

Sapropels
Mediterranean
Geochemistry
Gypsum
Stagnation

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Geochemistry of Pleistocene sapropels and associated sediments from the Eastern Mediterranean

S.E. Calvert

Department of Oceanography, University of British Columbia, Vancouver, British Columbia V6T 1W5, Canada.

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ABSTRACT

The mineralogical and chemical composition of Pleistocene sapropels and associated marl oozes from sites 125, 126, 127, 128 and 130 of Leg 13 of the Deep-Sea Drilling Project have been examined. The sapropels are black, pyritic, clay-rich sediments containing up to 20 and 53% by weight organic carbon and CaCO_3 , respectively. They also have relatively high Ba, Cu, Mo, Ni and Zn contents and measurable quantities of gypsum, the latter probably formed from sulphate ions released from oxidised pyrite. The organic material has a higher C/N_{org} ratio than that in the associated marl oozes. The bulk compositions of the sapropels can be explained by the admixture of organic material and carbonate and aluminosilicate phases closely similar to those in the associated marl oozes.

From estimates of the carbon accumulation rates and comparisons with the Black Sea, it is suggested that the sapropels were not formed as a direct consequence of the formation of stagnant bottom-water in the Eastern Mediterranean during glacial retreat. They are more likely a consequence of increased primary production as a result of the reversal in circulation in the Mediterranean brought about by excessive flood water runoff via the Nile River system. Further detailed measurements of the accumulation rates of the youngest sapropel and its associated facies are required to test the generality of these conclusions.

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RÉSUMÉ

Géochimie des sapropels du Pléistocène et des sédiments associés de Méditerranée orientale

La composition minérale et chimique des sapropels du Pléistocène, provenant des sites 125, 126, 127, 128 et 130 du Leg 13 du « DSDP » (Deep-Sea Drilling Project), ainsi que des marnes qui leur sont associées, a été examinée. Les sapropels sont des sédiments noirs, riches en pyrite et en argile, et contiennent jusqu'à 20%, en poids, de carbone organique et 53% de CaCO_3 . Ils sont relativement riches en Ba, Cu, Mo, Ni et Zn et contiennent des quantités mesurables de gypse, ce dernier étant probablement formé à partir du sulfate produit par l'oxydation de la pyrite. La matière organique a un rapport C/N supérieur à celui des marnes associées. La composition globale des sapropels peut être expliquée par un mélange de matière organique, de carbonates et d'aluminosilicates ressemblant fort à ceux trouvés dans les marnes associées. Les estimations de la vitesse d'accumulation du carbone et la comparaison avec la Mer Noire, suggèrent que les sapropels ne sont pas une conséquence directe de la stagnation des eaux profondes dans le bassin oriental de la Méditerranée pendant le retrait des glaces. Il est plus probable qu'ils résultent d'une augmentation de la production primaire à la suite du renversement du sens de circulation causé par une forte augmentation du débit du Nil. Des mesures détaillées de la vitesse d'accumulation du sapropel le plus récent ainsi que du « faciès » qui lui est associé, sont nécessaires pour généraliser ces conclusions.

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INTRODUCTION

Discrete centimetre- to decimetre-thick horizons of fine-grained, organic-rich sediment, known as *sapropels*, occurring in sequences of nanno-fossil oozes and marls, were discovered by piston coring in the eastern basin of the Mediterranean during the Swedish Deep-Sea Expedition (Kullenberg, 1952). Their distribution and general compositions have been described by Olausson (1960) and the detailed regional stratigraphy of several sapropel horizons recovered in other cores has been established by McCoy (1974), Hieke (1976) and Ryan and Cita (1977).

According to Kullenberg (1952) and Olausson (1961), the sapropels represent deposits formed during periods of bottom water stagnation in the eastern basin of the Mediterranean when sea level was lowered by the growth of the Pleistocene ice sheets, much as Bradley (1938) had earlier predicted. This view has largely prevailed (see Ryan, 1972; McCoy, 1974; Ryan, Cita, 1977), there being minor variations in the precise mechanism causing the stagnations. Up to 12 horizons of sapropel or sapropelic sediment have been recorded in the Holocene and Pleistocene sections in the Mediterranean (McCoy, 1974; Cita *et al.*, 1977), the youngest being 7,000-9,000 years old (McCoy, 1974) and the oldest being approximately 400,000 years old (Cita *et al.*, 1977).

Sapropelic sediment is also known to occur in the Black Sea (see Strakhov, 1971; Ross *et al.*, 1970); the youngest occurrence, dated by radiocarbon methods at 3,000-7,000 years BP, was deposited when anoxic conditions became established due to the influx of saline water through the Bosphorus into the oxic lake which existed during the maximum glacial stages (Degens, Ross, 1972). The composition of this unit has been described by Degens *et al.* (1970), Ross and Degens (1974) and Hirst (1974).

Older sapropelic sediments have been recovered in the Mediterranean on Legs 13 and 42A of the Deep-Sea Drilling Project (Ryan *et al.*, 1973; Hsü *et al.*, 1978) and

in the Black Sea isolated occurrences of such deposits were sampled on Leg 42B (Ross *et al.*, 1978). They are in many respects similar to the younger sapropels sampled by conventional coring methods. The old Mediterranean deposits are also considered to represent the sediments formed during stagnant phases of the eastern basin throughout the Pleistocene and Pliocene epochs.

This paper deals with the chemical composition of some of the sapropels sampled during Leg 13 of the Deep-Sea Drilling Project (Fig. 1). Although studies of the micropalaeontology, the mineralogy and the bulk composition of the Leg 13 sapropels are available, chemical information is sparse. More complete chemical data will allow a direct comparison between the Mediterranean sapropels and those occurring in the Black Sea, where their formation at particular stages in the hydrographic evolution of the basin is well-established, and will provide data with which a comparison can be made between these deposits and other modern organic-rich sediments.

Nesteroff (1973) has provided a description of the sapropels and sapropelic sediments recovered during Leg 13. The sapropel beds are black in colour and generally 1 to 3 cm thick (although much greater thicknesses are listed in Table 1 of Nesteroff (1973), it appears that they must refer to "sapropel sequences" rather than discrete sapropel beds). The sapropels generally overlie grey marl oozes with sharp contacts, and are succeeded by marl oozes or nannofossil oozes, also with sharp contacts. They may contain thin laminae of foraminiferids, which are wholly planktonic and include many apparently abnormal forms.

Two main types of sapropels can be distinguished. Pelagic sapropels are found on topographic highs and are present in sequences of normal pelagic nannofossil oozes. Turbidite sapropels occur in the sedimentary fill of trenches and depressions and are found in nannofossil and foraminiferal sediments showing abundant evidence of current reworking. These two categories of sapropel have been largely confirmed by Kidd *et al.* (1978), although the range of minor structures recorded in the occurrences from Leg 42A is much greater than that described by Nesteroff (1973).

The sapropel samples available for this study are from the Pleistocene *Gephyrocapsa oceanica* and the *Pseudomiliana lacunosa* zones (Fig. 2). The Glomar Challenger cores did not sample the Recent and Pleistocene sapropels that have been recovered by piston-coring. The terminology of sapropels and sapropelic sediments adopted in this paper is modified from the recommendations of Kidd *et al.* (1978). According to these authors, 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. Since the thicknesses of the individual layers sampled by DSDP personnel are not available, it is necessary to define a sapropel and a sapropelic sediment simply on the basis of the organic carbon content, namely 2 and 0.5%, respectively.

