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31. CARBON AND NITROGEN STABLE ISOTOPE RATIOS AT SITES 969 AND 974: INTERPRETING SPATIAL GRADIENTS IN SAPROPEL PROPERTIES[1]

Jeffrey C. Milder,[2] Joseph P. Montoya,[3] and Mark A. Altabet[4]

ABSTRACT

Discrete organic-rich layers (sapropels) representing 1–10 k.y. of depositional time are common throughout Pleistocene sediments from the Mediterranean Sea, and are thought to reflect temporary oceanographic changes such as enhanced organic matter preservation at depth or enhanced surface productivity. Pleistocene sections from two Mediterranean Sea sediment cores, one from the Mediterranean Ridge (Ocean Drilling Program Site 969) and one from the Tyrrhenian Sea (Site 974), were analyzed for carbon and nitrogen isotope ratios in order to identify the mechanisms for sapropel formation and their spatial extent. Compared with surrounding sediments, sapropels contained consistently higher organic carbon concentrations, lower $^{15}N/^{14}N$ ratios, and, contrary to previous findings, higher $^{13}C/^{12}C$ ratios. These trends are consistent with upwelling-induced increases in primary productivity and/or enhanced preservation triggered by deep-water anoxia during sapropel formation, and they are inconsistent with two mechanisms suggested previously: terrigenous inputs of organic matter and dissolved nutrients. The opposite sense of the $\delta^{13}C$ excursion between sites suggests that a single mechanism cannot explain all the Mediterranean sapropels, but that different mechanisms, perhaps all triggered by the same global or regional event, acted in different parts of the basin.

INTRODUCTION

Two competing sets of theories have been proposed to explain the Mediterranean sapropels. The preservation hypothesis suggests that changes in the water budget and possibly a switch to estuarine circulation during sapropel formation produced deep-water anoxia, which would have led to enhanced sediment organic content even with no increase in organic flux to the benthos. The productivity hypothesis argues that upwelling and/or increased terrigenous runoff during sapropel formation boosted surface-water nutrient concentrations, thus increasing primary productivity and the export of organic matter to the deep sea. Decreased surface salinity, caused by increased precipitation, glacial meltwater, and/or Black Sea spillover, could have triggered either or both of these mechanisms.

So far, many studies have demonstrated that freshwater flooding coincided with sapropel formation in both the eastern Mediterranean (e.g., Rossignol-Strick et al., 1982) and the Tyrrhenian Sea (e.g., Thunell et al., 1990), but few studies have been able to distinguish between enhanced preservation and enhanced productivity as causal mechanisms. Nitrogen stable isotope ratios preserved in sediments offer the possibility of detecting increases in nitrate availability in surface waters, which in turn would indicate elevated primary productivity levels. For example, Altabet and Francois (1994) found an inverse linear relationship between nitrate concentration and $\delta^{15}N$ of near-surface and core-top organic nitrogen samples across nutrient gradients in the Pacific and Indian Oceans.

However, only two studies have examined nitrogen isotope ratios in the Mediterranean sapropels. Calvert et al. (1992) found a systematic decrease in $\delta^{15}N$ in nine sapropels (S1 and S3–S10) near the mouth of the Nile, which they attributed to increased nitrogen supply to the surface layer accompanied by increased primary productivity. The alternative explanation—that primary productivity decreased while nitrogen concentration remained constant—is unlikely since nitrogen is usually the limiting nutrient in oligotrophic ocean environments. Sachs (1996) also observed lighter $\delta^{15}N$ in sapropels S2–S4 from Site 964 and sapropels S5–S7 from Site 969, but, on the basis of chlorin biomarker $\delta^{15}N$ values, he argued that these shifts represent decreased diagenesis (and thus enhanced preservation). Furthermore, he suggested that neither nutrient levels nor primary productivity increased during sapropel formation.

