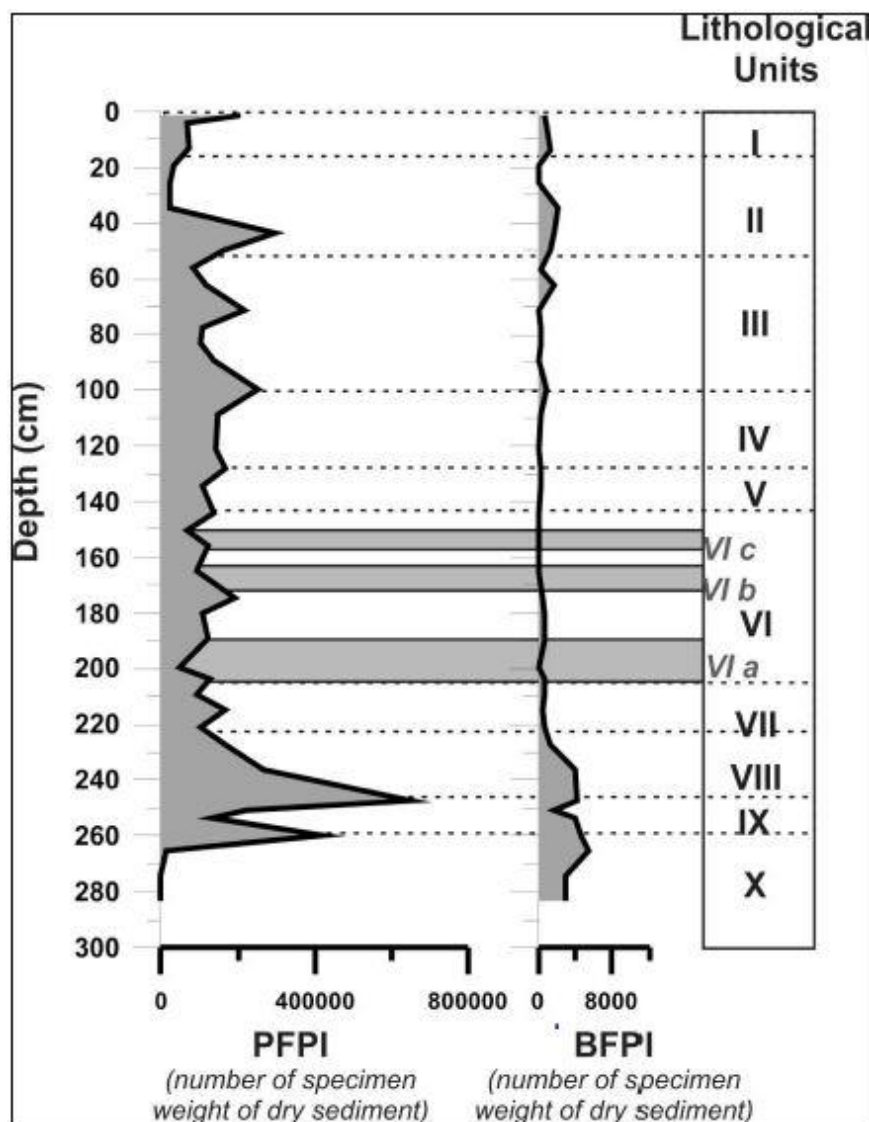


Figure 30: Down core variations of the Planktonic and Benthic Foraminifera Productivity Indexes (PFPI and BFPR, respectively). Dashed lines indicate the boundaries of the lithological units, referred on the right.

The planktonic assemblages consist of *Globigerinoides ruber alba*, *Gs. ruber rosea*, *Gs. sacculifer*, *Gs. trilobus*, *Orbulina universa*, *Globigerinella aequilateralis*, *G. calida*, *Hastigerina pelagica*, *Globoturborotalita rubescens*, *G. tenella*, *Globigerina bulloides*, *G. falconensis*, *Globigerinita glutinata*, *Turborotalita quinqueloba*, *Neogloboquadrina pachyderma*, *N. dutertrei* and *Globorotalia scitula*. The down core variations in the abundance of planktonic foraminifera species coincide with changes in the lithological units of the core sediments (Fig. 31). Cluster analysis (R-mode) revealed two clusters (Fig. 32).

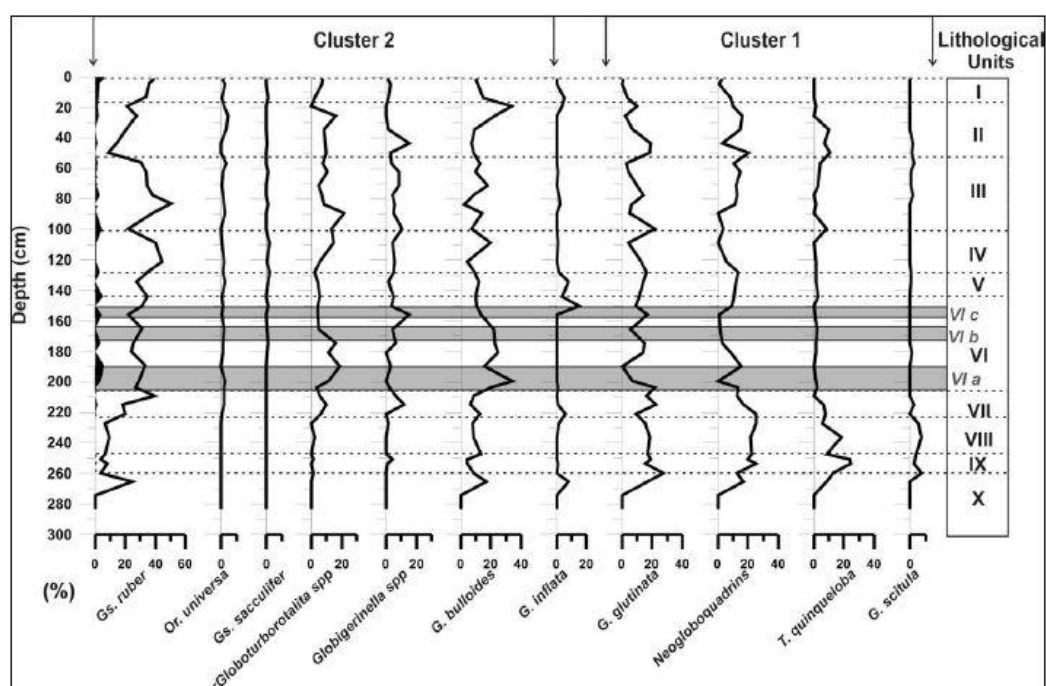


Figure 31: Down core variation of selected planktonic species versus depth. Dashed lines indicate the boundaries of the lithological units, referred on the right. Species belonging to Clusters 1 and 2 are also shown.

