MINERALOGICAL, GEOCHEMICAL AND METALLOGENETICAL FEATURES OF SEDIMENTS FROM DSDP SITE 378 IN THE AEGEAN SEA, N. CRETAN BASIN AND THEIR ORIGIN

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ABSTRACT

The geochemical, metallogenetical, and mineralogical characteristics were studied in the hemipelagic sapropelic sediments from Site 378, boreholes 378&378A(Leg.42A DSDP) in the north of Cretan basin revealing the existence of four lithologic units(I-IV).The upper 3 lithologic units contain detrital minerals that are predominantly consist of clays(principally illite& kaolinite),quartz and feldspars, whilst calcite is the most important authigenic mineral. The reducing environment rich in organic material most probably caused the production of mixed layers and authigenic sulfides in minor amounts. Most of the major and trace elements have a terrigenous origin that is related with the Rhodes - Karpathos -Crete drainage system. During the upper Pliocene and especially during the lower Pliocene(Unit III) the detritus input was enriched in mafic and ultramafic detritus whereas much of Si, V& Ba are biogenous and associated with the sapropelic organic material -rich sediments. Part of Mn especially in the upper part(Unit I) seems to be associated with a hydrothermal activity related with the submarine volcanic activity in S.Aegean during late Quaternary, whilst another proportion of Mn is related with the calcium carbonate-manganese phase which is quite common in sapropelic sediments. The basal Unit IV contains only a selenitic pure gypsum which is a product of the Messinian salinity crisis that resulted in the development of evaporites with a thick salt layer.

INTRODUCTION

Site 378 (Holes 378 and 378A) was located in the north Cretan Basin (Fig.1). The maximum penetration was 343.5m below surface(BSF) with termination in Messinian gypsum. The Quaternary sequence of nannofossil marls and ooze with numerous sapropels and sapropelic layers and the Pliocene nannofossil marlstones with many sapropels provide good opportunities to study the geochemical and mineralogical aspects of these sediments-rich in sapropels - in order to establish some clues associated with the origin of these sediments as well as with the origin of some of their most important major and trace elements.

The Quaternary sequence of mannofossil marls and ooze with sapropels and sapropelic layers accumulated rapidly up to 200 m/my. The more compacted and slightly cemented Pliocene nannofossil marlstones contain numerous

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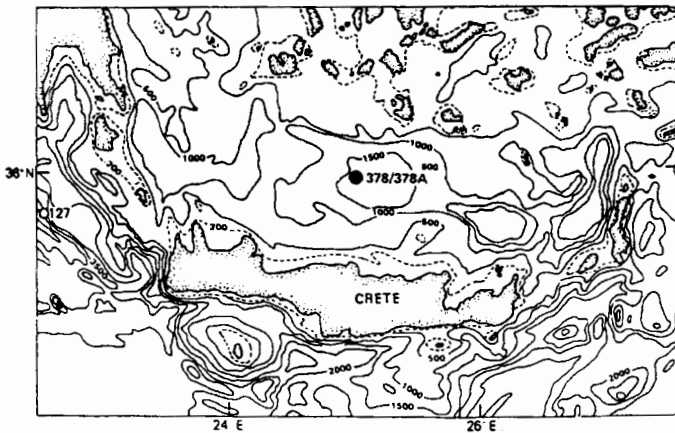
Fig. 1: Site location map (depth countours in m.) from Site 378/378 A, Cretan Basin DSDP (Shipboard Scientific Party, Init. Rept. DSDP Leg 42, 1978).

sapropels and burrows. At the base of the Pliocene,the accumulation rate dropped to about 9m/m.y. The late Miocene evaporites are represented mainly by coarse pure selenitic overlained by a brecciated dolomitic gypsum limestone.

THE GEOLOGICAL SETTING OF THE BROADER AREA

The Aegean arc is a broad folded belt extending from southwest Turkey to the Dinarides (Jongsma 1975).The north Cretan basin is an interdeep basin, one of the many units distinguished in the central part (Biju-Duval et.al. 1978).According to Hsu and Bernoulli(1978) the paleogeography of these units has suffered significant changes since the Messinian, marginal areas including the Cretan Basin were deformed, uplifted and energed during the Pliocene-Quaternary. An important tectonic event probably also occured during the late Eocene-Oligocene in the Crete - Karpathos - Peloponesus area which also involved the emplacement of nappes including ophiolites (Biju - Duval et.al.1978). During the Neogene the oceanic basin that experienced the most numerous anoxic events is probably the whole Mediterranean Sea(Thunell et.al.1974).The present results of DSDP Leg.42 indicate that the sapropels have been periodically deposited primarily in the eastern basin since the middle Miocene(Shipboard scientific party of Leg 42A DSDP 1978)

OBSERVATIONS AND PRELIMINARY CONCLUSIONS FROM THE SHIPBOARD SCIENTIFIC PARTY OF LEG.42A DSDP

According to the Shipboard Scientific Party four lithologic units are recognized at Site 378 based on the discontinous coring in Holes 378 and 378A. The upper three have a purely hemipelagic origin and are rich in calcareous and partly in siliceous tests.

Unit I (Fig.2a&b) consists of hemipelagic nannofossil marls and oozes of Quaternary age, and is 132m thick. They are dark gray in color and contain numerous intercalated sapropels and sapropelic layers. Planktonic and benthic foraminifera and nannoplankton assemblages constitute 30% to 50% of sediments. Unit I represents a hemipelagic desposition with periodic episodes of bottom stagnation,only little volcanic ash is present.

Unit II (fig.2a&b) consists of firm gray, nannofossil marlstones of late Piocene age. Dark sapropels and sapropelic layers are common and burrowing is rather intense. The composition depositional setting and accumulation

rate (up to 200m/m.y) are similar to those of Unit I. The most important difference is the diagenesis. The Pliocene sediments are compacted and cemented locally producing coherent marlstones. In this Unit there is a considerable increase in the siliceous components mainly in the form of siliceous microfossils (diatoms, radioloria, sponge spicules). This increase is reflected in the increase of the Si/Al ratio after 175m within Unit II(Fig.7)(see page 12).

Unit III (Fig.2a&b) represents early Pliocene gray nannofossil marlstones, with abundant organic rich sapropelic marl interlayers. In general the composition of this Unit is similar to Unit II but with substancially lower sediemention rate. As in Unit II, beside clay minerals, nannofossils and unspecified carbonates- the siliceous component is also important. A major difference with the previous Unit is a more abundant serpentine (3 to 5% as compared with 1% in Unit II) and talc (especially in the <2m fraction) (Table 3) which suggests that there was a change in composition of the detrital material reaching this basin between early to late Pliocene. The considerable increase in the Ti/Al,Mg/Al, Fe/Al, Ni/Al, Cr/Al relations which started within Unit II and reached higher values in Unit III (See Figs.5,6&7) agrees with the presence of serprentine and talc in considerable amounts in Unit III. It also supports the suggestion that the detrital input was enriched with terrigeneous components of mafic to ultramafic origin between early to late Pliocene.