In this study, we used both nitrogen and carbon stable isotopes to attempt to distinguish among various potential mechanisms for sapropel formation. Our approach is to use the nitrogen isotopes as indicators of nutrient availability, and therefore primary production, in surface waters, and to use the carbon isotopes to constrain the role of freshwater input as well as surface primary production in sapropel formation. In addition, we consider whether the sapropels reflect a single basin-wide event or several smaller events by examining an east–west transect consisting of Ocean Drilling Program Sites 969 and 974 plus Medsap Site 84641 near the mouth of the Nile River (Calvert et al., 1992; Fontugne and Calvert, 1992).

MATERIALS AND METHODS

Hole 969E was subsampled at five-centimeter intervals for each of 13 sapropels, plus overlying and underlying organic-poor sediments. Five sapropels were sampled from Holes 974B and 974D, with a 1-cm sampling interval from 5 cm above the sapropel to 5-cm below it, and a 5-cm sampling interval for the subsequent 50-cm above and below the sapropel. Table 1 lists the sapropels analyzed in this study and places the sapropels in their stratigraphic context.

Sediment from each interval was dried, ground, and weighed for isotopic analysis (10 µmol of carbon or 3 µmol nitrogen were used per analysis). Samples were then acidified with 10% HCl in a 2-mL plastic microcentrifuge tube to eliminate all carbonate compounds; ethanol was used to control bubbling during acidification. In order to ensure complete carbonate reaction, samples were acidified with excess HCl, stirred with a vortex mixer, and allowed to react overnight at

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[2] Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, U.S.A.

[3] The Biological Laboratories, Harvard University, Cambridge, MA 02138, U.S.A. Present address: School of Biology, Georgia Institute of Technology, Atlanta, GA 30332, U.S.A. j.montoya@biology.gatech.edu

[4] Department of Chemistry, University of Massachusetts, North Dartmouth, MA 02747, U.S.A.

Table 1. Sapropel samples analyzed in this study.

Sapropel no.	Core, section	Interval (cm)	Depth (mbsf)	Approximate age (k.y.)
161-969E				
S1	1H-1	26-37	0.26	9
S3	1H-2	117-124	2.67	81
S5	1H-3	68-100	3.68	123
S6	2H-1	34-79	5.24	175
S7	2H-1	123-129	6.13	193
S8	2H-2	37-51	6.77	234
A1	2H-3	32-46	8.22	297
A2	4H-2	29-33	25.69	1392
A3	4H-2	108-118	26.48	1455
A4	4H-3	28-34	27.18	1509
A5	5H-2	110-120	36.00	2042
A6	5H-3	96-111	37.36	2104
A7	5H-4	79-85	38.69	2165
161-974D				
T1	2H-3	82-89	5.32	211
161-974B				
T4	4H-5	21-32	31.71	767
T5	4H-5	94-113	32.44	778
T19	7H-5	24-26	58.06	1249
T20	7H-5	96-99	58.78	1266

Notes: Sapropel labels beginning with “S” represent late Pleistocene sapropels identified and correlated across the eastern Mediterranean by ODP (Shipboard Scientific Party, 1996a, table 3, p. 354), labels beginning with “A” denote eastern basin sapropels not numbered by ODP, and labels beginning with “T” indicate Tyrrhenian Sea sapropels numbered by ODP (Shipboard Scientific Party, 1996b, table 5, p. 65). Depth is given in meters below seafloor and refers to the top of the sapropel. Ages are estimated from Emeis and Leg 160 Shipboard Scientific Party (1996) and Comas et al. (1996).

60°C. Samples were then washed two or more times with deionized water to remove all chlorine and reacted chlorine compounds, dried overnight, and packed into tin capsules using forceps and a capsule press.

Isotopic analysis was performed on either a Carlo Erba elemental analyzer interfaced directly with a VG PRISM mass spectrometer or on a Europa CN analyzer interfaced with a Finnigan MAT 251 mass spectrometer. The δ^{15}N of each sample was measured relative to atmospheric dinitrogen, while the δ^{13}C was measured relative to the PeeDee Belemnite (PBD) standard. Analysis of replicate standards indicates that our isotopic measurements have a precision of ±0.2‰ or better. The two mass spectrometers used in this study have been extensively intercalibrated with a variety of organic and inorganic standards.