The first cluster comprises *G. glutinata*, *T. quinqueloba*, *Gr. scitula* and the group of *N. pachyderma* and *N. dutertrei* together with the indexes of planktonic and benthic foraminifera productivity (PFPI and BFPI, respectively). These planktonic foram species are considered as cold water indicators (Rohling *et al.*, 1993; Pujol and Vergnaud- Grazzini, 1995; Geraga *et al.*, 2010) and their high participation in the lower part of the core (200- 285 cm) suggests the prevalence of cold climatic conditions during the deposition of the lithological units VII -X. This interval is also characterized by high participation of both the planktonic and benthic foraminifera

fauna suggesting high levels of productivity in the surface waters and relatively high concentration in oxygen in the bottom waters.

The second cluster comprises *Gs. ruber*, *Or. universa*, the sum of *Globigerinella* spp. and the sum of *Globoturboatalita* spp. together with *G. bulloides* and *Gr. inflata*. The former species are considered indicators of warm waters (Rohling *et al.*, 1993; Pujol and Vergnaud-Grazzini, 1995; Geraga *et al.*, 2010). Their high participation in the upper part of the core between the top and 200 cm suggests the prevalence of warm climatic conditions during the deposition of the upper lithological units (I-VII). Furthermore, *G. bulloides* has been related to eutrophicated waters due to river discharges (Rohling *et al.*, 1993; Geraga *et al.*, 2010). The increased participation of this species between 150 cm and 200 cm core interval reveals a more humid climate during the deposition of the lithological unit VI. *Gr. inflata* has been related to eutrophicated waters due to water mixing especially during the winter (Pujol and Vergnaud-Grazzini, 1995). The participation of this species in the above interval is low. The increase in its abundance between 130 cm and 150 cm suggests an increase of water mass circulation during the deposition of the lithological unit V.

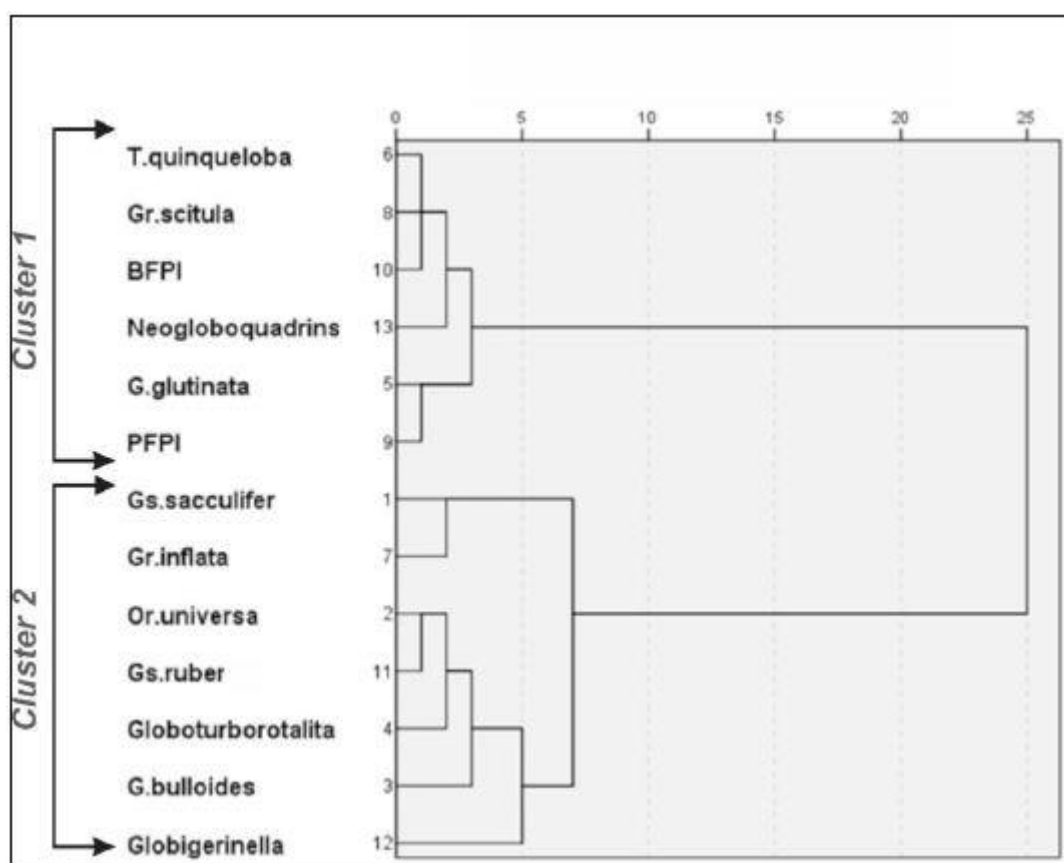


Figure 62: R-mode cluster analysis for the dataset of the microfauna

Furthermore, juvenile assemblages are present in the majority of the samples though their presence is higher in the upper part of the core (lithological unit I). Juvenile assemblages have been obtained in sediment cores revealed from the Tyro basin and they have been related to homogeneous deposits (Troelstra, 1987).

5.5 Organic/inorganic carbon and total C, H, N, S

The TOC values range between 0.40 and 2.62 and show a mean value of 1.13%. Specifically, the upper sediments of the core (0-130cm) varied in the range of 0.69% to 1.71%, whereas in the interval 130-202cm, the TOC gradually increases up to 2.62. Then the variable demonstrates an abrupt decline from 202cm to 223cm, which leads to the minimum values of the whole core with an average of 0.45% (223-288cm). In addition to TOC, CaCO_3 has a variability of approximately 21% to 42%.

The total H (hydrogen) displays some minor fluctuations which vary between 0.34-0.99%, while S (sulphur) has a distinct discontinuity (0-1.61%). Furthermore, total N (nitrogen) shows an analogous nature as TOC, where in the hiatus 142.5-202cm it presents the biggest values. Then the interval 0-130cm deviates from the latter with an average of 0.14% (except from a few spikes) as also as 202-285cm with a mean of 0.08% (Fig. 33).

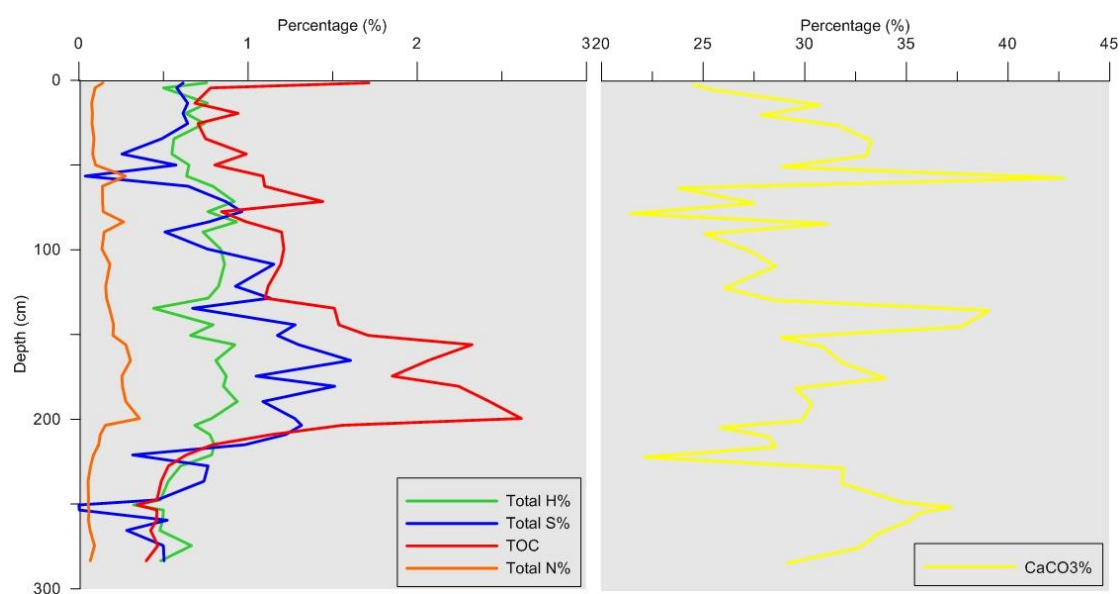


Figure 33: The vertical fluctuations of the elemental analysis for total organic carbon (TOC), H, N, S and CaCO_3 .