Although more numerous than in Units I and II the saprorpelic layers are poorer in organic material judging by their generally lighter colours. This suggests that Unit III sapropels represent a sea floor environment where the reducing conditions were less intense.

This suggestion is in agreement with the substancially lower sedimentation rates in this Unit resulting in a more oxigenated sea water.

Unit IV(See Figs.2a&2b and Table 2) consists mainly of white to yellowish pure gypsum overlain by a brecciated - dolomitic limestone. The gypsum crystals are coarse, elongated and appear to have grown upwards in rosette-like clusters. Considerable void spare exist between some of these clusters, giving the rock a vaggue appearence (Figs.3a&b). This presence of selenitic gypsum indicates that both the Aegean Basin and the Mediterranean were subjected to the Messinian salinity crisis. According to the Shipboard Scientific Party for Site 378 Leg 42A (1978) the absence of the typical Mediterranean evaporites"Lago Mare" facies above the gypsum formation in Site 378 is due to the fact that Messinian Aegean had no connection the the Black sea. According to the same authors the gypsum was deposited in a shallow subaqueous environment.

Units I, II and III are rich in sapropelic layers and sapropels(see above) but the origin of these formations and especially their geochemical origin is incompletely understood and is therfore the main target of this study.

According to Kullenberg (1952), Olausson (1961) and Calvert (1983) the saproperls represent deposits formed during periods of bottom water stagnation within the Eastern basin of the Mediterranean throughout the Pleistocene and Pliocene periods, when sea level was lowered by the growth of of the ice sheets. In this work it has been used for sapropels and sapropelic sediments the terminology proposed by Kidd et al (1978),namely that a sapropel is a discrete layer more than 1 cm thick in a pelagic sediment sequence and containing more than 2% by weight, organic carbon. A

sapropelic layer is similarly defined but contains more than 0.5% by weight organic carbon. Both have been deposited under anoxic conditions. Their bulk compositions indicate that sapropels represent mixtures of biogenous

carbonate and terrigenous aluminosilicates, closely similar to those in the inercalated marls and oozes, with variable amounts of admixted organic matter. According to Sigl et. al (1978) and to Deroo et. al (1978) the organic material of these Eastern Mediterranean sapropels including those from Cretan Basin mainly originated from continental sources as was confirmed also by Calvert (1983). This organic material had deposited under fully anoxic water, causing a preferential preservation of deposited carbon producing sapropels (Glenn and Arthur 1985, Calvert and Fontugne 1987).The available analysis for $C_{org.}$ contents for some of the studied cores show high values($C_{org.}$>1,8 %) which are expected for such sapropels (Olausson 1961,Kidd et. al. 1978).On the other hand the data from the Shipboard Scientific Party Leg.42A DSDP (1978) for $C_{org.}$ contents confirm the findings of Thunell et. al.(1984) that lower Pliocene sapropels appear to have a lower $C_{org.}$ content than the upper Pliocene ones. This is consistent with the conclusion of Sigl et. al.(1978) that there is a general decrease in $C_{org.}$ content with increasing age in several DSDP
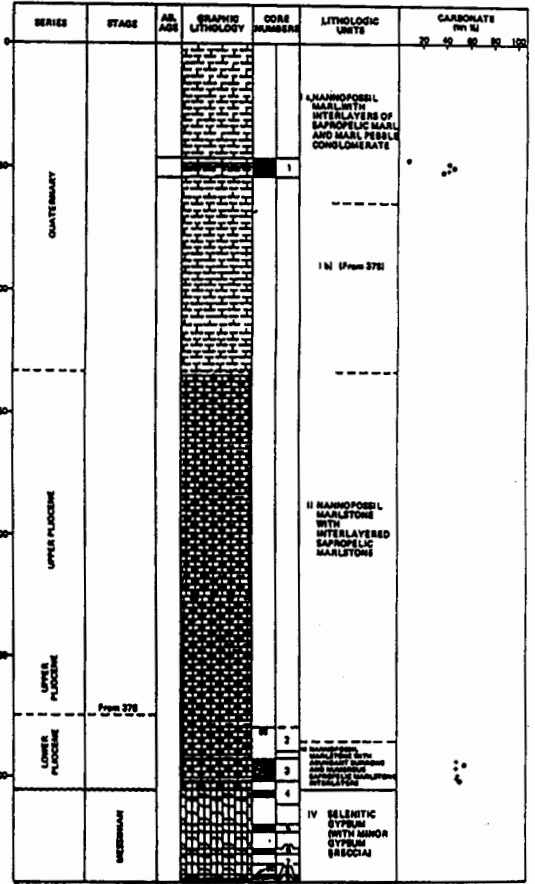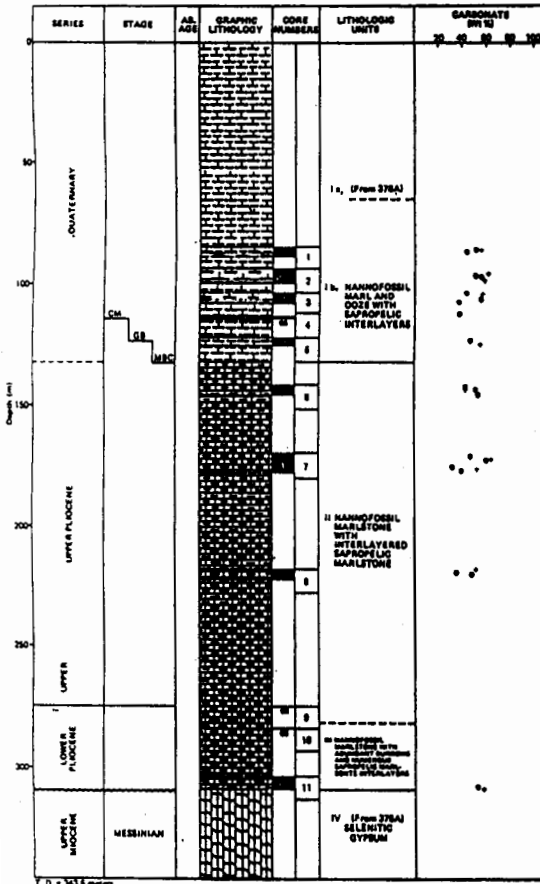

Fig. 2a & 2b: Lithologies at Site 378, core 378 (Fig. A) and core 378a (Fig. B) (From the Shipboard Scientific Party. In Init. Rert eg. 42 1978).

sites within the Mediterranean basin. Furthermore the strong terrigenous character of these sediments does not exclude that a significant component of organic matter has a terrigenous origin too.(Sigl et. al. 1978,Thunell et. al. 1984)

BULK ROCK MINERALOGY

The bulk rock mineralogy data are presented in a semi-quantitative basis and are based on the work of the Shipboard Scientific Party of Site 378 DSDP (1978),Sigl et al (1978), Melieves et. al. (1978) (Table 1).