An acetanilide standard of known elemental composition (71.09% C, 10.36% N) was used to calibrate the dependence of the mass spectrometer ion beam intensity on sample size. This relationship was then used to determine the carbon and nitrogen content of each sample. Two corrections were made to the raw isotope data to remove the effects of our analytical “blank,” representing organic contamination introduced during sample preparation and during combustion of the tin capsule, and a correction for the small isotopic offsets associated with different batches of reference gas as well as normal instrumental variation between runs. Our blank correction was a simple mass-balance calculation based on direct analysis of capsule blanks as well as a regression of the isotopic composition of standards as a function of mass. Repeated analyses of a sediment standard (δ^{13}C = –15.9‰, δ^{15}N = 5.5‰) and two isotopically characterized organic standards, peptone (δ^{13}C = –14.7‰, δ^{15}N = 7.0 ‰) and histidine (δ^{13}C = –8.4‰, δ^{15}N = –9.7‰) were used to derive the blank contribution and the isotopic offset for each analytical run.

We performed one-way analysis of variance (ANOVA) tests to detect isotopic and compositional differences between the cores, between sapropel and nonsapropel intervals within each core, and between the different sapropels at each site.

RESULTS

Samples from both Site 969 and Site 974 revealed clear correlations between the three measured parameters: percent organic carbon, $\delta^{13}C_{org}$, and δ^{15}N. Sapropel intervals of increased organic carbon content were marked by lighter δ^{15}N values and almost always by heavier δ^{13}C values. Tables 2 and 3 provide compositional and isotopic data for each sample; Figures 1 through 5 show data from representative sapropels and their surrounding sediments.

Organic Carbon and Nitrogen Concentrations

At Site 969, organic carbon content averaged 0.48% (standard deviation [S.D.] = 0.35%) during normal sedimentation and 4.69% (S.D. = 2.63%) during sapropel formation, with no consistent trends downcore. Sapropel values ranged from 2.5% to 9.2% organic carbon. Two exceptions were sapropels A1 and A5, which showed no elevation in organic carbon content despite being identified as sapropels (Shipboard Scientific Party, 1996a).

At Site 974, the organic carbon gradient between sapropel and background intervals was less pronounced, with sapropels averaging 1.61% (S.D. = 0.42%) organic carbon and surrounding sediments averaging 0.51% (S.D. = 0.19%). No downcore trends were apparent in either the sapropels or the background sediments.

Nitrogen was one to two orders of magnitude less abundant than carbon in all samples. Nonsapropel values averaged 0.018% (S.D. = 0.007%) at Site 969 and 0.030% (S.D. = 0.010%) at Site 974 while sapropel values averaged 0.179% (S.D. = 0.095%) at Site 969 and 0.088% (S.D. = 0.022%) at Site 974. Within sapropel intervals, nitrogen increased in approximate proportion to carbon, so that the C:N ratio did not change significantly across sapropel boundaries.

Nitrogen Isotope Ratios

At Site 969, δ^{15}N averaged 3.5‰ (S.D. = 1.5‰) in background sediments, 0.2‰ (S.D. = 1.5‰) in sapropels, and $\Delta\delta^{15}$N ($\delta^{15}N_{sapropel}$ – $\delta^{15}N_{background}$) ranged from +0.45‰ to–6.79‰. Although the mean δ^{15}N varied little from sapropel to sapropel, we found relatively large variations in δ^{15}N within narrow stratigraphic zones within the sapropels. At Site 974, δ^{15}N averaged 5.0‰ (S.D. = 0.6‰) in background sediments and 2.2‰ (S.D. = 0.8‰) in sapropels, and $\Delta\delta^{15}$N ranged from –2.80‰ to–3.08‰.

Compared to these values, the data of Calvert et al. (1992) from the eastern Mediterranean are markedly enriched in ^{15}N during background sedimentation (average $\delta^{15}N \approx +6$‰) and somewhat enriched during sapropel sedimentation (average $\delta^{15}N \approx +1$‰ to +3‰).