5.6 Geochemistry

A total of 48 elements were detected in all 20 samples throughout the whole core, including major, minor and trace elements (Table. 4).

<i>Al %</i>	<i>Ca %</i>	<i>Fe %</i>	<i>K %</i>	<i>Mg %</i>	<i>Na %</i>	<i>S %</i>	<i>Ti %</i>
<i>Ag ppm</i>	<i>As ppm</i>	<i>Ba ppm</i>	<i>Be ppm</i>	<i>Be ppm</i>	<i>Cb ppm</i>	<i>Ce ppm</i>	<i>Co ppm</i>
<i>Cr ppm</i>	<i>Cs ppm</i>	<i>Cu ppm</i>	<i>Ga ppm</i>	<i>Ge ppm</i>	<i>Hf ppm</i>	<i>In ppm</i>	<i>La ppm</i>
<i>Li ppm</i>	<i>Mn ppm</i>	<i>Mo ppm</i>	<i>Nb ppm</i>	<i>Ni ppm</i>	<i>P ppm</i>	<i>Pb ppm</i>	<i>Rb ppm</i>
<i>Re ppm</i>	<i>Sb ppm</i>	<i>Sc ppm</i>	<i>Se ppm</i>	<i>Sn ppm</i>	<i>Sr ppm</i>	<i>Ta ppm</i>	<i>Te ppm</i>
<i>Th ppm</i>	<i>Tl ppm</i>	<i>U ppm</i>	<i>V ppm</i>	<i>W ppm</i>	<i>Y ppm</i>	<i>Zn ppm</i>	<i>Zr ppm</i>

Table 4: The 48 elements that were detected in all the examples

Almost all of the elements present fluctuations, whether they are valuable or invaluable. Furthermore, they were normalized to Al, so as to exclude the terrestrial factor, and categorized into two groups. The elements that belong in the first group are described by a rather steady distribution, whereas in the second group the elements illustrate a more abnormal distribution. Almost all the ratios from the second group (As/Al, Ba/Al, Cd/Al, Fe/Al, Mn/Al, Mo/Al, Re/Al, Sr/Al, S/Al, Se/Al, U/Al, V/Al) show their distinct variations in the interval 149-205cm. Some vertical profiles can be seen in the Fig. 34.

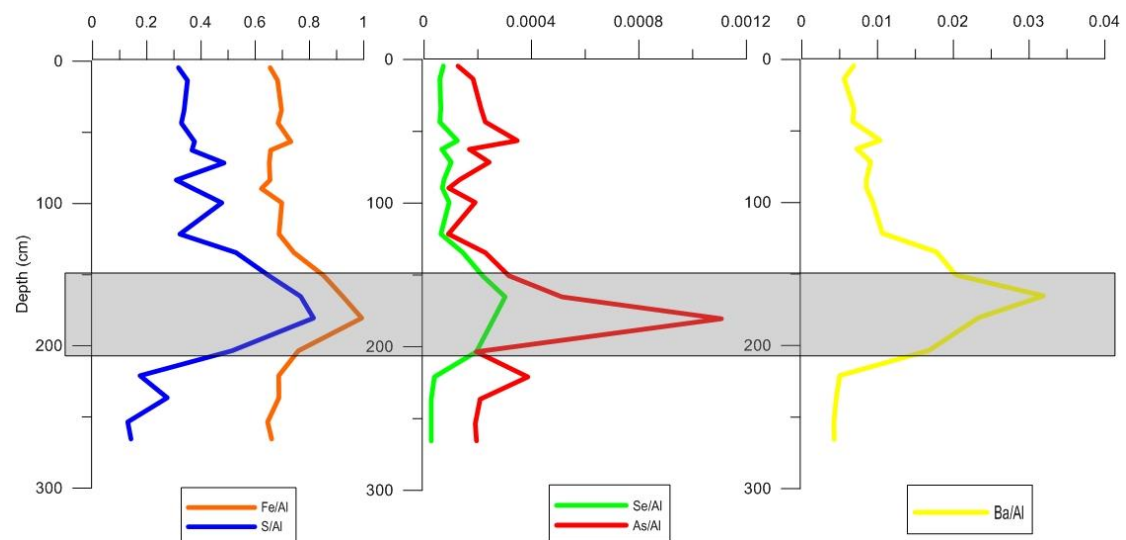


Figure 34: A few vertical profiles of normalized to Al elements. Shaded area refers to the interval 149-205cm.

6. DISCUSSION

The grain size distribution throughout the whole core indicates a few abrupt transitions from fine sediments, where the percentages of the sand are 0-3%, to coarser layers, where the percentages rise up to ~30%. Firstly we suggested that these sharp sedimentological transitions could be an indication of turbiditic deposits since it has been reported in many bibliographies (Cita et al 1984, Erba et al 1987, Rimoldi et al 1996, Rutten et al 1999, Olivieri et al 2013). Though, this possibility was rejected after consideration and further examination of the samples.

An explanation was that these layers were possibly biogenic sand due to some foraminifera bloom event during the time of the sedimentation. That could have caused this massive grain fluctuation in the core. Another hypothesis for the increase of the sand fraction is some aggregates that were observed in a few samples and couldn't segregate during the Mastersizer analysis (Fig. 35). Thus, it was interpreted by the computer program as a large amount of sand.