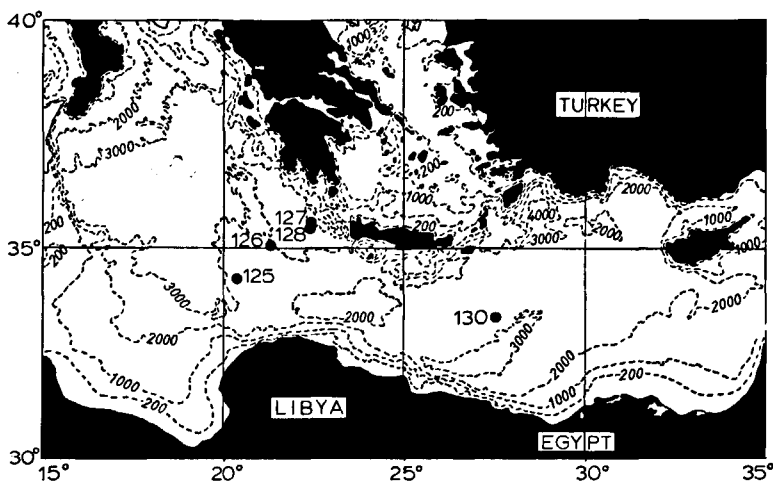


Figure 1
Location of DSDP Leg 13 drill sites in the eastern Mediterranean from which sapropel and associated sediment samples were obtained. Isobaths in metres.

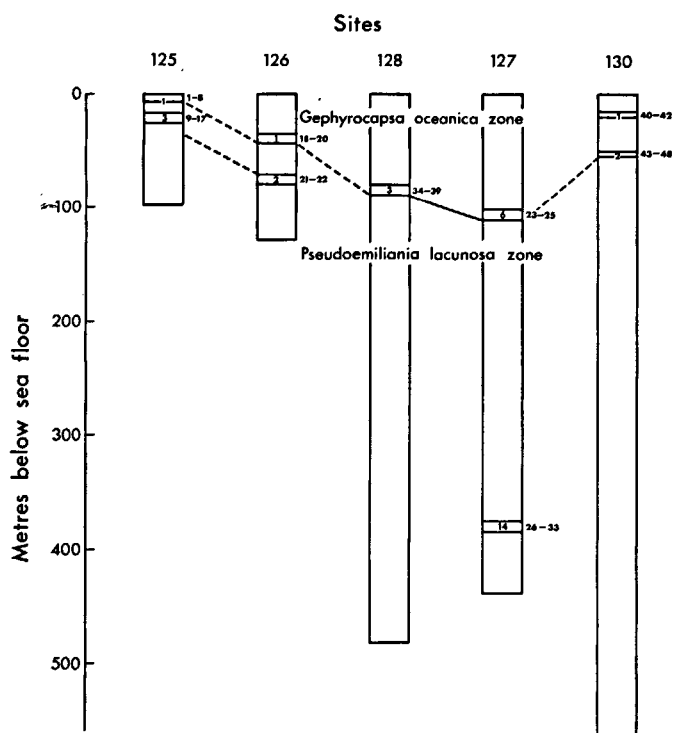


Figure 2

Stratigraphic position of the samples studied. Numbers within the columns refer to DSDP core numbers; numbers to right of columns refer to sample numbers in Table 1.

ANALYTICAL METHODS

Samples (3 cm³) of sapropelic and interbedded non-sapropelic sediment were obtained from the Deep-Sea Drilling Project at the Scripps Institution of Oceanography, La Jolla, California. On receipt, sub-samples were used for smear-slide and SEM examination and for chemical and mineralogical analysis. For the latter, sub-samples were dried at 100°C and ground to pass 200 mesh in a tungsten carbide mill. The chemical analyses were carried out by X-ray emission methods. For the major elements, 300 mg of sample were fused with a mixture of Li₂B₄O₇ and La₂O₃ at 1,100°C in a carbon crucible; the resulting glass bead was crushed to a fine powder with sufficient chromatographic cellulose to make up for the loss on ignition and pressed into a 32 mm disc with a cellulose backing. A wide range of international geochemical standards (USGS, CRPG, NIM, and ZGI) was used for calibration.

Separate 1 g subsamples of the ground powders were used for the minor element analyses using the method of Reynolds (1963). The set of international geochemical reference standards used for the major element analyses was used for calibration, plus an additional series for As and Mo prepared by spiking a silicate base with appropriate Specpure salts.

Chlorine and sulphur were also analysed by X-ray emission methods using separate 1 g sub-samples mixed with LiBO₂ and La₂O₃. The chlorine values were used to correct the final analyses for the diluting effect of sea salt in the dried powders and for the contribution of some of the major elements in the salt to their contents in the bulk sediment.

Organic and carbonate carbon were determined using a Leco gravimetric analyser. Total carbon was measured by dry combustion, using steel standards, and carbonate carbon was determined by weighing the CO₂ released from the samples by hot 10% HCl. Analar grade CaCO₃ was used as a standard. Organic carbon was estimated from the difference between these two measurements. Total nitrogen was determined by a micro-Kjeldahl method (Bremner, 1960), using (NH₄)₂SO₄ as a standard, and fixed nitrogen was measured by the method of Silva and Bremner (1966). Organic nitrogen was estimated from the difference between these two measurements.

CHEMICAL COMPOSITION OF THE SEDIMENTS

General features

The samples received were pale cream marls and oozes, grey and olive-green clays and black clays containing macroscopic gypsum crystals. Many of the sapropels (black) and the olive-green clays contained chocolate-to rust-brown streaks or laminae.

From the major and minor element data (Table 1), and the smear slide and X-ray diffraction data, the sediment samples represent nanofossil oozes (>60% CaCO₃) and marls (<60% CaCO₃), organic-rich, carbonate-poor clays and mixtures of these two types. Sampling of discrete sapropel layers was evidently not always possible, some samples of this ostensible sediment type visibly consisting of two quite different lithologies. Hence, the two end members are poorly represented in some of the cores.

Carbonate contents, from the total CO₂ values, range from 1 to 74% by weight. There appears to be no clear difference in total carbonate content between sapropels and sapropelic marls (Table 2); oozes and marls (<0.5% organic C) have on average higher carbonate contents, the range being 29 to 74% by weight. The carbonate is for the most part calcite; minor amounts of aragonite (pteropods) are present in some cores.

The relative Si and Al contents of the sediments (Fig. 3) serve to identify sapropelic and nanofossil marl and ooze sections having both different textures and different microfossil contents. Many of the samples from sites 127 and 128, from the Hellenic trench, have Si/Al ratios significantly higher than those from sites on the Mediterranean ridge. The ratios on the ridge cluster around a value of 2.5 in both sapropels and marls and oozes; such ratios are characteristic of clays and shales. The difference is consistent with the presence of abundant silt-sized quartz [samples 23-29 (site 127) and 34-39 (site 128)], as determined by smear slide and XRD examination, and silicoflagellates and minor diatoms (site 127, especially samples 31 and 32). The coarser-grained sediments at these sites occur as distinct laminae, which Nesteroff (1973) has interpreted as an indication of turbidity current deposition within the trench. Similar sedimentary structures are also present at site 126 where the Si/Al ratios are not anomalously high; however the coarser-grained sediment at this site

Table 1
 Chemical composition of sapropelic and associated sediments from the Mediterranean Sea. Major elements in weight %; minor elements in ppm.