Carbon Isotope Ratios

At Site 969, δ^{13}C averaged –24.7‰ in normal sediments, with considerable variation through the sediment column (S.D. = 1.9‰). However, within any single stratigraphic zone, δ^{13}C values were relatively constant. Sapropel δ^{13}C did not vary greatly, with an average value of –23.1‰ (S.D. = 0.97‰). The resulting average difference in δ^{13}C between sapropel and background sediments ($\Delta\delta^{13}C = \delta^{13}C_{sapropel}$ – $\delta^{13}C_{background}$) was 1.60‰, a highly significant difference (single-factor ANOVA, $p < 0.05$). Variations in $\delta^{13}C_{background}$ through the sediment column led to $\Delta\delta^{13}$C values ranging from 4.44‰ in sapropel A7 to –1.40‰ in sapropel S1; in three sapropels (S1, S6 and S8), $\delta^{13}C_{sapropel}$ was actually more negative than $\delta^{13}C_{background}$.

The δ^{13}C trends were more consistent at Site 974, where the δ^{13}C of background sediments averaged –25.8‰ (S.D. = 1.0‰) and the δ^{13}C of sapropels averaged –24.5‰ (S.D. = 0.67‰). The $\Delta\delta^{13}$C offset at this site varied between 0.98‰ and 1.66‰, with a mean of 1.32‰,

Table 2. Compositional and isotopic data for Site 969.