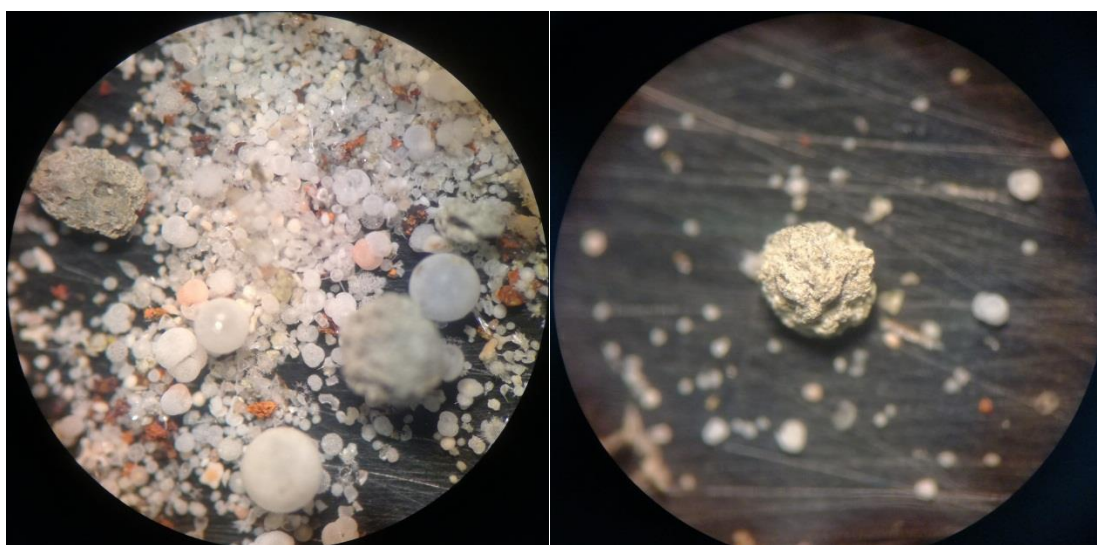


Figure 35: An optical depiction of the foraminifera ooze (left) and the aggregates (right), through the stereoscope (x4 lens). The sample is from a depth of 163.5-167cm of the TYRO5 core.

Hence we deduced that if the distribution curves of the samples with the maximized amounts of sand had two discrete and isolated peaks, then the source of the coarser material was exclusively by those aggregates. However, if the peaks of the distribution curve had a normal transition from one another then the source would be a result of both the aggregates and the foraminifera oozes. This theory was verified by observation of the samples (stereoscope) and by plotting them in a diagram, though further investigation is needed for the identification of the exact source (Fig. 36).

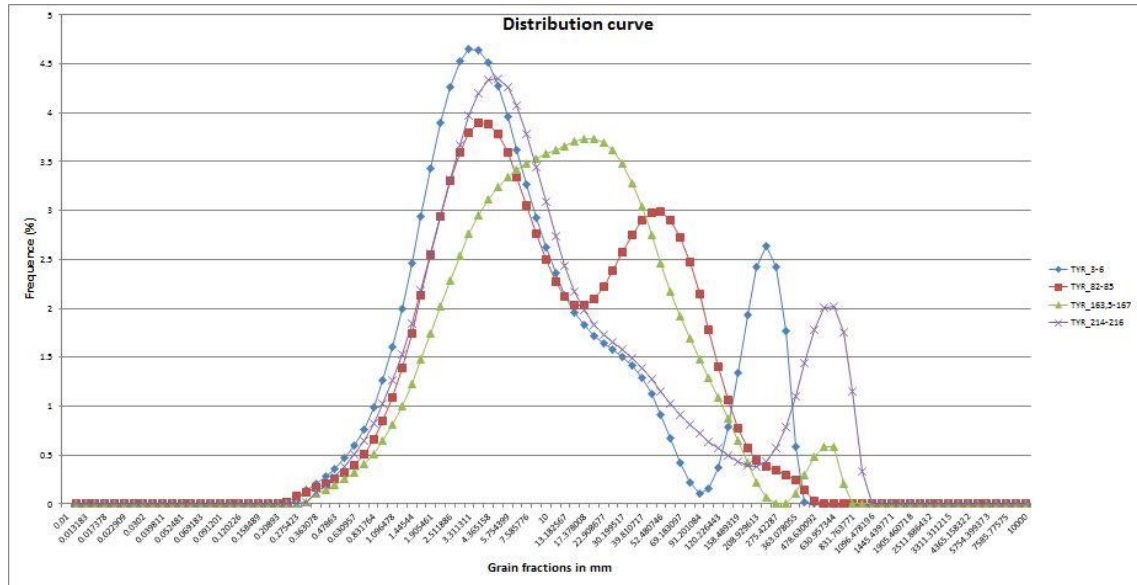


Figure 36: Four samples out of ten that had increased percentages of sand were plotted in a distribution curve. The blue line is an unequivocal example of the first theory, while the red line of the second theory.

Regarding the mineralogical association obtained in the examined sediment samples of TYR05 core, there is a correlation with the sediments of the eastern Mediterranean Sea (Nesteroff, 1973). In particular, halite, calcite, gypsum, dolomite and Mg-calcite are the dominant mineral phases in the sediments revealed from the Tyro basin (Nesteroff, 1973; ten Haven *et al.*, 1987; De Lange *et al.*, 1990) and other hypersaline basins (Corselli and Aghib, 1987; Wallmann *et al.*, 2002). This can be supported by the precipitation of these minerals via dissolution of the underlying evaporates. The steady presence of these minerals in the relative records of the present dissertation suggests the constant influence of the hypersaline environment developed in the area as well as the dark/greenish color that dominates, in the core (Geraga et al 2016).

Illite and chlorite, which are present in almost all the examined samples, are among the common clay minerals observed in the sediments of the sea southern of Crete and they are considered as the alteration products of the metamorphic rocks cropping out in Crete and other islands in the same area (Ehrmann *et al.*, 2007). Furthermore, illite has been related a terrigenous source transported by rivers discharging into the Aegean Sea (Geraga et al 2016) (Fig. 37).



Figure 37: Schematic map of the Mediterranean showing different basins and main rivers flowing to the Mediterranean. Sediment sources and major clay mineral inputs are indicated by theoretical arrows in green (riverine supply) and orange (aeolian input) (Martinez Ruiz et al 2015).

The coarser grain fractions in all the examined samples mirror a content which is abundance in quartz. According to Calvert and Fontugne, 2001, in eastern Mediterranean the proportion of quartz is reduced in the sapropelic sediments as a result of low wind strength during times of sapropel formation. Along with sapropel deposits of east Mediterranean, pyrite is also a common mineral as a result of microbial SO_4 reduction and subsequent reaction of reduced S with Fe, mainly during the formation of the layer (Passier et al., 1999; Calvert and Fontugne, 2001). Aragonite is also associated to the sapropel formation and a couple possible mechanisms explaining its presence are the high growth of *Florisphaera profunda*, the detrital origin and the sulphate reduction, during the sapropel interval (Thomson et al., 2004).

The mineralogical composition obtained from the 127 cm to 209 cm core interval, which comprises pyrite, aragonite, low quartz content and absence of Mg-calcite (Calvert and Fontugne, 2001) provides direct evidence that the lithological units V and VI include sapropelic deposits. This is further supported by the rare presence or even absence of the benthic foraminifera fauna in this interval suggesting the prevalence of anoxic bottom waters at the core site (Geraga et al., 2010). According to Rohling (1994) sapropels contain more than average amounts of pyrite and low to absent benthic fauna, which indicates low bottom water oxygen conditionst. The same pattern but of a weaker signal is obtained also from the 42 cm to 82 cm core interval within the unit III.