Lab. Code	Site	Core	Section	Interval (cm)	Si	Al	Ti	Fe	Ca	Mg	K	P	S	CO ₂	C	N _{tot}	N _{org.}	As	Ba	Cu	Mn	Mo	Ni	Pb	Rb	Sr	Y	Zn	Zr
1	125	1	3	35-36	16.60	5.08	0.25	2.46	18.80	2.48	1.39	0.03	0.13	20.83	0.07	0.024		3	1,136	58	548	3	49	3	59	681	13	274	112
2	125	1	3	46-47	12.31	4.36	0.20	4.15	19.17	2.21	1.00	0.07	0.15	20.75	1.11	0.102		62	1,271	88	2,414	6	84	7	49	1,207	18	131	84
3	125	1	3	50-51	13.53	4.65	0.22	2.41	20.59	2.81	1.16	0.03	0.14	23.43	0.24	0.033	0.024	4	591	66	1,007	3	40	3	50	693	17	114	105
4	125	1	3	66-67	12.89	4.49	0.21	3.16	19.82	2.29	1.15	0.07	0.35	22.00	0.57	0.062		3	2,350	77	791	5	48	4	47	766	21	69	94
5	125	1	3	73-74	15.06	5.01	0.24	2.50	19.20	3.21	1.36	0.03	0.64	21.49	0.23	0.026		3	569	56	630	4	41	3	51	554	12	63	114
6	125	1	4	97-98	15.12	4.81	0.24	2.32	19.51	2.84	1.29	0.03	0.15	21.45	0.14	0.023	0.012	3	687	46	816	3	37	7	52	634	9	53	100
7	125	1	4	101-102	12.57	3.91	0.20	2.23	21.28	2.39	1.15	0.03	0.41	23.06	1.11	0.098		3	1,451	67	626	6	62	2	46	858	13	56	95
8	125	1	4	110-111	15.32	4.98	0.29	2.60	17.82	2.39	1.52	0.05	0.39	19.10	0.19	0.032	0.019	3	687	35	706	3	33	3	59	695	17	58	114
9	125	3	1	125-126	10.81	3.76	0.17	1.88	25.10	2.38	0.97	0.03	0.11	27.43	0.05	0.021		3	653	98	652	3	59	2	43	1,202	26	93	71
10	125	3	1	133-134	15.91	5.35	0.31	4.05	11.16	2.67	1.59	0.07	1.76	10.63	5.90	0.361	0.347	3	1,810	404	415	42	168	30	97	522	31	274	114
11	125	3	1	144-145	9.94	3.21	0.14	2.25	25.64	2.24	0.76	0.03	1.13	26.88	1.34	0.092		13	607	82	486	13	56	2	34	1,094	16	42	64
12	125	3	4	30-31	13.50	4.61	0.24	2.23	21.64	2.57	1.21	0.05	0.18	23.43	0.16	0.025	0.015	3	1,081	111	635	3	59	7	55	964	31	66	99
13	125	3	4	44-45	11.82	3.72	0.22	3.95	12.36	2.20	1.21	0.20	2.02	10.05	10.27	0.658		5	2,541	290	481	82	261	10	46	500	44	220	93
14	125	3	4	60-61	7.77	2.45	0.11	1.39	29.84	2.21	0.61	0.03	0.48	32.41	0.16	0.024	0.019	3	503	46	557	13	30	5	28	1,440	16	38	54
15	125	3	5	33-34	15.98	5.02	0.32	2.58	17.41	2.63	1.73	0.04	2.33	19.47	0.17	0.016		3	517	17	476	3	22	2	61	688	14	48	110
16	125	3	5	47-48	13.27	4.38	0.23	2.46	20.76	2.57	1.49	0.03	0.20	22.81	0.21	0.036	0.025	3	685	07	620	3	63	13	57	968	37	66	106
17	125	3	5	55-56	9.27	3.05	0.14	6.06	14.95	1.91	0.91	0.04	5.30	10.78	10.04	0.597	0.592	47	1,821	101	523	168	247	2	29	564	8	91	71
18	126	1	1	133-134	8.96	2.76	0.13	2.44	23.66	2.27	0.80	0.08	1.90	23.54	3.60	0.239		4	1,791	61	520	55	64	2	30	903	10	137	44
19	126	1	2	13-14	13.01	4.27	0.20	3.27	18.89	2.50	1.26	0.05	1.80	18.55	2.35	0.184		3	1,483	63	561	46	76	2	50	860	17	162	79
20	126	1	2	28-28	14.20	4.87	0.23	3.19	17.82	2.62	1.36	0.03	1.48	18.48	0.54	0.071		7	859	62	580	23	76	12	62	867	21	91	82
21	126	2	5	70-71	12.43	3.88	0.18	1.86	24.35	2.57	0.91	0.03	0.13	26.40	0.27	0.032		3	530	61	756	6	55	13	45	1,121	16	42	80
22	126	2	5	110-111	11.64	3.67	0.17	2.75	20.93	2.30	1.00	0.04	1.89	20.50	3.32	0.226		3	1,738	62	569	59	83	2	46	1,048	19	56	69
23	127	6	2	50-51	22.04	4.51	0.32	2.92	11.22	2.03	1.44	0.03	1.03	12.14	0.86	0.101	0.082	3	613	37	462	26	55	8	62	415	27	61	142
24	127	6	3	50-51	19.81	5.61	0.34	3.35	11.49	2.57	1.78	0.03	1.20	11.73	1.11	0.126	0.100	4	681	42	521	10	73	7	78	466	32	77	137
25	127	6	3	122-123	19.08	4.55	0.29	2.20	14.94	2.62	1.49	0.03	0.11	16.72	0.34	0.054		3	662	37	591	3	63	13	59	634	24	73	121
26	127	14	3	2-3	16.81	3.23	0.22	1.95	17.60	2.76	0.96	0.03	0.27	20.35	0.25	0.048	0.035	3	569	25	1,586	3	50	2	38	710	15	39	115
27	127	14	3	10-11	20.40	5.39	0.32	3.35	10.37	2.62	1.76	0.03	1.22	11.18	0.96	0.092		3	610	36	4,755	3	95	12	77	448	25	87	139
28	127	14	4	35-36	16.71	3.56	0.20	1.95	18.89	2.94	0.88	0.04	0.17	21.56	0.38	0.056	0.043	3	528	27	940	4	54	2	42	835	18	40	113
29	127	14	4	42-43	15.56	4.12	0.25	2.69	15.99	2.89	1.48	0.04	0.15	18.33	0.21	0.053	0.036	3	509	35	4,782	3	63	2	56	643	15	50	94
30	127	14	4	45-46	16.67	5.15	0.26	3.96	14.17	3.05	1.62	0.03	1.16	15.47	1.02	0.137		22	559	54	1,059	32	124	14	67	588	23	67	84
31	127	14	5	50-51	20.26	3.58	0.23	4.08	10.32	2.51	1.29	0.03	2.08	9.39	0.70	0.069		3	493	42	560	3	73	2	46	803	10	53	76
32	127	14	6	10-11	15.26	4.09	0.22	2.72	17.21	2.99	1.29	0.05	0.67	18.08	1.19	0.125		3	610	86	844	45	104	13	56	837	26	64	94
33	127	14	6	15-16	19.10	5.43	0.32	2.65	11.25	2.71	1.99	0.02	0.17	12.61	0.28	0.051	0.025	3	588	52	647	8	83	9	86	510	30	80	131
34	128	3	4	115-116	12.61	3.31	0.16	2.30	23.14	2.77	1.03	0.05	0.73	24.79	0.50	0.064	0.050	3	719	51	824	20	58	14	42	984	22	45	68
35	128	3	4	134-135	13.11	3.24	0.20	2.44	17.50	2.45	1.26	0.05	0.96	19.69	1.91	0.173	0.157	3	617	59	4,758	20	75	2	48	690	16	51	76
36	128	3	5	10-11	15.14	3.52	0.21	2.70	16.42	3.00	1.15	0.05	0.95	17.97	3.32	0.295		3	617	67	6,493	27	91	3	44	582	15	53	68
37	128	3	5	136-137	16.44	4.86	0.26	3.07	15.55	2.79	1.45	0.04	1.24	15.58	1.76	0.165		7	630	41	586	3	78	2	63	704	14	58	76
38	128	3	6	90-91	15.76	3.45	0.19	2.46	18.60	2.62	0.89	0.04	1.22	18.66	2.67	0.201		3	620	41	490	42	65	2	39	653	11	46	76
39	128	3	6	110-111	21.51	4.86	0.29	3.25	9.46	2.62	1.72	0.06	1.60	9.20	2.11	0.186		3	585	35	487	38	71	2	66	316	15	63	100
40	130	1	2	85-86	22.09	8.88	0.85	6.43	1.77	2.12	2.13	0.04	1.82	0.51	0.95	0.068		3	529	45	754	3	70	6	71	149	30	121	227
41	130	1	2	109-110	12.40	4.21	0.28	4.36	19.46	2.70	1.20	0.03	2.63	18.18	1.54	0.118		13	1,099	41	775	13	78	2	30	762	15	110	96
42	130	1	2	120-121	15.94	5.73	0.49	5.80	12.18	2.48	1.54	0.05	3.03	9.51	1.54	0.101		128	953	51	779	14	93	2	50	500	26	136	67
43	130	2	3	15-16	16.55	5.52	0.50	3.96	13.92	2.44	1.44	0.04	1.25	14.15	0.34	0.034	0.022	3	585	59	689	6	39	6	52	823	35	74	184
44	130	2	3	25-26	11.04	3.67	0.11	3.72	21.04	2.30	0.78	0.07	2.35	20.24	3.30	0.245		7	547	80	741	14	106	2	29	1,032	58	56	111
45	130	2	3	33-34	22.25	7.79	0.89	6.06	5.48	1.93	1.74	0.06	1.67	3.66	0.88	0.066		3	615	52	767	13	60	7	57	358	39	104	265
46	130	2	3	65-66	16.72	5.64	0.40	3.34	15.52	2.45	1.47	0.03	0.64	16.39	0.32	0.040	0.029	3	531	46	718	7	34	7	55	963	38	69	167
47	130	2	3	72-73	14.32	5.28	0.30	5.21	1.82	1.42	1.22	0.05	4.24	0.59	20.21	1.275		9	412	218	295	228	197	4	38	125	20	131	190
48	130	2	3	83-84	11.62	4.27	0.20	2.89	22.07	3.27	0.95	0.10	0.68	25.81	0.25	0.028		3	534	47	765	3	58	6	33	826	10	44	85