Core, section, interval top (cm)	Sapropel no.	Depth (mbsf)	C (%)	N (%)	C/N	δ^{13}C (‰)	δ^{15}N (‰)
160-969E-							
1H-1, 0	S1	0.00	0.12	0.008	15.27	–23.77	5.22
1H-1, 5	S1	0.05	0.30	0.016	18.46	–21.31	4.92
1H-1, 10	S1	0.10	0.23	0.016	14.56	–21.91	4.81
1H-1, 15	S1	0.15	0.19	0.013	14.66	–22.07	5.14
1H-1, 20	S1	0.20	0.21	0.013	16.22	–22.36	4.97
1H-1, 25	S1	0.25	0.35	0.021	16.43	–21.82	4.41
1H-1, 30	**S1**	**0.30**	**3.96**	**0.148**	**31.25**	**–23.61**	**0.84**
1H-2, 100	S3	2.50	0.55	0.004	180.74	–26.83	2.26
1H-2, 105	S3	2.55	1.12	0.016	226.86	–27.09	5.27
1H-2, 110	S3	2.60	0.70	0.004	223.75	–27.26	0.30
1H-2, 115	S3	2.65	0.94	0.026	41.93	–23.34	3.36
1H-2, 120	**S3**	**2.70**	**5.71**	**0.190**	**35.10**	**–21.52**	**0.34**
1H-2, 123	**S3**	**2.73**	**2.07**	**0.043**	**56.88**	**–23.86**	**2.90**
1H-2, 130	S3	2.80	1.71	0.031	64.71	–24.84	3.70
1H-3, 50	S5	3.50	0.84	0.015	67.07	–24.32	4.18
1H-3, 55	S5	3.55	0.56	0.012	46.67	–26.60	5.10
1H-3, 60	S5	3.60	0.68	0.014	48.46	–26.43	4.65
1H-3, 65	S5	3.65	0.67	0.020	33.60	–26.14	3.39
1H-3, 70	**S5**	**3.70**	**7.10**	**0.282**	**25.21**	**–22.08**	**–0.59**
1H-3, 75	**S5**	**3.75**	**8.03**	**0.277**	**29.00**	**–22.61**	**–0.71**
1H-3, 80	**S5**	**3.80**	**7.90**	**0.345**	**22.94**	**–21.76**	**–0.69**
1H-3, 85	**S5**	**3.85**	**8.59**	**0.282**	**30.42**	**–22.38**	**–1.09**
1H-3, 90	**S5**	**3.90**	**9.54**	**0.312**	**30.56**	**–23.02**	**–0.88**
1H-3, 95	**5S**	**3.95**	**7.94**	**0.285**	**27.90**	**–22.33**	**–0.77**
1H-3, 100	**S5**	**4.00**	**3.61**	**0.208**	**17.38**	**–22.18**	**–0.27**
1H-3, 105	S5	4.05	0.29	0.028	10.27	–22.36	3.27
1H-3, 110	S5	4.10	0.18	0.025	7.27	–23.49	3.81
1H-3, 115	S5	4.15	0.15	0.020	7.58	–23.47	4.10
1H-3, 120	S5	4.20	0.17	0.016	10.92		5.10
2H-1, 20	S6	5.10	0.17	0.019	9.01	–22.75	2.47
2H-1, 25	S6	5.15	0.16	0.020	8.17	–22.64	2.23
2H-1, 30	S6	5.20	0.21	0.013	16.38	–25.44	4.82
2H-1, 35	**S6**	**5.25**	**2.62**	**0.143**	**18.29**	**–24.03**	**–0.42**
2H-1, 40	**S6**	**5.30**	**1.12**	**0.072**	**15.60**	**–22.73**	**0.54**
2H-1, 45	**S6**	**5.35**	**2.52**	**0.126**	**19.99**	**–23.74**	**0.22**
2H-1, 50	**S6**	**5.40**	**0.92**	**0.050**	**18.33**	**–22.30**	**2.12**
2H-1, 55	**S6**	**5.45**	**3.71**	**0.200**	**18.52**	**–23.93**	**–1.42**
2H-1, 60	**S6**	**5.50**	**2.41**	**0.144**	**16.75**	**–22.69**	**–1.30**
2H-1, 65	**S6**	**5.55**	**2.47**	**0.142**	**17.37**	**–23.24**	**–1.49**
2H-1, 70	**S6**	**5.60**	**5.55**	**0.208**	**26.72**	**–23.14**	**–0.49**
2H-1, 75	**S6**	**5.65**	**2.54**	**0.142**	**17.90**	**–23.12**	**0.05**
2H-1, 80	S6	5.70	0.52	0.028	18.64	–21.91	3.25
2H-1, 85	S6	5.75	0.30	0.019	15.70	–22.70	4.05
2H-1, 90	S7	5.80	0.20	0.022	9.08	–22.47	2.89
2H-1, 100	S7	5.90	0.17	0.020	8.58	–23.56	3.66
2H-1, 105	S7	5.95	0.17	0.020	8.40	–23.44	3.11
2H-1, 110	S7	6.00	0.18	0.021	8.36	–23.81	4.87
2H-1, 115	S7	6.05	0.20	0.023	8.76	–23.57	4.27
2H-1, 120	S7	6.10	0.17	0.024	7.29	–21.52	3.00
2H-1, 125	**S7**	**6.15**	**6.49**	**0.178**	**36.52**	**–22.47**	**0.56**
2H-1, 130	**S7**	**6.20**	**7.44**	**0.191**	**38.95**	**–22.90**	**0.03**
2H-1, 135	**S7**	**6.25**	**3.19**	**0.178**	**17.94**	**–21.77**	**–0.80**
2H-1, 140	S7	6.30	0.41	0.032	12.77	–22.00	2.51
2H-2, 20	S8	6.60	0.15	0.019	7.85	–21.80	3.38
2H-2, 25	S8	6.65	0.15	0.019	7.78	–22.90	1.91
2H-2, 30	S8	6.70	0.15	0.021	6.99	–23.08	3.96
2H-2, 35	S8	6.75	0.28	0.022	12.75	–24.68	4.52
2H-2, 40	**S8**	**6.80**	**5.13**	**0.144**	**35.73**	**–24.32**	**0.73**
2H-2, 45	**S8**	**6.85**	**2.76**	**0.154**	**17.94**	**–23.49**	**0.03**
2H-2, 50	**S8**	**6.90**	**3.35**	**0.134**	**24.99**	**–24.02**	**3.37**
2H-2, 55	S8	6.95	0.65	0.035	18.60	–23.01	3.20
2H-2, 55B	S8	6.98	1.28	0.031	41.51	–24.04	3.83
2H-3, 20	A1	8.10	0.24	0.012	19.59	–27.59	5.43
2H-3, 25	A1	8.15	0.24	0.008	30.40	–27.39	0.87
2H-3, 30	A1	8.20	0.15	0.021	7.14	–27.02	5.77
2H-3, 35	A1	8.25	0.19	0.006	32.94	–28.09	3.07
2H-3, 40	A1	8.30	0.14	0.006	21.43	–27.35	
2H-3, 45	A1	8.35	0.25	0.011	23.74	–26.72	–0.42
2H, 3, 50	A1	8.40	0.22	0.015	14.54	–26.70	3.31
2H-3, 55	A1	8.45	0.14	0.020	6.88	–22.57	1.66
2H-3, 60	A1	8.50	0.15	0.023	6.70	–22.93	4.23
4H-2, 20	A2	25.60	0.17	0.010	17.51	–27.17	4.69
4H-2, 30	**A2**	**25.70**	**9.18**	**0.409**	**22.45**	**–22.60**	**–2.30**
4H-2, 35	A2	25.75	0.39	0.022	17.76	–25.23	2.32
4H-2, 80	A2	26.20	0.57	0.018	32.27	–27.57	4.27
4H-2, 85	A2	26.25	0.56	0.016	34.39	–27.49	6.66
4H-2, 130	A3	26.70	0.89	0.017	60.46	–24.92	4.04
4H-3, 10	A4	27.00	0.74	0.018	49.11	–24.25	4.95
4H-3, 15	A4	27.05	0.86	0.014	70.73	–24.41	–1.49
4H-3, 20	A4	27.10	0.82	0.017	56.32	–24.60	2.92
4H-3, 25	A4	27.15	0.94	0.023	48.09	–23.99	4.80