Based on macroscopic observations of the core as regards to the stratigraphy, the layers Via, VIb and VIc appear as the more likely proxy to the presence of sapropels. This hypothesis relates fully with the measurements of N%, H% and S% that have their highest values in the interval 142.5-210cm in the TYRO5 core. Respectively, the highest amounts of TOC (>2%) are found between 155 and 202cm, which hints a sapropel unit (VI). While a variety of definitions of the term “sapropel” have been suggested, we accepted both Kidd et al (1978) and Van Santvoort et al (1996), who refer to it as a discrete layer, thicker than 1cm, set in open marine environment and containing greater than 2% organic carbon or a significantly higher percentage than that of the surrounding hemipelagic sediment (Rutten et al 1999). This reflects our results perfectly since we have higher amounts than 2%, which are also higher from the surrounding hemipelagic sediments (<0.5%). The term “sapropelic” is used for sediments with values of organic carbon that vary from 0.5% to 2%. These organic-rich sediments probably exist due to strong density stratification that prevail in our basin, eventually prevented ventilation of the deeper parts of the basin, leading to bottom anoxia (Gansse & Troestrle, 1987). Thus, the intervals 0-152cm and 202-229cm are sapropelic, the unit 155-202cm consists of sapropels (except a small layer that is sapropelic, 173-176cm) and the last ~50cm are typical oxic hemipelagic eastern Mediterranean sediments.

However, in view of the data hitherto of this study and taken into consideration the strong geo-dynamic regime of the study area (Troelstra, 1987) there was a dilemma of whether or not these layers were resultant of different sapropels or to post depositional layers of the same sapropel. It was assumed in many papers by Jongsma et al, De Lange and ten Haven (1983) that the sedimentation rate was quite high and the age of the sediments (up to 400cm depth) could exceed 80000ka. Hence, the sapropels would be different. This assumption was rejected by McCoy and Stanley (1984), who believed in a high re-sedimentation rate, as there were similar evidences in nearby basins. We concluded to support the theory of the latter. Considering previous studies on different anoxic basins of the eastern Mediterranean along with the high re-sedimentation rate we propose that our sapropel corresponds to S1.

The S1 sapropel is the youngest (Cita et al., 1977) and has been deposited between 5000 and 9000 years ago (Troelstra et al., 1991; Thomson et al., 1995; Van Santvoort et al., 1996). This sapropel is being subjected to diagenesis because of the diffusion of oxygen into its uppermost reaches, thus oxidizing organic matter and giving rise to extensive remobilisation of redox-sensitive metals (Rutten et al 1999). It was deposited under relative warm climatic conditions and is characterized by anoxic bottom waters as it is suggested by the absence or low participation of the benthic forams. Furthermore in these layers *G. bulloides* participates in the planktonic associations with percentages around 20% to 30% while the participation of the *Neoqloboquadrins* varies among the investigated sites from 0 to 20-30% (Geraga et al 2016). The same trends have been obtained in the studied core interval (Figs. 4 and 5).

Another speculation that the S1 sapropel is involved in our TYRO5 core is the positive peaks of Mn from the bulk geochemistry analysis. Mn-rich layers have been observed to occur under steady-state conditions and just above sapropel units (van Santvoort et al 1996). The Tyros basin is one of those occasions and presents one discrete manganese peak at 133-136cm (P1) and two smaller at 98-101cm(P2) and 55-58cm (P3) (Fig. 38).

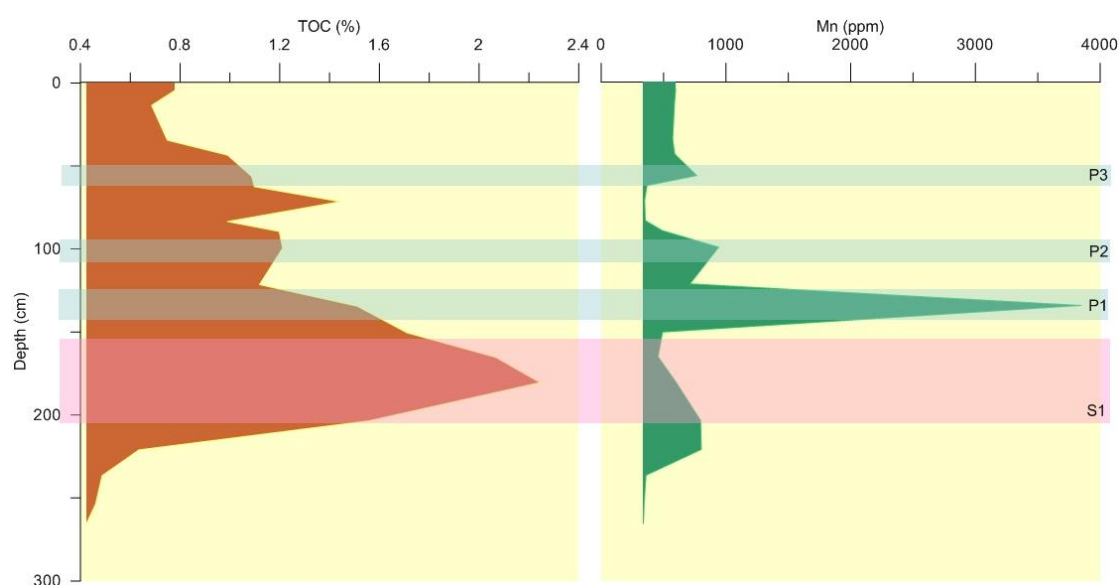


Figure 38: The vertical profiles of Mn and TOC. Light shaded area reflects the sapropel interval, while the dark shaded area the highest peak on Mn above the sapropel.

As reported by van Santvoort et al (1996) and Rutten et al (1999), two Mn peaks have been observed in few anoxic brine lakes. The first/lower peak is right above S1 sapropel and the second/upper peak is a few centimeters closer to the sediment surface. Higgs et al. (1994) and Thomson et al. (1995) assumed that the upper Mn peak resulted from a bottom water re-oxygenation at the end of sapropel formation (similar to the formation of Mn-rich layers in the world ocean, proposed by Mangini et al., 1991). The lower peak interpreted as diagenetic and subsequently formed by the action of a progressive oxidation front. Hence, this implies that the deep eastern Mediterranean sediments are yet to adjust to the changes which occurred at the end of S1 sapropel formation and that it is the lower Mn peak which at present is actively forming. Others suggested that both peaks were diagenetic and the upper peak is the one that still actively forms (van Santvoort et al 1996).

In our case one discrete peak can be observed (P1), which is possibly equivalent to the one referred right above the S1 sapropel. The other two peaks could be either because of two different origins or as a result of re-sedimentation (of the P1 or P2). More investigation is needed such as pore-water analysis to verify any of those theories.

Sapropels have been found in sedimentary sequences from the entire eastern Mediterranean and have a notably tendency towards higher enrichments in Ba, Mo, S, Re, As, Cu, Ni, Sb, and Fe, reflecting the strong sulfidation in an anoxic water column (Rohling 1994, Brumsack 2006). In literature the ratios that present their highest values in sapropels and used as redox-proxies are Fe/Al, Sr/Al, Ba/Al, Ni/Al, Mo/Al, V/Al, Co/Al, Cu/Al, As/Al, Se/Al, Re/Al and can be all verified by the results of the TYRO5 core (Fig. 39), (Calvert et al 2001). Also, Ti/Al, K/Al, Rb/Al and Zr/Al along with quartz, Mg-calcite and illite tend to be lower in sapropels, but in our samples these ratios display a rather uniform distribution, such as Ti/Al and Zr/Al, which can be related to a homogeneous grain distribution as a result of the high re-sedimentation rate (Rutten et al 1999, Calvert et al 2001).