These data show the following relations:

i) Calcite is the predominant mineral phase in the bulk rock analysis often reaching 60% to 80% provided that all CaO in the bulk chemical analysis(Table4) corresponds to CaCO_3. Most of the calcite has a biogenous authigenic origin.

ii) Clay Minerals is the second most abundant phase ranging between 10% to 60% in the studied samples.

iii) Detrital quartz is the third most abundant mineral phase, followed by detrital fieldspars mainly Na - Feldspars.

iv) Small reflections of Dolomite Halite,and Serpertinite are ubiquitous with Dolomite being more prominent. Below a depth of 170m there is a systematic tendency towards higher contents of Serpentinite and dolomite which also is reflected in chemical analysis by the increase of elements associated with those minerals,especially in Unit III, eg. Mg, Ni, and Cr, for Serpentinite, and Mg for Dalomite. There are also traces of Gypsum.

v) Gypsum is the only phase in sample core no.4-1 (Fig.3a&3b) representing Unit IV. A chemical microanalysis of the core 4-1 sample (Table 2)

Table 1: Bulk mineralogy from sample sediments of site 378 (Holes 378/378A) on a semi-quantitative basis (Data from the Shipboard Scientific Party of Leg. 42A DSDP (1978)

CORES	CALCITE	CLAYS	FELDSPARS	QUARTZ	DOLOMITE	SERPENTINITE	HALITE	GYPSUM	DEPTH(in m.)
1/3/(102-106)	****	**	**	*	tr.	tr.	tr.	✶	50
1/5(74-78)	****	**	**	*	tr.	tr.	tr.	✶	55
1/1(105-109)	****	***	*	*	tr.	tr.	tr.	✶	90
1/1(125-129)	****	**	*	*	tr.	tr.	tr.	✶	93
2/4(22-26)	****	**	*	*	tr.	tr.	tr.	✶	95
2/5(122-126)	****	**	*	*	tr.	tr.	tr.	✶	102
3/3(50-54)	****	**	*	*	tr.	tr.	tr.	✶	110
4CC	****	**	*	*	tr.	tr.	tr.	✶	122
5/1(53-57)	****	***	*	*	tr.	tr.	tr.	✶	125
6/3(93-97)	****	**	*	*	tr.	tr.	tr.	✶	145
6CC	****	**	*	*	tr.	tr.	tr.	✶	150
7/4(74-80)	****	***	*	*	tr.	tr.	tr.	✶	175
7/5(80-84)	****	**	*	*	tr.	tr.	tr.	✶	179
8/2(18-22)	****	***	*	*	*	tr.	tr.	✶	220
3/2(12-16)	****	***	*	*	*	*	tr.	tr.	295
3/6(11-15)	****	**	*	*	*	*	tr.	tr.	302
11/4(22-26)	****	**	*	*	*	*	tr.	tr.	305
11/4(125-129)	****	***	*	*	*	*	tr.	tr.	312
4/1(12-14)	✶	✶	✶	✶	✶	✶	✶	****	315

****=Abundance> 60%
***=Abundance 30-60%
**=Abundance 10-30%
*=Abundance < 10%
t.=Traces
✶=Not Detected

**Table 2**: Microanalysis of samples from core 4/1, Unit IV, Site 378A

| OXIDES	SAMPLE 1	SAMPLE 2
SiO2	N.D	N.D
Al2O3	O15	O16
MgO	O36	O32
CaO	33.85	33.72
FeO	N.D	N.D
Na2O	N.D	N.D
K2O	N.D	N.D
TiO2	N.D	N.D
MnO	N.D	N.D
Cr2O3	N.D	N.D
NiO	N.D	N.D
SO3	45.46	45.49
TOTAL	79.82	79.69
N.D=Not detected		

confirms the XRD findings that it represents a pure gypsum.

vi) According to Emelyanov et al(1978) authigenic sulfides are the dominant heavy minerals and constitute the 75-93% of the heavy mineral suite,whereas the detrital heavy minerals include hornblende, amphiboles, epidotes, micas, garnets and opaque iron minerals. The reducing conditions revealed by most of site 378 sediment, supports the presence of authigenic sulfides.

vii)The monotonous mineralogical assemblage especially after Pliocene (Units I and part of Unit II) suggests, that the sources of terrigenous and biogenic materials have not changed since the late Pliocene. However, in Unit III there is a considerable increase in serpentine and talc con-
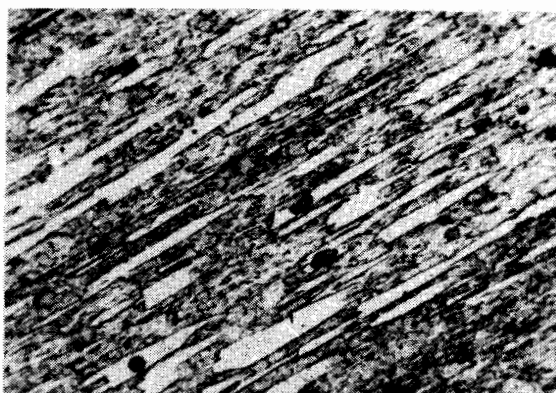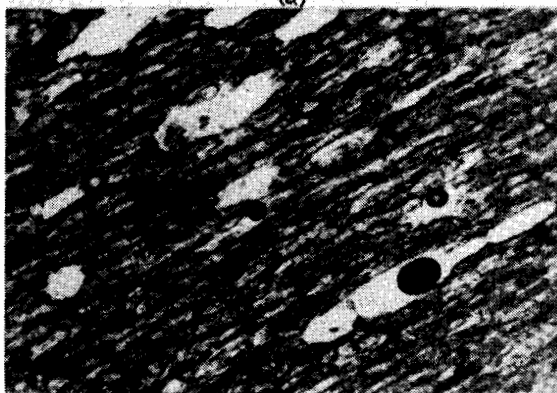
Fig. 3(a) & 3(b). Gypsum crystals from sample 4-1 of Unit IV under scaning electron microscope. It is obvious their elongated shape. They grow upwards in rosette like clusters. There is also an abundance of void spaces between the clusters.

tent a fact which also is reflected in the geochemistry of samples coming from this Unit. This suggests that between early to late Pliocene the detrital input was enriched with ultramafic to mafic terrigenous material. The alteration products of ultrabasic and basic rocks occuring on the islands of Karpathos and Rhodes (Varnavas 1989) is a very probable source of this terrigenous material.