Table 2

Mean compositions of sapropels, sapropelic marls and marls. Major elements in weight %; minor elements in ppm.

Element	Sapropels (n=11)	Sapropelic marls (n=18)	Marls (n=19)
Si	13.49	16.39	15.94
Al	3.96	4.93	4.72
Ti	0.21	0.33	0.27
Fe	3.62	3.74	2.50
Ca	15.39	14.73	19.46
Mg	2.35	2.47	2.76
K	1.14	1.41	1.30
P	0.07	0.04	0.04
S	2.27	1.31	0.44
CO ₂	14.61	15.08	21.27
C	6.10	1.12	0.22
N	0.41	0.10	0.03
As	7	15	3
Ba	1269	856	639
Cu	129	57	69
Mn	1052	1266	954
Mo	73	14	3
Ni	130	77	49
Pb	5	6	5
Rb	47	55	52
Sr	646	677	820
Y	23	22	21
Zn	117	81	73
Zr	92	112	190

is composed of foraminiferal tests. This is consistent with the location of the site in a depression in the Mediterranean ridge which, unlike sites 127 and 128, would not receive coarse-grained terrigenous detritus by bottom-current transport.

Gypsum

The relationship between Ca and CO₂ (Fig. 4) shows that samples containing less than 1% S cluster around a regression line representing pure CaCO₃. Points representing samples containing more than 1% S fall away from this line due to the presence of variable

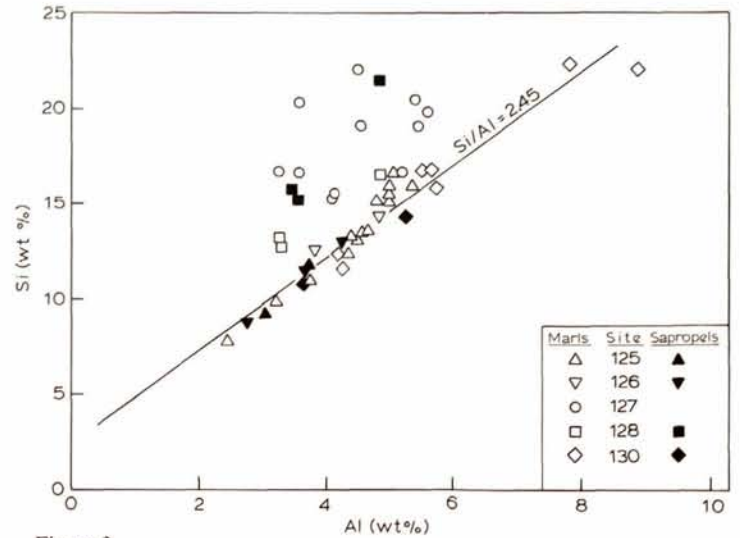


Figure 3

Relationship between Si and Al contents of sapropelic and associated sediments. The regression line has been calculated omitting the data from sites 127 and 128. See the text.

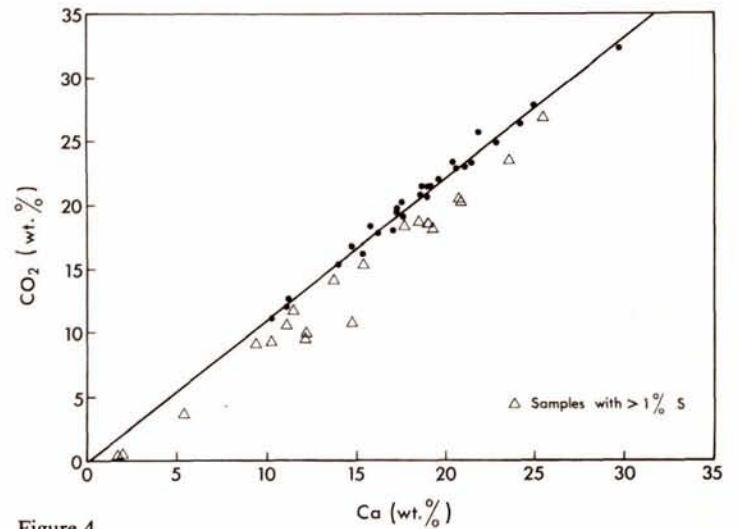
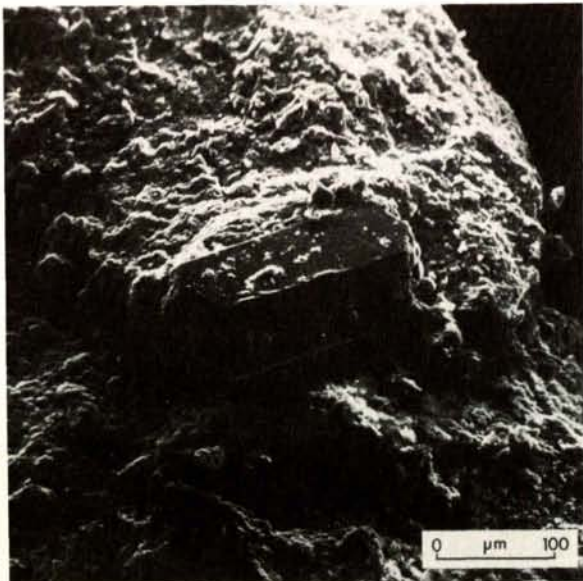


Figure 4

Relationship between Ca and CO₂ contents of sapropelic and associated sediments.



A



B

Figure 5
Scanning electron micrographs of (A) gypsum and (B) pyrite crystals in sapropels.

amounts of gypsum. With a single exception, all samples containing more than 1% S are sapropelic marls (>0.5% C) or sapropels (>2% C) and cover almost the entire range of total carbonate contents of the suite of samples analysed.