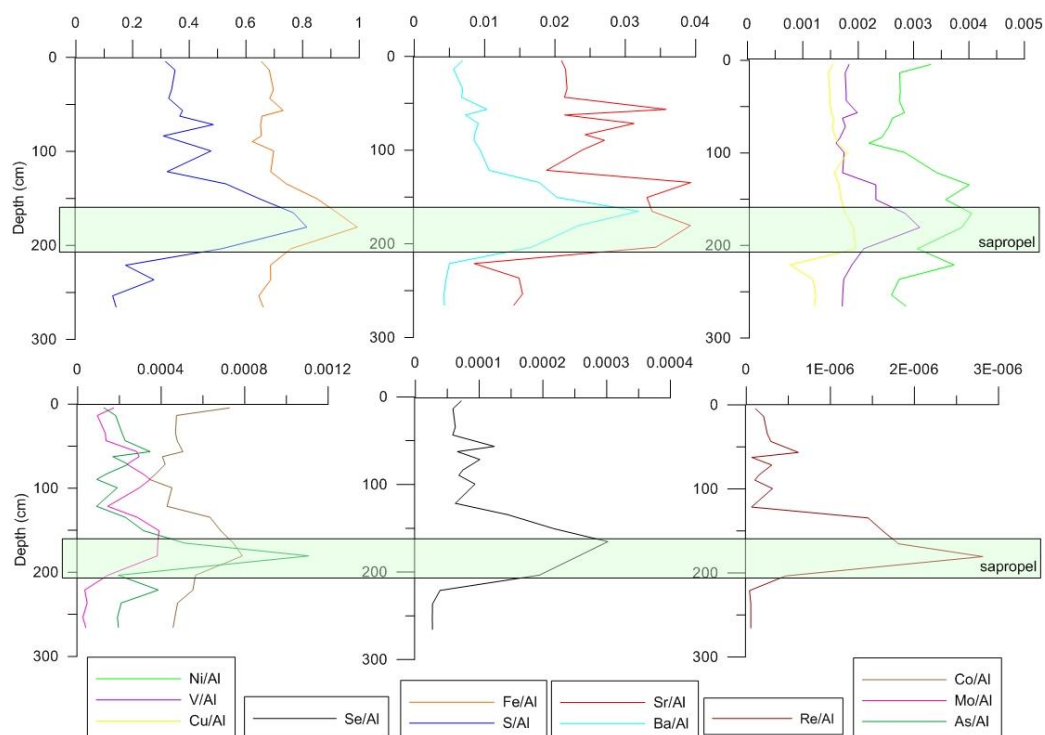


Figure 39: Vertical profiles of the redox-proxies. Shaded area reflects the sapropel unit (S1).

Carbonates are important for the concentration of Ca, Mg and Sr, whereas aluminosilicates determine the concentration and distribution of Si, Al, K, Li, Y and Be, and to a lesser extent that of Fe, Cr, Ti, Mg, Zn and Zr. In sapropels, organic carbon and sulphur seem to be closely related. Mo, P, Fe, V, Cu, Zn, Co, Ni and Cr are closely associated with organic and sulphidic compounds. The concentration versus depth profile for organic carbon in two sapropels points to a rapid establishment of conditions that gave rise to sapropel formation, followed by a gradual transition back to "normal" conditions (Pruysers et al 1991).

Sediments result from the accumulation of particulate matter which may originate either from atmospheric or riverine inputs (clays, altered minerals), or from formation in the water column (carbonates, opal, organic matter and Mn-Fe oxyhydroxides), (Freydier et al 2001). As stated by Wehausen & Brumsack, (1999) there are different scenarios about the possible origin of the lithogenic materials that end up in the Mediterranean depending on the climate conditions (Fig. 40). Also, many major elements (Si, Al, Fe, K, Ca, Mg, Na, Ti, Mn, and P; can be affected by biological processes or diagenesis, while some trace metal show high concentration levels in plankton (like Zn, Ni, Cd, or Cu), not necessarily associated with the organic fraction after burial (Brumsack 2006).