Table 2 (continued).

Core, section, interval top (cm)	Sapropel no.	Depth (mbsf)	C (%)	N (%)	C/N	δ13C (‰)	δ15N (‰)
160-969E-							
4H-3, 30	**A4**	**27.20**	**8.19**	**0.290**	**32.96**	**–23.59**	**4.88**
4H-3, 35	A4	27.25	1.04	0.027	45.97	–23.51	5.79
4H-3, 40	A4	27.30	1.21	0.022	63.58	–24.83	3.68
5H-2, 90	A5	35.80	1.10	0.020	63.19	–24.70	5.90
5H-2, 95	A5	35.85	0.72	0.017	50.05	–24.95	3.71
5H-2, 100	A5	35.90	0.81	0.017	56.47	–24.22	3.35
5H-2, 105	A5	35.95	0.92	0.017	63.82	–23.70	1.74
5H-2, 110	A5	36.00	0.95	0.021	53.24	–23.60	4.60
5H-2, 115	A5	36.05	0.97	0.018	61.22	–24.01	4.19
5H-2, 120	A5	36.10	0.70	0.012	69.22	–24.34	–0.65
5H-2, 125	A5	36.15	0.59	0.011	63.43	–24.73	3.82
5H-2, 130	A5	36.20	0.59	0.010	69.93	–24.52	3.24
5H-2, 135	A5	36.25	0.31	0.005	73.24	–25.05	0.42
5H-2, 140	A5	36.30	0.69	0.012	69.28	–25.08	4.00
5H-3, 80	A6	37.20	0.25	0.013	22.84	–26.75	2.69
5H-3, 85	A6	37.25	0.24	0.013	22.03	–26.65	3.99
5H-3, 90	A6	37.30	0.22	0.013	20.08	–26.61	3.21
5H-3, 95	A6	37.35	0.35	0.023	17.66	–26.87	3.06
5H-3, 100	**A6**	**37.40**	**3.80**	**0.109**	**40.73**	**–24.13**	**–0.76**
5H-3, 105	**A6**	**37.45**	**2.12**	**0.026**	**93.96**	**–25.59**	**0.70**
5H-3, 110	**A6**	**37.50**	**1.70**	**0.027**	**74.68**	**–24.78**	**1.68**
5H-3, 115	A6	37.55	0.40	0.017	26.65	–26.95	2.62
5H-3, 120	A6	37.60	0.41	0.017	28.63	–27.02	1.89
5H-4, 60	A7	38.50	0.38	0.013	33.27	–27.23	2.71
5H-4, 65	A7	38.55	0.65	0.027	28.71	–26.82	2.02

Note: Bold = sapropel intervals.