The gypsum occurs as euhedral crystals, up to 500 μm in size (Fig. 5A) and is generally untwinned. The amount of this phase in the sapropels has been estimated from the amount of Ca in excess of that required to balance the amount of CO_2 present (Fig. 4), assuming that the only other Ca-bearing phases present are calcite and aragonite. This excess Ca is positively correlated with the concentration of total S (Fig. 6), which further substantiates the occurrence of the Ca as gypsum. The amount of gypsum present, from the excess Ca values, ranges from 4 to 21%. The concentration of S derived from the estimates of the amount of gypsum present is highly positively correlated with the measured total S values.

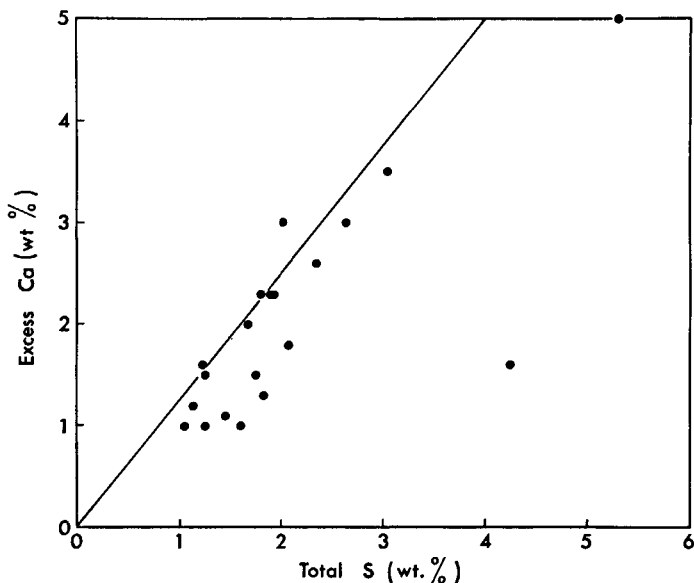


Figure 6
Relationship between total sulphur and excess calcium in the sapropelic sediments. Line drawn represents the relationship between Ca and S in ideal gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Some proportion of the total S in the sediments is also present as pyrite (Fig. 5B); judging by the proportion of the S which is present as gypsum, the amount of pyrite in the sapropels does not exceed 1%, according with the smear slide examinations. This is puzzling in view of the high Fe/Al ratios of the sapropels compared with the intervening marls and oozes. The ratios in the oozes fall in the range 0.48 to 0.65, values typical of fine-grained aluminosilicate debris, whereas the ratios in the sapropels are higher, reaching 1.97. The Fe/Al ratio is positively related, moreover, to the total S content (Fig. 7), apparently pointing to the presence of a substantial amount of pyrite in the sapropels. This would reach 10% if all the S were present as pyrite. Some of the scatter in Figure 7, especially at low S values, is due to the presence of an additional Fe-bearing phase, also having high Ti contents, probably a ferromagnesian silicate or an oxide. These sample points are confined to site 130.

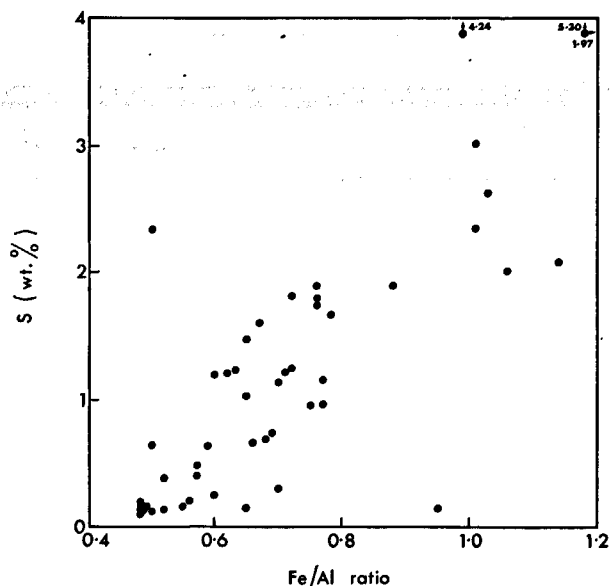
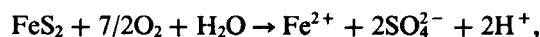


Figure 7
Relationship between total sulphur and the Fe/Al ratio in the sapropelic and associated sediments.

The presence of gypsum in the Mediterranean sapropels has been ascribed to: 1) authigenic growth (Kullenberg, 1952); 2) oxidation of sulphide during storage of the cores (Olausson, 1961); and 3) penecontemporaneous deposition of gypsum and pyrite in environments where "reduction is less marked than in sapropels containing pyrite alone", the formation of gypsum being due to bacterial oxidation of H_2S (Robert, Chamley, 1974).

The relationship between the excess Ca and S contents and between the excess Fe (as expressed by the Fe/Al ratio) and S contents of the sapropels allows some distinction to be made between these possibilities. It appears that the sulphur present was originally introduced into the sediment as a sulphide, by the formation of iron monosulphide or pyrite in organic-rich, anoxic sediment, and that this has been subsequently oxidised. The oxidation of pyrite proceeds by the following reaction (Kleinmann, Crerar, 1979):



producing low pH conditions, as occurs for example in sulphide-bearing mine waste, and sulphate ions. In this case, the Ca released from dissolving biogenous carbonate combined with the sulphate and precipitated as gypsum. The Fe released in this reaction was subsequently oxidised and remains in the sediment as an oxyhydroxide phase; as noted earlier, many of the sapropels are actually rust-brown in colour or contain yellow to brown laminae.

Gypsum has not been reported in the sapropels of the Black Sea although pyrite is present and carbonate is abundant (Ross, Degens, 1974; Hirst, 1974; Calvert, Batchelor, 1978). This is explained by the fact that the Black Sea has remained fully anoxic since the formation of the youngest sapropel (3,000-7,000 years B.P.) so that no opportunity for the oxidation of pyrite has occurred.

Carbon and nitrogen

Organic carbon and total nitrogen contents of the sapropels, sapropelic marls and marls and oozes range between 0.08 and 20.21% and between 0.016 and 1.275%, respectively. Using the definitions of sapropel and sapropelic sediments given above, a total of 11 samples are sapropels and 18 are sapropelic marls. As noted earlier, the samples available for study are in many cases mixtures of sapropelic and carbonate material. It seems likely that many sapropels contain more organic material and that the range of organic carbon values found here reflects the effects of mixing. Sigl *et al.* (1978) have reported organic carbon values reaching 16.7% in a Pliocene sapropel recovered during Leg 42A.

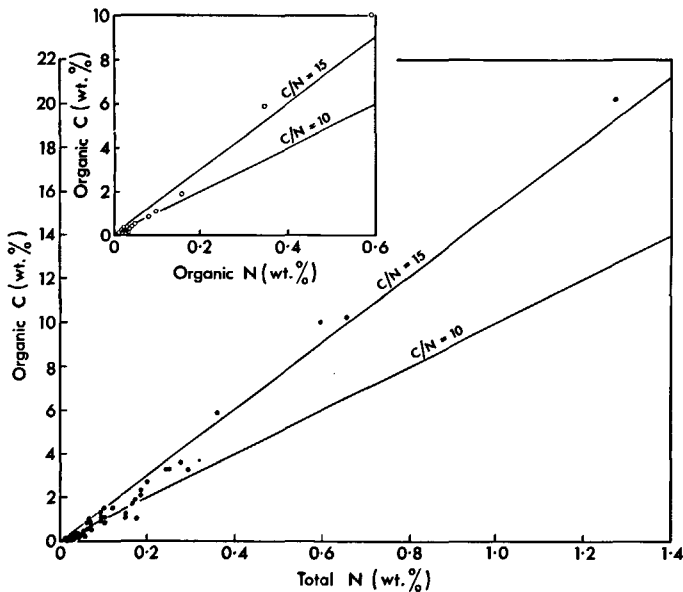


Figure 8
Relationship between organic carbon and nitrogen contents of the sapropelic and associated sediments.