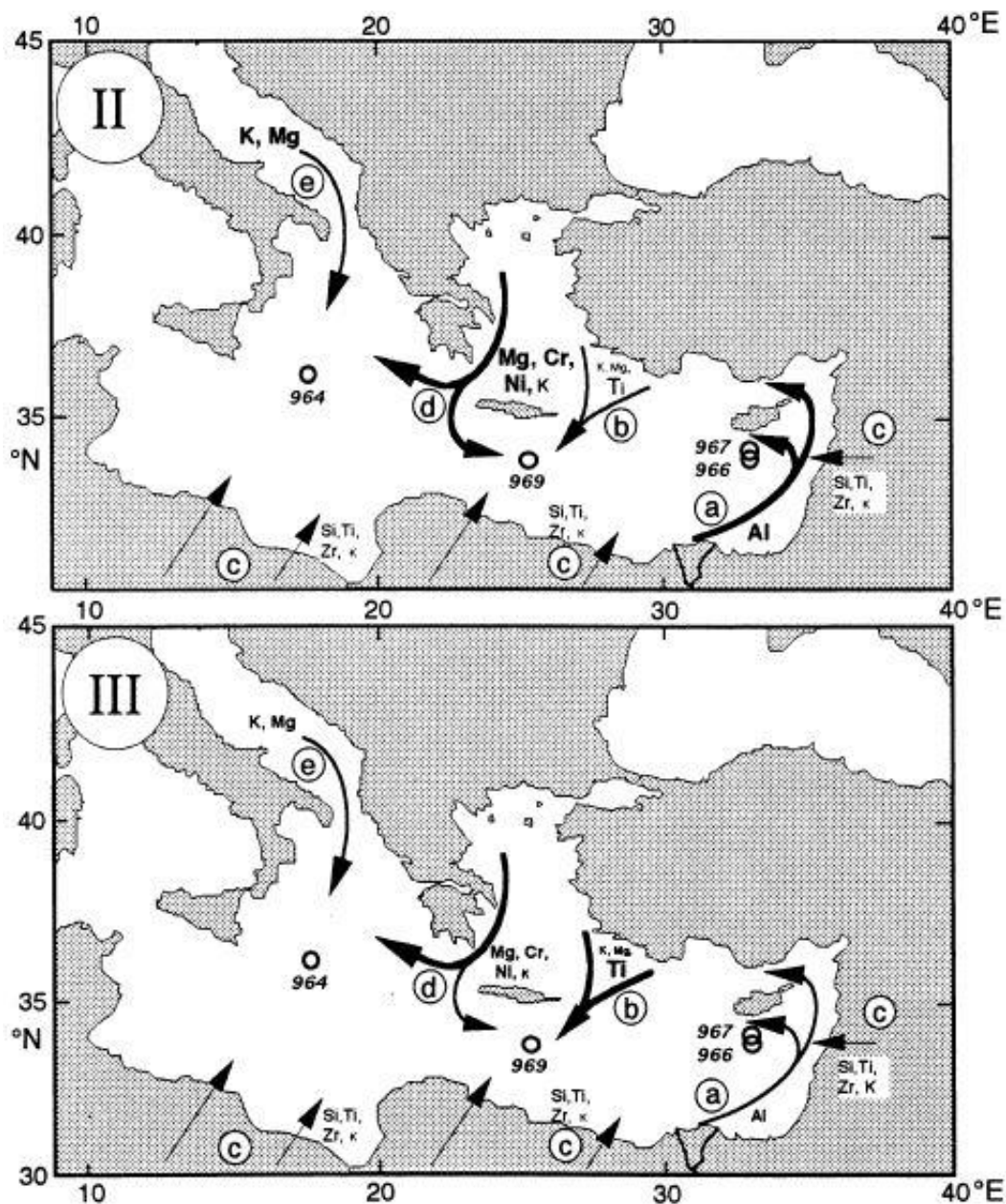


Figure 40: Scenario II= eutrophic condition and sapropel deposits (strong insolation maxima), Scenario III=oligotrophic conditions and reddish sediment deposits (weak insolation maxima). The site 969 is very close to our sampling site in the Tyros basin. (Wehausen & Brumsack, 2000)

All the factors that resulted from the different analyses that we conducted in our samples were finally computed in the SPSS software. A few methods were applied in the examined samples to see which one represents our case the best (R-factor, Q-factor, Hierarchical cluster). The first two were rejected because of their chaotic results, while Hierarchical cluster analysis (R-mode) was proved to be the most suitable. So the tree diagram was constructed using the Ward's method based on Squared Euclidian distance (Fig. 41).

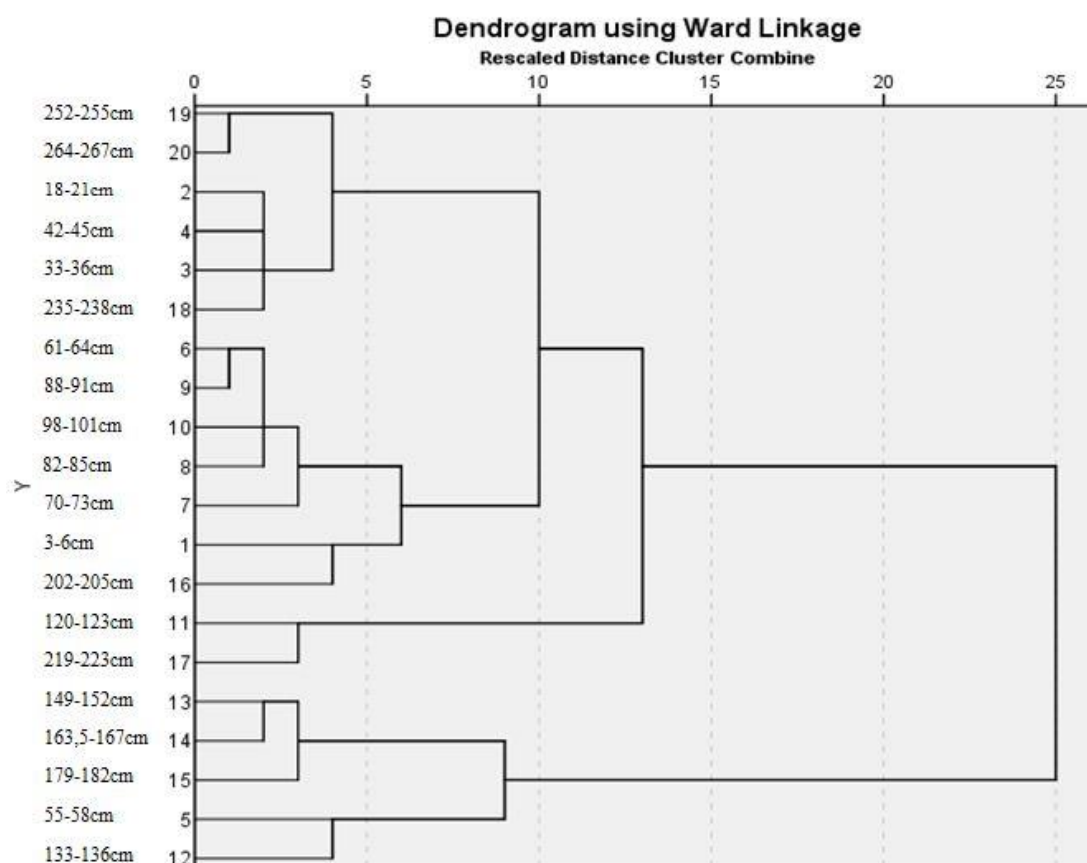


Figure 41: R-mode cluster analysis for the dataset of all the previous analysis (granulometry, XRD, foraminifera, Toc and bulk geochemistry) based on the samples as variables.

The dendrogram (according to the sample variable) verified all the previous theories, which were mainly focused to the sapropel unit and the pre/post-depositional characteristics. According to the correlation between the intervals 133-182cm, which corresponds to the sapropel unit, and the much alike layer 55-58cm that is sapropelic, we can suggest two possible explanations. Either it implies that the interval 55-58cm is a re-depositional unit/layer of the S1 sapropel, as it depicts the same peaks as the latter (Fig. 42), or it could depict a climatic phenomenon that had a similar outcome as the sapropel. Though, because of the lack of literary in Tyros basin it is impossible to validate any of those theories without a much more meticulous study, such as the radiocarbon dating of these layers and the stable isotopic analyses.