Table 3. Compositional and isotopic data for Site 974.

Core, section, interval top (cm)	Sapropel no.	Depth (mbsf)	C (%)	N (%)	C/N	δ13C (‰)	δ15N (‰)
161-974D-							
2H-3, 37	T1	4.87	0.67	0.02	40.42	–25.26	2.61
2H-3, 42	T1	4.92	0.62	0.04	17.63	–24.77	4.74
2H-3, 47	T1	4.97	0.45	0.04	13.35	–24.72	4.91
2H-3, 52	T1	5.02	0.67	0.04	21.57	–24.10	4.81
2H-3, 57	T1	5.07	0.56	0.04	15.14	–24.35	4.94
2H-3, 62	T1	5.12	0.52	0.04	16.79	–24.72	5.09
2H-3, 67	T1	5.17	0.47	0.03	15.92	–25.83	5.25
2H-3, 72	T1	5.22	0.45	0.03	15.09	–25.92	
2H-3, 77	T1	5.27	0.57	0.04	18.14	–25.78	5.13
2H-3, 78	T1	5.28	0.52	0.04	16.71	–26.15	5.20
2H-3, 79	T1	5.29	0.74	0.04	22.53	–25.40	5.02
2H-3, 80	T1	5.30	0.57	0.03	20.53	–26.00	4.70
2H-3, 81	T1	5.31	0.84	0.05	19.62	–25.55	4.14
2H-3, 82	**T1**	**5.32**	**2.76**	**0.07**	**46.06**	**–25.80**	**2.34**
2H-3, 83	**T1**	**5.33**	**1.49**	**0.08**	**21.08**	**–24.67**	**1.67**
2H-3, 84	**T1**	**5.34**	**1.70**	**0.09**	**21.42**	**–24.48**	**1.45**
2H-3, 85	**T1**	**5.35**	**1.94**	**0.10**	**22.74**	**–24.76**	**1.30**
2H-3, 86	**T1**	**5.36**	**1.06**	**0.06**	**19.50**	**–24.44**	**1.22**
2H-3, 87	**T1**	**5.37**	**1.50**	**0.08**	**21.09**	**–24.54**	**1.32**
2H-3, 88	**T1**	**5.38**	**1.78**	**0.11**	**18.62**	**–24.32**	
2H-3, 89	**T1**	**5.39**	**1.60**	**0.10**	**18.12**	**–24.59**	**1.86**
2H-3, 90	T1	5.40	0.85	0.05	18.54	–25.34	3.57
2H-3, 91	T1	5.41	0.77	0.04	24.50	–25.89	4.47
2H-3, 92	T1	5.42	0.55	0.04	17.88	–26.28	4.32
2H-3, 97	T1	5.47	0.54	0.03	20.54	–25.88	4.68
2H-3, 102	T1	5.52	0.51	0.03	19.62	–26.31	4.95
2H-3, 107	T1	5.57	0.72	0.03	27.93	–25.36	4.80
2H-3, 112	T1	5.62	0.50	0.03	20.07	–26.09	
2H-3, 117	T1	5.67	0.64	0.02	30.63	–26.00	4.79
2H-3, 122	T1	5.72	0.51	0.02	25.28	–26.82	5.15
2H-3, 127	T1	5.77	0.72	0.03	33.82	–25.96	4.98
2H-3, 132	T1	5.82	0.74	0.03	30.73	–26.29	
2H-3, 137	T1	5.87	0.50	0.03	20.37	–27.30	
161-974B-							
4H-4, 121	T4	31.21	0.19	0.02	12.00	–24.83	5.19
4H-4, 126	T4	31.26	0.21	0.02	10.79	–24.96	5.28
4H-4, 131	T4	31.31	0.44	0.02	23.82	–25.33	4.94
4H-4, 136	T4	31.36	0.21	0.02	11.68	–25.08	5.16
4H-4, 141	T4	31.41	0.21	0.02	10.88	–26.75	5.17
4H-5, 1	T4	31.51	0.27	0.03	11.49	–25.16	5.12
4H-5, 6	T4	31.56	0.25	0.03	10.39	–24.96	4.91
4H-5, 11	T4	31.61	0.22	0.01	20.14	–27.27	5.04
4H-5, 16	T4	31.66	0.35	0.03	14.88	–26.34	4.67
4H-5, 17	T4	31.67	0.31	0.03	12.91	–25.60	4.59
4H-5, 18	T4	31.68	0.44	0.03	17.36	–25.21	4.52
4H-5, 19	T4	31.69	0.29	0.04	9.39	–25.03	4.74
4H-5, 20	T4	31.70	0.44	0.03	15.20	–25.40	4.42