CLAY MINERALOGY

The Clay Minerals relations were further studied in the Institute de Mineralogie of the University of Liege. The <2μ fraction was examined by X-ray diffraction technique . A first run was completed in rontine through three usual tests (air dried, solvated with ethlene glycol vapours, heated to 500°C). Afterwards some samples were subjected to bostreatment kationic saturations in order to achieve a more accurate identification particularly at the level of swelling clay components.

Oriented mounts for X-R-diffraction were prepared by leaving dilute aqueous suspensions of the <2μ fraction to dry in air on glass slides. X-ray diffractograms were obtained using a Philips diffractometer with Cuka radiation. Semiquantitative determinations were carried out by using the techniques applicable by J.THOREZ in the Institut De Mineralogie in the

Table 3: Clay mineralogy by XRD of site 378/378A sediments (On a semi-quantitative basis)

MINERALS	MICA/ILLITE	SMECTITE	CHLORITE	KAOLINITE	MIXED LAYERS}	TALC	VARIOUS MINERALS*	AMPHIBOLES	DEPTH(in m.)
CORES									
1/3(102-106)	48	5	7	18	14	6	3		50
1/5(74-78)	42	7	8	20	12	6	5		55
1/1(105-109)	58	12	10	7	10	3	2	Tr.	90
1/1(125-129)	56	8	9	8	17	3	Tr.		93
2/4(22-26)	60	3	18	6	6	6	3		95
2/5(122-126)	57	3	14	8	7	9	3		102
3/3(50-54)	61	2	5	22	6	1	3		110
5/1(53-57)	51	3	4	22	5	7	7		125
6/3(93-97)	54	5	6	24	8	1	3		145
6CC	47	4	6	27	8	8	1		150
7/4(74-80)	53	2	9	13	10	7	5		175
7/5(80-84)	56	6	5	20	8	5	2		179
8/2(18-22)	42	4	7	17	16	9	5		220
3/2(12-16)	54	3	3	22	8	8	2		295
3/6(11-15)	51	1	3	24	8	11	2		302
11/4(22-26)	59	2	5	14	8	9	3		305
11/4(125-129)	58	4	4	13	10	9	3		312

*The mixed layers are mainly CHLORITE/ILL. (14C/I) and to a lesser degree ILL/SCMEC.
**The various minerals include mainly Palygorskite, Serpentinite and Clinoptilolite.
Tr.=Traces

University of Liege.

The results of this semiquantitative analysis are presented in TABLE (3). The main conclusion derived from this analysis are given below.

a) The predominant mixed layers are CHLORITE/SMELTITE (14C/I) and to a lesser degree ILL/SMCT. In general they have low contents and more or less are uniform throughout the boreholes.

b) Illite is the dominant clay mineral having a rather uniform distribution throughout the boreholes.

c) Kaolimite contents are quite high and rather uniform throughout of the boreholes.

d) Chlorite contents are rather low and there is a weak tendency of having higher contents with decreasing depth.

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e) The amount of smectite is generally low with a weak tendency of having higher contents with decreasing depth.

f) Talc is a very important mineral in the <2μ. fraction showing quite often values higher than smectite. There is a tendency for high talc values to increase at larger depths (Fig.4) supporting the suggestion that the

Fig. 4: Moving average data for Talc % (Table 3) versus Depth, based on 18 data points and a moving period of 2. It is evident that after 150 m and with increasing depth there is a strong tendency of increase the Talc %.

detrital input reaching the basin during lower Pliocene mainly, was enriched in terrigenous components of ultramafic origin.This tendency is supported by chemical data too as shown below.

g) In a few samples especially in the lower part of the boreholes traces of palygorskite are present. There are also minor reflections of amphiboles, serpentinite and sometimes clinoptilolite in some samples which can not be quantified.

The presence of appreciable amounts of mixed layer minerals, the very low content of palygoskite the low contents of smectite in combination with high contents of illite (mainly) and kaolinite all seem to confirm the findings and conclusions by Sigl et.al (1978) "that clay minerals brought into the sea may be weathered by an euxinic environment, perhaps with the exception of kaoliniten under the influence of organic matter contained in sapropels". The above date confirm also the findings of the same authors that the clay minerals in the sapropelic sediments of site 378/378A in North Cretan basin suffered increased alteration under the influence of organic matter (stage 3 to stage 4 of alteration according to Sigl et. al (1978) which produced mixed layers after the degradation of clay minerals). According to the same authors this alteration mainly takes place at the water-sediment interface whilst no diagenetic, modification happens after burial. This is a broader characteristic of the Pliocene-Pleistocene Mediterranean Sapropels according to Thunell et. al.(1984) who attributed this characteristic mineralogy to an in situ diagenetic alteration of original clays in an anaerobic environment and not to the clasical burial diagenesis. This is quite possible in site 378/378A where the maximum depth of burial (approximately 315m) is rather low in order to have significant diagenetic changes in clay minerals.

GEOCHEMISTRY OF THE SEDIMENTS AND ORIGIN OF THEIR MOST IMPORTANT CHEMICAL CONSTITUENTS

In the present study major and minor elements were determined by an X-Ray Fluorescence Spectrometer (Philips PW 1400) in Southampton University, Department of Geology. Details concerning the ca libration processes, limits of detection, precision and accuracy for each element as well as the operational conditions are given by Papavassiliou (1979) and Baig (1982).

The bulk chemical composition of site 378/378A sediments is given in TABLE 4.

In order to give, a meaningfull interpretation of the interelement relationships and evidences concerning the origin of the most important

chemical constituents a combination of a pure geochemical approach and statistical methods including correlation coefficient matrix were employed. The results from these two methods are given in Tables 5&6.

General chemical characteristics of the sediments.

In order to normalize the values for the nonbiogenic part of the sediments (removing biogenic carbonate or opal) values of elements such as Al, Ti, Mg, Na, K, Fe are commonly reported as the atomic ratios (DONNELLY et.al 1977) for Ti/Al, Mg/Al, Fe/Al, etc. Also some other important ratios which can may reveal the chemical origin of important constituents of the sediments such as Fe/Mn were calculated and are presented in Table (6).Also,

Table 4a: Major elements composition of sediments from hole 378/378A, DSDP, in weight %.