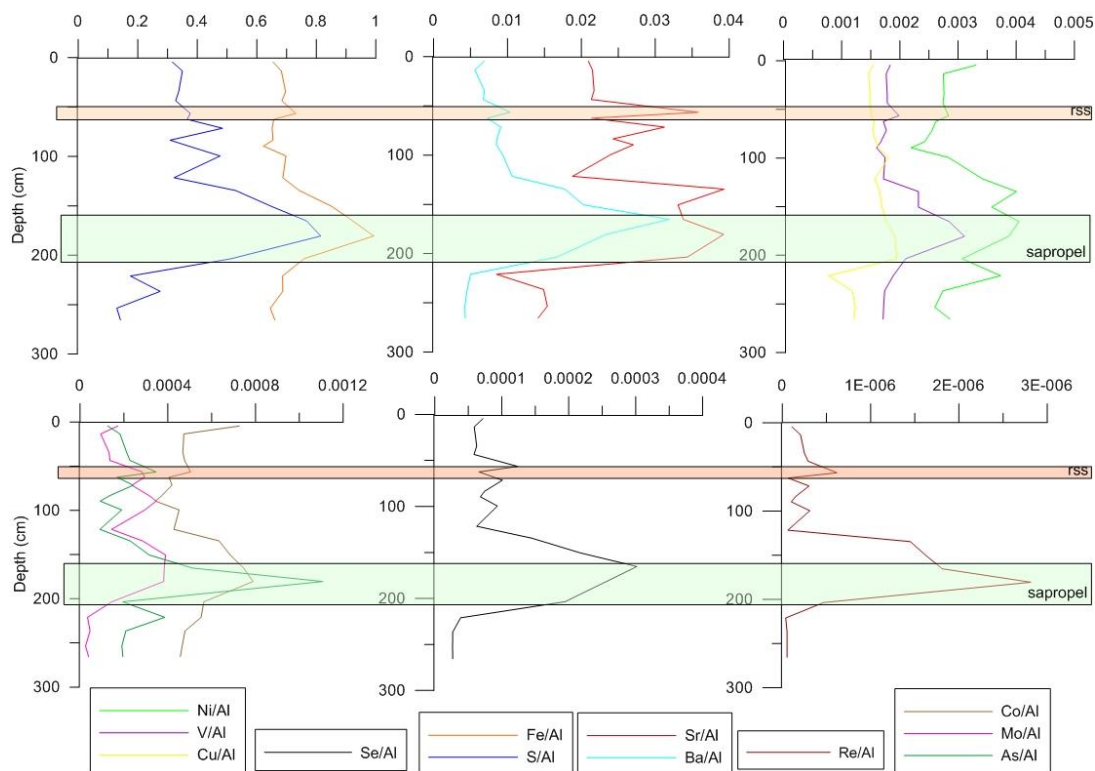


Figure 42: Vertical profiles of the redox-proxies and their highest values. Green shaded area=sapropel, Orange shaded area=possible resedimentation of the lower sapropel (rss)

The rest of the samples are divided into three groups. The first group is comprised by the intervals 3-6cm, 61-101cm and 202-205cm, the second group contains the layers 120-123cm and 219-223cm, and finally the third includes units 18-45cm and 235-267cm.

The first two groups can be combined because they both have a post-depositional nature. The layers 120-123cm and 219-223cm indicate the intervals that enclose the main sapropel unit, which along with the intervals 61-101cm and 202-205cm show the environment as to the pre and post depositional nature of the S1 sapropel in our anoxic basin. They differ from the sapropel unit because of:

- Their significant decline in most of the geochemistry elements that act as sapropel-proxies, such as Ba, Se, Re, Sr, As etc.
- The total organic carbon (TOC) drop to sapropelic values (0.6-1.5%).

The last group (18-45cm and 235-267cm) is probably the most neutral due to the fact that it approaches the characteristics of the “typical” oxic Mediterranean hemipelagic sediments. So here we have an even greater reduction to the previous variables and the notable increase of the foraminifera (especially the benthic), which shows the transitional phase of our core to a stable state (Fig. 43). Lastly it is very interesting how the top layer (3-6cm) has an analogous nature as the pre and post depositional units, possibly indicating that we are on the verge of a new event.

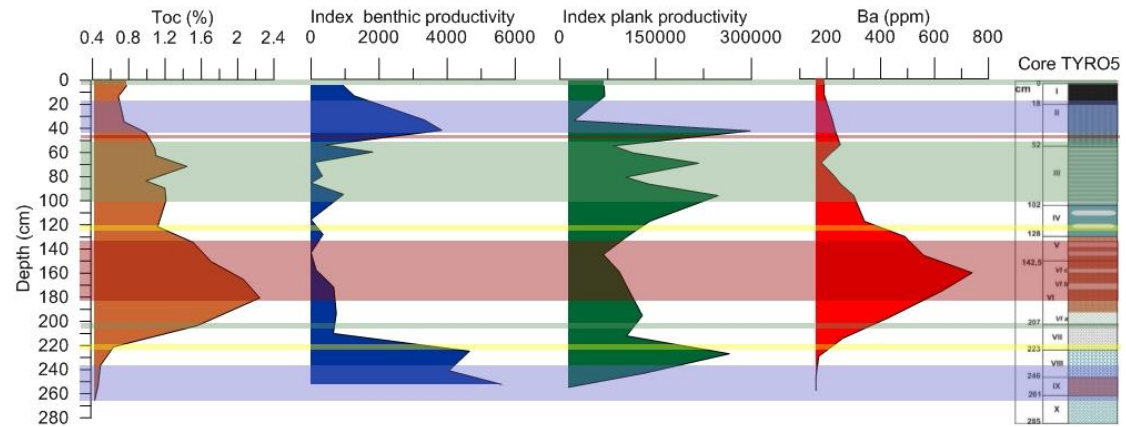


Figure 43: Some variables that fluctuate between the groups showing the diversity between them, as well as the transitional character of the sediments in relation to the core (TYRO5). Red shade= sapropel (or in case of 55-58 a possibly critical climatic phenomenon), Green/Yellow shade= pre-post deposits, Blue shade= transition to “typical” oxic eastern Mediterranean sediments.

7. CONCLUSIONS

The presently anoxic Tyros basin, located in the western part of Strabos Trench, is one of the few brine basins that exists in the Eastern Mediterranean Sea. One core (TYRO5) was recovered from the Tyros basin, at approximately 3000m below the sea-surface. A series of analyses were performed on the sediment samples from the TYRO5 core (285cm long) including granulometry, mineralogy, micropaleontology, elemental analysis and bulk geochemistry.

Firstly we deduced that the core sediments present a relatively complex sedimentary sequence. The grain size distributions showed variation every few centimeters where thin layers of sand emerged. Despite our first thought being that these small sections were related to turbidites, after more investigation we suggested that they were a result of either aggregates that couldn't isolate during the process of the analysis or/and biogenic sand due to a foraminifera bloom.

The mineralogical composition of the sediments shows the influence of the brine which is developed in the basin and is characterized mostly by evaporate minerals. In literature it is also reported that these evaporate minerals belong to the Messinian age (~5.5ma) and are exposed in the slope sides of the Tyros basin.

The microfauna assemblages present fluctuations in their abundances which coincide with changes in the lithology of the core. However, most of the examined samples show that the core sediments deposited under warm climatic conditions. Furthermore, the micropaleontological together with the mineralogical findings suggested that the core includes sapropelic layers, which was expected considering the anoxic nature of our basin.

This was later verified by the results of the elemental analysis, where the values of the total organic carbon (TOC) in the biggest part of our core had a range of 0.5-2% and in the interval 155-202cm it was exceeding 2%. Therefore, the majority of the TYRO5 core consisted of sapropelic to sapropel sediment alternations.

Finally, the geochemistry results proved that the Tyros basin has an anoxic nature and it is enriched in organic sediments due to high concentrations of Fe/Al, Sr/Al, Ba/Al, Ni/Al, Mo/Al, V/Al, Co/Al, Cu/Al, As/Al, Se/Al, Re/Al, which are all reported as strong redox-proxies. Also right above the sapropel unit a significant positive peak of

Mn (P1) was observed and it was indicated to be the S1 sapropel since previous studies presented a couple peaks on top the S1. Though, because in our case only one strong peak occurs with the other two peaks (P2, P3) to be considerably lower it was not possible to determine safely if these peaks exist due to the strong re-sedimentation processes of the area (P2, P3 as re-sedimentation deposit of P1) or due to a much more excessive presence of the Mn.

A more integrate viewpoint of the Tyros basin will “surface” after a few more analysis such as the stable isotopic analysis of O, C and the radiocarbon dating C¹⁴.

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