The relationship between organic C and total N (Fig. 8) shows that C/N ratios are highly variable where C values are low, and that the ratio increases with increasing C content. The range of C/N ratios is from 2.4 to 16.8 with a continuous change in the ratio over the range of C contents.

The low C/N ratios in organic-poor sediments are produced to some extent by the presence of a significant fraction of inorganic fixed N (see also Müller, 1975; 1977). C/N_{org} ratios are consequently higher, although the range is still quite wide, from 5.8 to 16.9. Figure 9 shows that there is no overlap in the range of C/N ratios in true sapropels and marls even when the correction for the inorganic fixed N fraction is made. The proportion of fixed N in the sediments appears to be different for different sites. Fixed N content is positively related to the Al content (Fig. 10), which is a reflection of the contribution of this N fraction to the sediment by fine-grained aluminosilicate debris (Müller, 1977). At sites 127 and 128, substantially more fixed N is present at a similar Al content compared with sediments at sites 125 and 130. This in turn is a reflection of the greater abundance of fine-grained mica,

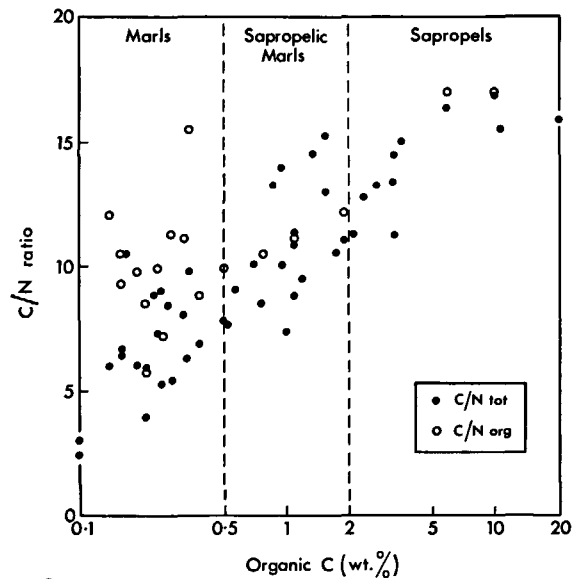


Figure 9
Relationship between organic carbon contents and the C/N ratio in the sapropelic and associated sediments.

which fixes ammonium ions in interlayer positions (Marshall, 1964), in the Hellenic trench sites compared with the sites on the Mediterranean ridge (Zemmel, Cook, 1973).

The highly variable C/N_{org} ratios of the sediments can be interpreted in two ways. The low ratios in the oozes and marls may be produced by the adsorption of nitrogenous organic material by clays which protect it from further bacterial degradation (Müller, 1977). The contrast in C/N_{org} ratios between sapropels and marls would then be due entirely to a difference in the amount of clay in the two types of sediment. That this is not the case is shown by the relatively small difference in Al content between the sapropels (3.96%, $n = 11$) and the marls (4.72%, $n = 19$; Table 2). Alternatively, we may be dealing with two different sources of organic material, a marine source, having a low C/N ratio, in the marls, and a terrestrial source, having a high C/N ratio, in the sapropels.

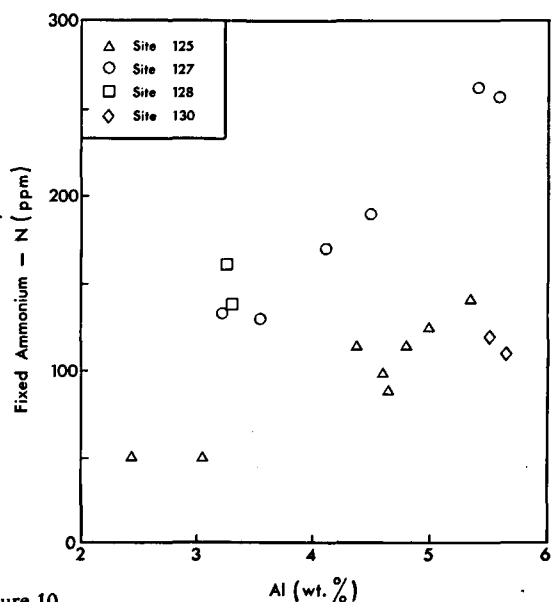


Figure 10
Relationship between total Al and fixed nitrogen contents of the sapropelic and associated sediments.

Minor elements

The minor element data (Table 1) show that there are notable differences between the various sites examined. Considering the full range of sediment types, the highest Ba, Cu, Mo, Ni and Zn values are found at sites 125 and 126, and in particular core 3 from site 125. The As contents are highly variable, the high values being confined to samples which are brown in colour due to the presence of ferric oxyhydroxides which may absorb As from sea water. The Mn contents are also quite variable; one sapropel sample has a high content while the most organic-rich samples have very low contents. Lead, Rb, Y and Zr contents generally reflect the amount of aluminosilicate present in the samples, the variations being related to the relative abundance of clay, carbon and carbonate.

Comparing the various sediment types, it is clear that the sapropels, on average, have higher Ba, Cu, Mo, Ni and Zn contents, whereas the marls contain more Rb, Sr and Zr (Table 2). The sapropels show a similar degree of enrichment of Cu, Mo, Ni and Zn as other organic-rich, fine-grained sediments compared with normal muds and shales (Table 3). Calvert (1976) has discussed the metal-enrichment of nearshore organic-rich sediments and the available information suggesting the probable sources of the metals. Positive correlations between metal and carbon contents are often taken to imply that the metals are associated with the organic fractions of many sediments (*see* Curtis, 1966). Such correlations are found in Black Sea sapropels (Volkov, Fomina, 1971), Mediterranean sediments (Kochenov *et al.*, 1965; Baturin *et al.*, 1967; Pilipchuk, 1972) German Bight muds (Little-Gadow, Schafer, 1974) and in the Namibian shelf sediments (Calvert, Price, 1983). Although a correlation of this type may in fact be misleading, in view of the close correlation between the grain-size and the carbon content of a sediment (Calvert, 1976), Nissenbaum and Swaine (1976) and Calvert and Morris (1977) have shown that some extracted organic fractions of several near-shore sediments do have substantial minor metal contents. These metals are not,

Table 3
Minor metal contents of sapropelic sediments, nearshore muds and shales (ppm).

Element	1	2	3	4	5	6	7	8
Ba	1269	198	—	—	472	375	496	580
Cu	129	68	45	30	97	18	32	45
Mo	73	53	26	33	175	—	—	3
Ni	130	108	26	67	67	29	38	68
Pb	5	12	—	24	21	22	21	20
Rb	47	49	—	—	24	150	90	140
Sr	646	523	—	—	740	183	309	300
Y	23	23	21	—	36	—	24	41
Zn	117	68	71	147	82	—	87	95
Zr	92	78	76	82	79	168	192	160

1. Eastern Mediterranean sapropels (*this paper*).
2. Namibian shelf diatom oozes (Calvert, 1976).
3. Saanich Inlet diatom muds (Gross, 1967).
4. Black Sea modern muds (Glagoleva, 1961; 1970; Kochenov *et al.*, 1965; Pilipchuk, Volkov, 1966; Belova, 1970; Lubchenko, 1970).
5. Black Sea sapropels (Calvert, Batchelor, 1978).
6. Gulf of Paria muds (Hirst, 1962).
7. Barents Sea muds (Wright, 1972).
8. Shales (Wedepohl, 1971).

however, contributed directly by the organic material, at least in the case of planktonic material, since the concentrations of metals in plankton are much lower than those in the sediments. Post-depositional reactions are suspected as the mechanism of enrichment in these cases (Calvert, Morris, 1977).

The enrichment of Mo in the Mediterranean and the Black Sea sapropels is particularly marked (Table 3). Such enrichments are characteristic of modern fine-grained, organic-rich sediments which accumulate in permanently or intermittently anoxic environments (Calvert, 1976) where iron monosulphides co-precipitate Mo in the sulphide-bearing water. Calvert and Morris (1977) have shown that the humic acid fraction of the diatom oozes of the Namibian shelf also contains very high levels of this metal, the enrichment being considerably greater than that of Cu, Ni, Pb and Zn.