ELEMENTS	Si	Ti	Al	Fe	Mg	CaO%	CaCO3%	Na	K	Mn	P	DEPTH(in m.)
1\3(102-108)	14.15	0.27	5.84	3.74	3.32	39.17	48.91	1.32	0.44	0.290	0.0700	50.00
1\5(74-78)	16.76	0.29	5.48	3.06	3.51	40.32	71.96	1.35	0.60	0.30	0.09	55.00
1\1(105-108)	18.57	0.32	7.01	3.41	3.11	32.21	57.49	1.36	0.84	0.26	0.11	90.00
1\1(125-129)	16.16	0.26	5.54	3.31	3.20	42.02	75.00	0.92	0.31	0.32	0.11	93.00
2\4(22-26)	14.53	0.26	5.41	2.58	2.85	46.82	83.20	0.78	0.58	0.23	0.09	95.00
2\5(122-126)	17.25	0.26	6.16	3.30	3.06	37.84	67.74	1.27	0.70	0.16	0.07	102.00
3\3(50-54)	15.09	0.26	6.23	3.06	2.53	44.23	75.94	0.92	0.31	0.20	0.10	110.00
4CC	16.77	0.26	6.46	3.61	3.11	35.86	60.47	1.59	0.86	0.14	0.06	122.00
5\1(83-87)	17.52	0.27	6.92	3.43	3.16	34.55	61.68	1.81	0.39	0.16	0.10	125.00
6\3(93-97)	15.71	0.26	6.21	3.17	3.82	40.93	73.05	1.10	0.59	0.15	0.10	145.00
6CC	13.09	0.24	5.21	2.84	2.74	49.88	89.02	0.91	0.56	0.26	0.06	150.00
7\4(74-80)	17.90	0.25	6.41	3.36	3.14	36.71	65.52	1.36	0.40	0.16	0.06	175.00
7\5(80-84)	16.75	0.26	5.97	2.83	2.80	41.82	74.84	1.07	0.55	0.16	0.09	180.00
8\2(18-22)	24.35	0.20	4.66	2.51	2.07	28.84	51.47	1.91	0.87	0.05	0.07	220.00
3\2(12-16)	18.27	0.33	6.03	4.49	3.83	32.43	57.86	1.29	1.05	0.00	0.07	295.00
3\6(11-15)	17.43	0.34	5.90	3.30	3.07	38.40	66.53	1.02	0.58	0.00	0.10	302.00
11\4(22-26)	16.53	0.31	5.76	3.35	3.30	40.37	72.05	0.99	0.57	0.66	0.13	305.00
11\4(125-129)	21.29	0.35	6.77	5.13	4.67	22.59	40.32	1.82	1.25	0.05	0.14	312.00

Table 4b: Minor elements composition of sediments from hole 378/378A, DSDP. Minor elements in ppm.

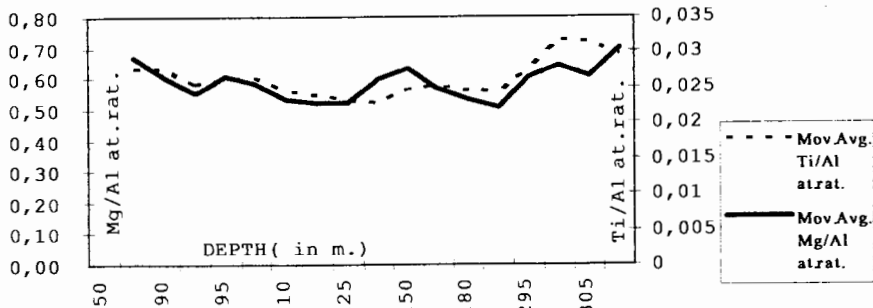| ELEMENTS	Cr	Ni	V	Zn	Ba	La	Ce	Nb	Sr	Y	Zr	Nb	Th	U	Pb	DEPTH(in m.)
1\3(102-108)	173	238	95	72	469	29	46	0	1.216	26	121	8	0	0	3	50.00
1\5(74-78)	140	122	84	59	176	32	53	11	1.119	30	147	11	3	0	14	55.00
1\1(105-108)	169	155	106	72	244	40	40	22	858	29	141	11	0	0	9	90.00
1\1(125-129)	146	154	92	64	225	59	70	0	1.273	29	125	8	0	0	3	93.00
2\4(22-26)	150	173	89	58	157	28	45	17	1.471	32	142	10	4	2	8	95.00
2\5(122-126)	186	215	108	16	502	31	56	16	1.287	33	130	10	0	0	13	102.00
3\3(50-54)	140	130	90	60	183	43	16	0	1.187	27	115	8	0	0	1	110.00
4CC	162	145	121	75	389	32	32	13	837	26	116	9	0	0	5	122.00
5\1(83-87)	154	169	110	78	504	31	41	0	893	24	102	7	0	0	0	125.00
6\3(93-97)	173	210	213	70	455	34	65	1	1.194	28	116	8	0	0	4	145.00
6CC	128	124	81	55	166	22	37	4	1.532	26	129	9	0	0	17	150.00
7\4(74-80)	159	139	109	67	311	50	50	0	1.051	26	116	8	0	0	2	175.00
7\5(80-84)	143	122	86	57	177	36	41	7	1.297	24	129	8	0	0	5	180.00
8\2(18-22)	167	173	324	72	1.045	22	52	19	972	29	103	6	0	0	3	220.00
3\2(12-16)	326	302	124	101	439	16	47	24	955	28	120	9	0	0	3	295.00
3\6(11-15)	224	191	110	65	154	23	56	17	1.091	27	135	11	0	0	13	302.00
11\4(22-26)	241	207	104	70	191	21	67	0	943	25	104	8	0	0	9	305.00
11\4(125-129)	374	350	156	120	744	33	53	23	466	30	102	9	0	0	0	312.00

Fig. 5: Moving average data for Mg/Al & Ti/Al (expessed as atomic ratios) versus depth. See Fig. 4 for more comments.

mean ratios for Shale (Krauskopf 1967), terrigenous material in ocean basins (Bostrom et.al.1976) and deep sea clays (Turekian & Wedephol 1961) are given for comparisons.

Table 5: Interelement relations in sediments from site 378/378A) Correlation coeffi-
cients ma based on 18 analysed samples.

Correlations coefficients r>0,708 are significant at the 0,001 significant level
Correlations coefficients 0,59<r<0,708 are significant at the 0,001 significant level
Correlations coefficients 0,543<r<0,59 are significant at the 0,02 significance level
Correlations coefficients 0,46<4<0,543 are significant at the 0,05 significance level
Correlation coefficients r<0,46 are not significant
Values within parenthesis are negative

Table 6: Important ratios from site 378/378A DSDP sediments. Fe/Al, Cr/Al, Mg/Al, Ti/
Al & Ni/Al are expressed as atomic ratios*

CORES	Fe/Al	Cr/Al	Fe/Ti	Ni/Al	Mg/Al	Ti/Al	Si/Al	Fe/Mn	DEPTH(in m.)	UNIT
1\3 (102-106)	0,304	0,0015	13,85	0,0018	0,62	0,026	2,93	12,20	50	*
1\5 (74-78)	0,272	0,0013	10,62	0,0010	0,71	0,03	3,06	10,27	55	*
1\1 (105-109)	0,234	0,0013	10,66	0,0010	0,49	0,026	2,71	13,11	90	*
1\1 (125-129)	0,274	0,0013	12,73	0,0012	0,61	0,025	2,77	10,34	93	I
2\4 (22-26)	0,264	0,0014	11,38	0,0015	0,61	0,027	2,74	12,87	95	*
2\5 (122-126)	0,266	0,0016	12,11	0,0016	0,56	0,026	2,80	21,19	102	*
3\3 (50-54)	0,237	0,0012	11,77	0,0010	0,50	0,024	2,42	15,30	110	*
4cc	0,270	0,0013	12,89	0,0010	0,53	0,024	2,91	25,79	122	*
5\1 (53-57)	0,239	0,0012	12,70	0,0011	0,51	0,022	2,58	21,44	125	**
6\3 (93-97)	0,247	0,0014	12,19	0,0016	0,68	0,024	2,53	21,13	145	**
6cc	0,273	0,0013	12,25	0,0011	0,58	0,026	2,51	11,30	150	II
7\4 (74-80)	0,255	0,0013	12,07	0,0010	0,54	0,025	2,79	21,12	175	**
7\5 (80-84)	0,229	0,0012	10,88	0,0009	0,52	0,025	2,81	15,72	180	**
8\2 (18-22)	0,260	0,0019	12,55	0,0017	0,49	0,024	5,23	31,37	220	**
3\2 (12-16)	0,360	0,0028	13,61	0,0023	0,70	0,031	3,03	49,88	295	***
3\6 (11-15)	0,275	0,0020	9,88	0,0015	0,58	0,033	2,95	37,33	302	***
11\4 (22-26)	0,280	0,0022	10,81	0,0016	0,63	0,03	2,91	41,87	305	III
11\4 (125-129)	0,366	0,0029	14,66	0,0024	0,77	0,029	3,14	102,6	312	***
SITE 378/378A AVG.VALUES	0,272	0,0016	12,09	0,0014	0,59	0,026	2,93	26,38		
AVG.SHALE(KRAUSKOPF 1967)	0,280	0,00050	10,44	0,0006	0,11	0,027	3,20	55,29		
AVG.T.M(BOSTROM et.al.1976)	0,290	0,00064	10,21	0,0005	0,22	0,033	2,95	55,68		
AVG.DEEP SEA CLAYS (TUREKIAN&WEDEPHOL 1961)	0,373	0,00056	14,13	0,0012	0,28	0,031	2,86	9,70		

* In order to normilize the values for the non-biogenic sediments removing biogenic
carbonate or opal) values of Mg, Cr, Fe, Ni & Ti are reported as the atomic ratios
of Mg/Al, Cr/Al etc. (Donnelly and Wallace 1976).

The study of the chemical data in Table(6) and the matrix of correlation
coefficients in Table (5) shows that there are two co-varrying groups of
elements representing different types of terrigenous alaminosilicates,
and a smaller but significant group representing the biogenous sapropelic
phase on one hand and the biogenous caleareous phase on the other hand.

Thus the very high to high degree of correlation between Al, Ti, Mg, Fe,
Cr, Ni, Zn & P represents an aluminosilicate phase which, except the
chlorite and the significant chlorite/ smectite mixed layer contains also,
significant amounts of detrital minerals having a mafic to ultramafic
origin. Indeed the presence of significant amounts of serpentinite and
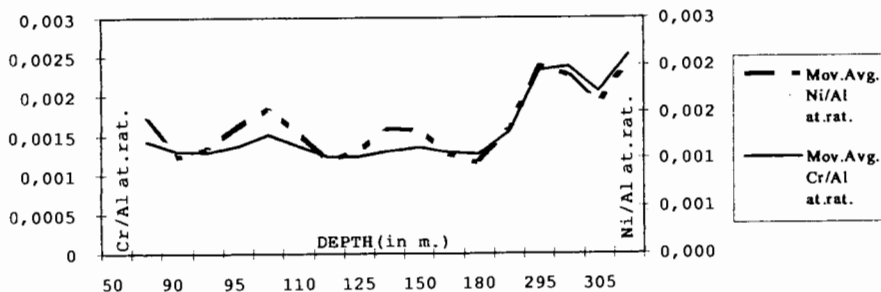talc especially in Unit III confirms the above observations. This phase is

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Fig. 6: Moving average data for Cr/Al &Ni/Al (expressed as atomic ratios) versus depth. See Fig. 4 for more comments.
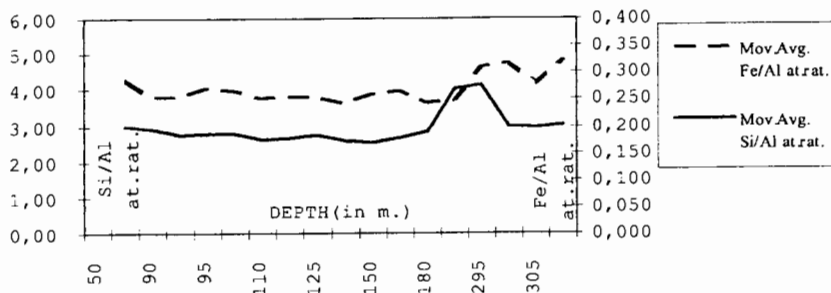

Fig. 7: Moving average data for Si/Al & Fe/Al (expressed as atomic ratios) versus depth. See Fig. 4 for more coments.

becoming more important with depth below the middle of Unit II and shows its higher contribution in Unit III. The significant increase of the Fe/Al, Mg/Al, Cr/Al, Ni/Al and the noticeable increase of the Ti/Al atomic ratios started within Unit II after 180m sub-bottom depth and showing highest values in Unit III (after 220m sub bottom depth, (Figs 5,6 & 7) fully supports this observation. It is evident that the detrital input reaching sites 378/378A was enriched with terrigenous components of mafic to ultramafic origin which becomes even more obvious between early to late Pliocene.