The enrichment of Ba in the Mediterranean sapropels is also marked (Table 2), and its concentration is significantly greater than that in other organic-rich or detrital sediments (Table 3). The contrast with the Namibian shelf diatom oozes is particularly striking in view of the suggestion of Brongersma-Sanders (1967) that diatoms are responsible for delivering relatively large amounts of this element to such sediments (*see* also Calvert, Price, 1983). The biological enrichment and transport of barium has previously been invoked to explain the relatively large enrichments in some pelagic clays (Goldberg, Arrhenius, 1958). The Mediterranean sapropels bear a closer resemblance to deep-sea sediments than to near-shore organic-rich sediments in terms of their Ba contents; this may be due to the presence of biogenic or authigenic barite, although a positive identification of this phase has not been made. Note in addition that diatom frustules make up a relatively minor component of the sapropels.

The occasional high Mn content of some sapropels and sapropelic sediments are not considered to be due to the presence of a manganoan carbonate, as it is in the Black Sea sapropel described by Calvert and Batchelor (1978). Rather, it is probably present as an oxyhydroxide, associated with an iron oxyhydroxide in the secondarily oxidised horizons.

The remaining minor elements in the sapropels are either depleted, or have similar concentrations, relative to the marls. Strontium is present mainly in carbonate debris and to a minor extent in plagioclase feldspar, the dominant mineral in the silt and fine sand fractions, while Pb, Rb, Y and Zr are indicators of the fine-grained aluminosilicate fraction.

DISCUSSION

The sapropels in the Eastern Mediterranean are organic-, sulphur- and minor metal-rich clays, containing variable amounts of biogenous carbonate, intercalated in nannofossil oozes and marls. They have higher C/N ratios than the associated marls and they contain authigenic gypsum and pyrite. On the basis of their bulk compositions, it can be concluded that the

sapropels represent mixtures of biogenous carbonate and terrigenous aluminosilicates, closely similar to those in the intercalated marls and oozes, with variable amounts of admixed organic matter.

The presence of sediments with high concentrations of organic matter in the central, deep areas of the Eastern Mediterranean, where carbonate oozes are currently accumulating, clearly requires unusual depositional conditions. Changes in the supply rate and/or the efficiency of preservation of organic matter are required to produce sediments containing up to 20% by weight organic carbon in water depths of around 3,000 m. Moreover, the immediate source of the organic matter, whether terrestrial vegetation or marine planktonic material, is unresolved.

The organic matter in the Pleistocene sapropels examined in this paper has a high C/N ratio. Such high ratios are normally taken to be characteristic of terrestrial organic matter (Trask, 1953; Emery, 1960) which is relatively poor in proteinaceous material compared with marine organisms, both plant and animal. However, the C/N ratio in marine deposits is sensitively affected by the accumulation rate and the bulk composition of the sediment. In rapidly-accumulating nearshore sediments and in pelagic carbonate oozes, the C/N ratio increases with burial because nitrogen is lost more readily upon decomposition than is carbon. On the other hand, in pelagic clays, the C/N ratio decreases with burial because a relatively nitrogen-rich fraction is protected from bacterial degradation by being incorporated into the interlayer positions in clay minerals (Müller, 1977). While there appears to be no clear difference in the amount of fine-grained aluminosilicates in the sapropels and associated carbonate-rich sediments of the Eastern Mediterranean, there may have been preferential losses of nitrogen from the sapropels relative to the marls because of a higher accumulation rate, a higher ratio of organic matter to clay minerals and a higher initial burial rate of the deposited organic matter compared with the associated carbonate-rich sediments. Hence, the C/N ratio would not necessarily be diagnostic of the source of the organic matter without an independent evaluation of the degree of diagenetic alteration of the original input.

Terrestrial contributions to the organic material in some of the Eastern Mediterranean sapropels have been claimed by Sigl *et al.* (1978), based on the presence of fragments of higher plants and high C/N ratios, and by Deroo *et al.* (1978) based on characteristic spectra of *n*-alkanes, the composition of humic fractions and particular pyrolysis products. Such conclusions have not been substantiated or examined further; analyses of the stable carbon or nitrogen isotopic composition of the organic material and more detailed lipid analyses are required to test their general validity.

The term sapropel has been used for a considerable time in the limnological literature to connote an organic-rich sediment formed under anoxic conditions. In an extensive review of the various uses of the term Wasmund (1930) defined sapropel as a black, organic-

rich deposit containing mainly, but not exclusively, macrophytic plant remains which have been decomposed anaerobically. Where such deposits are forming, the bottom water in the lake invariably contains dissolved H₂S and benthos is consequently absent. In contrast, *gyttja* is an organic-rich deposit composed of planktonic organic remains (both plant and animal) which have been decomposed aerobically and where a benthic fauna has contributed to this decomposition. In this case, the bottom water in the lake contains oxygen, although anoxic conditions can be developed below the lake bed. Gyttjas are characteristically olive-green, grey or brown in colour as distinct from the intense black pigmentation of sapropels, the latter produced by the presence of fine-grained iron monosulphide which forms authigenically in the anoxic water and sediment.

In the geological literature, the term sapropel is frequently used to describe a deposit of an anoxic marine basin which is the precursor of black shale. Such rocks generally have high organic matter and pyrite contents and many are metal-rich (*see* Vine, Tourtelot, 1970). The link with modern sediments is evidently made by identifying a black sediment with a high organic matter content as the product of deposition under fully anoxic marine conditions, i.e., in a hydrographically-restricted basin with little deep-water renewal where free H₂S occurs in the bottom water. As noted by Thiede and Van Andel (1977), such usage of the term does not conform with the original meaning. The direct correlation between restricted, anoxic basins and black shales is, however, misleading. In the first place, the colour of modern black sediments is due to the presence of finely-divided iron monosulphide, either greigite or mackinawite (Berner, 1967), which is rapidly oxidised by atmospheric oxygen. Such phases form by the reaction between iron and dissolved sulphide in anoxic waters and sediments, and are precursors of pyrite which does not impart black colouration to sediments. On the other hand, black shales (and Mediterranean sapropels) owe their colouration to the presence of carbonised organic matter, or bitumen in the loose sense; their colour does not change on exposure to air. The original colour of the shales and the Mediterranean sapropels is therefore unknown and their present colour can give no clue to their environment of formation.

The second characteristic of black shales which supposedly identifies their environment of formation is the organic matter content. It is commonly implied that anoxic environments are conducive to the preservation of deposited organic matter which would otherwise be more rapidly oxidised by dissolved oxygen, mediated by aerobic bacteria, in oxic environments. Richards (1970) has reviewed the available information on the concentration of organic matter in the anoxic waters of restricted basins and finds no compelling evidence that it is higher in such situations. Moreover, the modern sediments of some permanently anoxic fjords (Strøm, 1936) and the Black Sea do not appear to be especially organic-rich (Doff, 1970; Hamilton-Taylor, 1974; Strakhov, 1962; 1971); certainly there is no evidence of sediments containing levels of 20% organic carbon in

such basins (note that the pre-modern sapropel in the Black Sea does have high organic matter concentrations; this will be discussed below). The efficacy of sulphide-bearing waters in preserving deposited organic material has not been adequately demonstrated. Although the efficiency of the bacterial breakdown of organic material is lower in anoxic environments compared with their oxic counterparts, carbon is nevertheless utilised by sulphate-reducing bacteria so that organic matter must be remineralised under such conditions.