This is quite obvious too with the use of the modelling the chemical composition of the sediments. This is a method proposed and used succesfully by Bostrom et. al.(1974),Bostrom et. al.(1976),Bostrom et. al.(1990) (Fig.8).This method is essentially a target factor analysis (Malinowski 1991),that is, real factors are used instead of abstract ones as in the conventional factor analysis.

From these figures it is clear that a sediment model composition approaching a terrigenous material consisting of continental crust matter enriched in ultramafic and mafic material can explains better the composition of Unit III samples compared with the normal terrigenous material reaching the ocean basins,See Fig.8 for more details. This figure implies that only a small proportion of V and Ba could be associated with other non - terrigenous components(i.e biogenous) within these sapropelic sediments.

The high to very high degree of correlation between Si, Na, Ba, V, K and Rb on the other hand represents the second aluminosilicate phase with the biogenous sapropelic phase. These correlations are probably accounted for
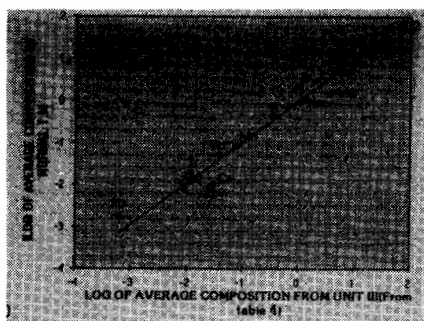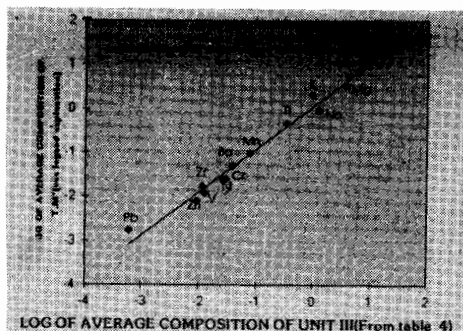
(a)   (b)

Figs.8(a)&(b): Modelling sediments from Unit III from Site 378 according to the method by Bostrom et.al.(1974), Bostrom et.al.(1976), Bostrom et. al.(1990).The diagonal line represents the best fit to the most important major and trace elements. All values represents log10(concentration %). Elements below to the diagonal line must have an additional source to the (Y) (vertical) ordinate of the graph. Elements above the diagonal line represents compo- nents which possibly were partially lost from the sediments during the diagenesis or before the sedimentation of the biological material (Bostrom et.al.1974).From these figures it is obvious that whilst the normal terrigenous material (T.M) reaching the ocean basins can explain satisfactory the origin of the most elements from Unit III, it can not explain satisfactory the origin of Mg, Ni and Cr (Fig.8a).These elements need an additional source to this model. It is proposed a different model of terrigenous material (T.M*)which is prevailing in the area of S. Aegean and Cretan Basin. This terrigenous material consists of 75 % shale and 25 % of continental crust as the normal T. M, with the difference that the local continental crust around the areas of S. Aegean and Crete is enriched in mafic and ultramafic material i.e having the composition 45 % average granite+25 % average basalt+30 % average ultramafic material instead the composition of the normal average continen- tal crust consisted of 50 % average granite+50 % average basalt (Krauskopf 1967).As is obvious from Fig.8b a such model can explain satisfactory the origin of Mg, Ni, and Cr too. On the other hand Pb and K in both cases it seems that are in deficiency and partially were lost during the early diagenesis.

by the presence of mica/illite which is the most abundant clay mineral especially in the <2µ. fraction(Table 2). However the strong correlation between Si, Na, V, Ba is partly attributed to the biogenous sapropelic phase rich in organic material. The association of elements like V and Ba, with organice material derived mainly from planctonic sources is well established especially in areas of high biogenous productivity (Calvert 1976, Bostrom et al 1976). The fact that biogenous siliceous components are present and sometimes in considerable amounts in the 378/378A sediments according to the Shipboard Scientific Party of Site 378/378A Cretan Basin, supports these associations. However the Si/Al atomic ratios from examined sediments (Table6) shows that a significant bioegnous siliceous component i.e. Si/Al 3 according to Bostrom and Fisher 1971, Bostrom et al 1976,is present only in Unit III (3.32) after the 220m sub-bottom depth) as it is evident also in Fig (7).

Finally the very strong positive correlation of CaCO3 with Sr repre- sents the biogenous caleareous phase which mineralogically also is promi-

nent. The geochemical association of Sr with calcite is well known. The medium to strong positive correlate between Mn, CaCO3 and Sr could be explained by the fact that part of Mn in 378/378A sediments is present as manganese (II) carbonate or a mixed calcium-manganese carbonate a phase found in mildly recuding and oxidizing sediments where there is free oxygen in the overlying water (Calvert 1976).Similar associations within sapropelic seidments from the Black Sea have been reported by Calvert and Batchelor (1978).

The Fe/Mn ratio (Table 6) and its plot against depth (Fig.9) is also worthwile to comment. It is evident from Table(4) that Mn contents in-crease considerably towards the top of drillhole 378/378A, especially in the upper part of Unit I. This increase corresponds to the considerable decrease, of Fe/Mn ratio towards the top of the borehole especially in the upper part of Unit I (Table 6)& Fig(9). In conclusion it is clear that the
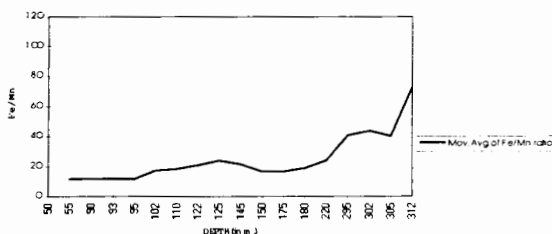

Fig. 9: Moving average data for the Fe/Mn versus depth. (See Fig. 4 for more comments). The significant decrease of this ratio with decreasing depth is obvious (See text for explanations)

top sediments of site 378/378A are considerable enriched in Mn compared to various materials that have reached the sea such as average Terrigenous material (Bostrom et. al 1976), average shale (KRAUSKOPF 1967), average eastern Mediterranean sediments (Fe/Mn: 34.06 Show and Bush 1978) and Aegean Shelf Sediments (Fe/Mn:50 Smith and Cronan 1975).