The formation of Mediterranean sapropels has been widely ascribed (Olausson, 1961; Chamley, 1971; Ryan, 1972; Nesteroff, 1973; McCoy, 1974; Cita *et al.*, 1977; Ryan, Cita, 1977; Vergnaud-Grazzini *et al.*, 1977; Stanley, 1978; Rossignol-Strick *et al.*, 1982) to the presence of anoxic bottom water presumably by direct analogy with ancient black shales. The problem posed by this correlation is to identify the mechanism that can produce a sediment containing 20% by weight organic carbon, or roughly 35% by weight organic matter, in water depths of around 3,000 m by preferentially preserving the deposited organic material without at the same time altering the accumulation rates of any of the other sediment components. That conditions in the Eastern Mediterranean during the late Pleistocene were unusual oceanographically is incontrovertible. Based on the oxygen isotopic composition of planktonic foraminifera in the sapropels, the near-surface waters were markedly brackish (Williams *et al.*, 1978; Williams, Thunell, 1979). Moreover, the stable carbon isotopic composition of benthonic foraminifera in the marls close to the bases of the sapropel units shows that the deep waters in the eastern basin contained higher concentrations of metabolic carbon (Luz, 1979) and consequently were also oxygen deficient (Shackleton, 1979).

The presence of a surface low-salinity layer in the eastern basin of the Mediterranean has been identified as the single most important factor in promoting anoxic conditions in the deep water, the stable density stratification inhibiting deep-water renewal from the western basin (Bradley, 1938; Kullenberg, 1952; Olausson, 1961; Ryan, 1972; McCoy, 1974; Ryan, Cita, 1977). However, since the sill at the Strait of Sicily is now 560 m deep, and was only slightly shallower during the post-Pleistocene sea level rise, it seems doubtful whether the presence of a surface low-salinity layer would lead to the formation of anoxic bottom water throughout the eastern basin. Moreover, even if such conditions were established, the evidence from modern anoxic basins suggests that exceptionally organic-rich sediments would be unlikely to form unless some other factors also changed.

This problem may be examined using the general relationships between carbon production, sedimentation rate and carbon burial recently established by Müller and Suess (1979). Thus, assuming a sedimentation rate of a sapropel of $2 \text{ cm (1,000 yr)}^{-1}$, an average value obtained by Mangini and Dominik (1979), a dry sediment density of 2.7 g cm^{-3} , a porosity of 0.8, and a primary production rate of $75 \text{ gC m}^{-2}\text{yr}^{-1}$ (Platt, Subba Rao, 1975), the organic carbon content of a

resulting sediment would be approximately 0.5%, within a factor of three of the carbon values in the marls and oozes reported here. Similarly, the potential carbon accumulation rate can be estimated from the relationship between the water depth and the ratio of the carbon flux to production rate established by Suess (1980). The resulting rate ($\sim 1 \text{ gC m}^{-2}\text{yr}^{-1}$) would yield a carbon content of 10% by weight, assuming all the deposited carbon were preserved. As indicated previously, some loss of carbon would be expected even under fully anoxic conditions because of the activities of sulphate reducers so that the 10% value would certainly not be realised. Hence, I conclude that it is not possible to produce a sapropel containing substantially more than a few percent carbon at the present production rate in the Mediterranean.

An alternative mechanism for producing organic-rich sediments in the Eastern Mediterranean not considered in the many discussions of this problem is an increased flux of carbon to the sea floor brought about by a higher primary production rate. Some modern coastal upwelling environments are sites of extremely high production and the bottom sediments in such areas are markedly organic-rich. For example, off the Peru-Chile and Namibian continental margins, anoxic, olive-green diatom oozes, devoid of benthos, and containing up to 20% by weight organic carbon, are found (Reimers, 1982; Calvert, Price, 1983). The bottom waters are depleted in dissolved oxygen and the sediments are anoxic due to the large fluxes of carbon to the sea floor; the carbon is not preserved because of stagnation.

Olausson (1961) and Ryan (1972), using the oxygen isotopic records in cores, have established that the various sapropels in the Eastern Mediterranean accumulated mainly during what are referred to as "warming trends", periods of temperature increase, when glaciers were retreating rapidly. Moreover, the oxygen isotope signal in planktonic foraminifera records the presence of low-salinity surface water during such periods, pointing to a marked increase in runoff.

Rossignol-Strick *et al.* (1982) have established that the period of formation of the youngest Mediterranean sapropel (8,000-12,000 years B.P.) was one of greatly increased rainfall in equatorial Africa which led to an exceptionally high discharge of floodwaters *via* the Nile (see Butzer *et al.*, 1972). Williams and Adamson (1974), Street and Grove (1976), Gasse and Street (1978) and Adamson *et al.* (1980) had earlier established that lake levels in Northern Africa and the Levant were much higher around 10,000 to 12,000 years ago and Hamilton (1976) and Shackleton (1977) maintain that forests were much more extensive during this same pluvial period.

The low-salinity surface layer of the extent claimed by Olausson (1961), Ryan (1972), Stanley (1978) and Rossignol-Strick *et al.* (1982) would probably have caused a profound change in the circulation of the Mediterranean. At the present time, evaporation greatly exceeds precipitation in the eastern basin and the circulation is anti-estuarine, surface water from the Atlantic replenishing the evaporative losses and deep Mediterranean water being lost through Gibraltar Straits. The Mediterranean is consequently a nutrient-

starved basin, the products of the water-column regeneration of organic matter, which normally accumulate in deep ocean waters, being exported to the Atlantic.

During periods of flooding, it is likely that the circulation became estuarine, with an outward surface flow through the Gibraltar Straits driving a subsurface flow of deeper Atlantic water into the Mediterranean. It would then have been a nutrient trap and the eastern basin in particular would have been more productive as a consequence of the upwelling and entrainment of the deeper nutrient-enriched water into the euphotic zone. Added to this effect would have been the possible additional supply of nutrients from the fresh-water runoff. The increased production would in turn have led to an increased flux of carbon to the sea floor, the formation of sapropelic sediments and the depletion of the oxygen content of the bottom water (although oxygen-rich water would have been supplied from the western basin *via* the Straits of Sicily as a consequence of the estuarine circulation) and of the sediments. Such conditions would have been conducive to the formation of iron sulphide phases in the sediments and, if anoxic conditions were present at the sediment surface because of the high sedimentation rate, the benthos would have been restricted.

A distinctive sapropel, containing up to 20% organic carbon, in the Black Sea (Ross, Degens, 1974) is only slightly younger than the youngest sapropel in the Mediterranean. The beginning of sapropel deposition took place when the Black Sea began receiving seawater from the Mediterranean *via* the Bosphorus sill when sea level had risen to within 10 to 20 m of its present level (Curry, 1965). This changed a deep oxic lake into a stagnant marine basin. Sapropel deposition ceased in the Black Sea, however, roughly 3,000 years ago and the modern sediment is not sapropelic. The conditions responsible for the formation of the sapropel here are not understood; however, it was clearly not the anoxic condition of the deep water. It seems more likely that primary production increased during the early period of

exchange of sea water with the lake and the concomitant displacement and mixing of the deep water. Boon *et al.* (1979) have discovered that the distinctive sterol, dinosterol, is abundant in the sapropel and suggest that dinoflagellate blooms were common during this period. This could indicate that phytoplankton production was greatly increased for a period in the evolution of the Black Sea basin and that the sedimentation rate of organic material was much higher than it is today. Likewise, increased production appears to have accompanied the change in the circulation of the Mediterranean because of extensive post-glacial flooding.

It is concluded that, in order to more carefully examine some of the problems outlined in this paper, a detailed examination of the composition of the most recent sapropel (6,000 to 9,000 yrs B.P.) is required. It is necessary to identify organic marker compounds that can be used to characterise unequivocally terrestrial and marine organic matter sources and to determine the accumulation rates of the organic material and other sediment components in sapropel and the associated marl oozes. More information on the composition of the sediments, and its variability throughout the Eastern Mediterranean, must be accumulated before further speculation on the origin of this unusual facies is made.

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