This Mn enrichment is hard to attribute to the classical mechanism described by Lynn and Bonatti (1965) which usually operates in a more oxidizing environment whereas the physicochemical conditions in the upper part of drillholes 378/378A are reducing as indicated by the deposition of sapropelic interlayers within the sediments.

These findings therefore tend to support the conclusions of Varnavas(1989) and Bostrom and Arvanitides(1994) that the submarine hydrothermal metallogenesis associated with the collision of two plates in the southern sea region is responsible of Mn and other metals (Ba, Zn, etc) in the surface sediments in the fore-arc basins such as Maleas, Iraklion (where site 378 is located) and Karpathos.

Varnavas(1989) presented a number of data (i.e. Mn, Fe, Zn, Cu, Ba, P) and other evidences (i.e. the marked enrichement of Mn in the fore-arc basins of the sea of Crete relative to the trenches of the Aegean,which coincides with significantly higher heat flow values in the former that in the latter area) which strongly support the suggestion of the existence of the hydrothermal activity which is already well established in other areas too i.e. Santorini. The same author believes that the findings of the work of Emelyanov et. al(1978) that 75% to 93% of the heavy mineral fraction in the sediments from the under study Site(DSDP 378) drilled in the Iraclion

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basin are sulfides, confirm his conclusion. Bostrom and Arvanitides(1994) found furthermore that some 98% of all volcanic Mn and 66% of all volcanic Ba have been lost selectively from the Santorini Caldera thus overflowing into the Aegean. VARNAVAS (1989) concluded also that "because the sea of Crete is under the process of extention with parallel injections of magmatic material along the planes of normal faults (JONGSMA et.al/1977) the metal-bearing hydrothermal solutions resulting from the leaching of this material are reponsible for the metal enrichments found in those sediments".

Furthermore the author confirms that the high contents of Ni and Cr not only in the surface sediments from Cretan Basin but especially around the land of Karpathos are related to the alteration of detrital products of basic and ultrabasic rocks occuring on the island of Karpathos and Rhodes. It is obvious that these rocks and the Cretan mafic rocks explain the enrichment of elements like Mg, Ni, Cr in the terrigenous material reaching site 378(Emelyanov et-al.1978, Coumes and Boltenhagen(1978). Data from Table 6 and Fig.8 suggest that this detrital input was particularly important in Unit III (and partly in Unit II) i.e. between early to late Pliocene. Later on there was either a compositional change in the terrigenous material or more probably, a dilution of this material by other phases due to the considerable higher sedimentation rates observed in Units I and II (See also introduction).It should be recalled however that the nature of the volcanic products may vary in space and time depending on the source depth at a subdacting slab.(Mitropoulos,1993).

CONCLUSIONS

The mineralogical and geochemical data suggest the following conclusios:

a) Calcite, clay minerals, detrital quartz and Na-feldspars(in descending order) are the major minerals, whilst dolomite and serpentinite (especially within Unit III) are important minor minerals.

b) Illite is the dominant clay mineral in the <2μ fraction followed by chlorite/ smectite mixed layers and kaolinite. Talc is a very important mineral and increases with depth below 170 m. And especially within Unit III.

c) The euxenic environment that formed the sapropelic sediments had a considerable effect on clay mineralogy. The high contents of mixed layer minerals, illite and kaolinite and the low contents of smectite confirm the conclusions reached by Sigl et. al.(1978) that clay minerals brought into the sea are weathered by organic materials in the reducing environment except possibly for kaolinite and illite.

d) The selenitic gypsum in Unit IV is a pure gypsum a product of the Messinian salinity crisis that affected the most of Mediterranean basin and resulted in the development of thick evaporites.

e) Most of the major and minor elements have a terrigenous origin and mainly from the Rhodes - Karpathos - Crete drainage system. During the upper Pliocene and the especially during the lower Pliocene(Unit III),the detrital imput was enriched in ultramafic to mafic material. The low sedimentation rates in Unit III, compared with Units I&II underlines this tendency. This has been established by:

i) The significant increase of the Fe/Al,Ti/Al,Ni/Al and Cr/Al atomic

ratios during the upper Pliocene and especially in lower Pliocene(Unit III)below 170 m.

ii)The strong positive correlations between Fe, Mg, Ti, Ni and Cr.

iii)The modelling of Unit III sediments chemical composition with terrigenous material having a continental crust component enriched in mafic and ultramafic material. This modelling well explains the chemical composition of these sediments, especially for Mg, Ni and Cr compared with the normal terrigenous material reaching the ocean basins (Bostrom et. al. 1974,1976 & 1990).

iv)The increase of serpentinite in, bulk mineralogy, and the significant increase of talc in the <2μ. fraction especially in Unit III.

The most probable source of this differentiated terrigenous material are the basic and ultrabasic rocks occuring in Karpathos and Rhodes as well as the Cretan ophiolites.

f)The statistical data presented confirms the conclusion that a proportion of Si, Ba and V has a biogenous origin and is associated with the sapropelic organic material-reach sediments that are abundant in Site 378.The existence of abundant siliceous microfossils is reflected in the considerable increase of the Si/ Al ratio, especially below 200 m. with ratios >3 which according to Bostrom and Fisher(1971),Bostrom et. al.(1976) suggest the existence of much biogenous silica.Also association between biogenous CaCO3 and Sr has been observed.

g)The geochemistry of Mn story leads to an important conclusion. The high Mn contents at shallow depths (i.e significant decrease of the Fe/Mn ratio with decreasing depth) in combination with the existence of reducing environment within the sapropelic sediments (which excludes the precipitation of Mn oxides) confirms previous conclusions by Varnavas 1989 that a submarine hydrothermal activity operated at the plate boundaries of Iraclion, Karpathos fore-arc basins and on the Aegean island arc, is responsible for this Mn enrichment and partly for Zn enrichment in the Unit I(late Quaternary)sediments.

This conclusion is supported by the fact that the important submarine volcanic activity in the broader area was intence especially during the late Quaternary when the southern part of the Aegean Island arc (Santorini area) became active, Bostrom and Arvanitides (1994). Emelyanov et. al.(1978) concluded from a study of the heavy mineral composition of the Mediteranean Neogene sediments, hat the volcanic constituents on site 378 sediments became important during the late Quaternary. It seems furthermore likely that some Mn is present as Mn (II) carbonate or mixed calcium-manganese phase.

h)The organic carbon data confirm previous conclusions that the organic mater might have partly a significant terrigenous character whilst the lower Pliocene sapropels appear to have a lower organic carbon content than the upper Pliocene sapropels.

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