Table 3 (continued).

Core, section, interval top (cm)	Sapropel no.	Depth (mbsf)	C (%)	N (%)	C/N	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
161-974B-							
4H-5, 21	**T4**	**31.71**	**0.83**	**0.03**	**28.95**	**–25.66**	**2.52**
4H-5, 22	**T4**	**31.72**	**0.57**	**0.04**	**15.42**	**–24.98**	**2.55**
4H-5, 23	**T4**	**31.73**	**1.02**	**0.06**	**20.25**	**–25.30**	**4.37**
4H-5, 24	**T4**	**31.74**	**1.76**	**0.07**	**31.41**	**–24.69**	**2.03**
4H-5, 25	**T4**	**31.75**	**1.29**	**0.07**	**21.20**	**–23.85**	**1.07**
4H-5, 26	**T4**	**31.76**	**1.28**	**0.06**	**23.29**	**–23.66**	**1.88**
4H-5, 27	**T4**	**31.77**	**1.34**	**0.07**	**22.35**	**–23.37**	**2.09**
4H-5, 28	**T4**	**31.78**	**1.81**	**0.09**	**23.06**	**–23.54**	**1.39**
4H-5, 29	**T4**	**31.79**	**1.40**	**0.08**	**20.20**	**–23.32**	**1.67**
4H-5, 30	**T4**	**31.80**	**1.57**	**0.09**	**21.30**	**–23.19**	**1.42**
4H-5, 31	**T4**	**31.81**	**1.68**	**0.11**	**18.53**	**–23.29**	**2.67**
4H-5, 32	**T4**	**31.82**	**1.31**	**0.07**	**20.34**	**–23.85**	**2.90**
4H-5, 33	T4	31.83	0.66	0.04	18.89	–25.12	4.62
4H-5, 34	T4	31.84	0.74	0.04	21.95	–24.85	5.19
4H-5, 35	T4	31.85	0.54	0.03	23.15	–26.27	4.13
4H-5, 36	T4	31.86	0.40	0.03	18.54	–25.63	4.68
4H-5, 41	T4	31.91	0.57	0.03	19.65	–25.59	4.70
4H-5, 46	T4	31.96	0.60	0.04	19.83	–25.44	5.31
4H-5, 51	T4	32.01	0.27	0.03	10.56	–25.36	4.63
4H-5, 56	T4	32.06	0.40	0.02	21.13	–25.14	4.79
4H-5, 61	T4	32.11	0.51			–26.51	
4H-5, 66	T5	32.16	0.51	0.024	21.32	–26.37	5.07
4H-5, 71	T5	32.21	0.40	0.010	39.55		6.05
4H-5, 76	T5	32.26	0.37	0.008	46.50	–28.08	5.79
4H-5, 81	T5	32.31	0.52	0.031	16.88	–26.47	5.9
4H-5, 85	T5	32.35	0.58	0.029	20.10	–25.85	5.82
4H-5, 89	T5	32.39	0.60	0.035	17.15	–26.76	5.49
4H-5, 90	T5	32.40	0.77	0.036	21.38	–26.29	5.35
4H-5, 91	T5	32.41	0.64	0.037	17.33	–26.48	4.86
4H-5, 92	T5	32.42	0.74	0.045	16.52	–26.24	5.26
4H-5, 93	T5	32.43	1.08	0.058	18.61	–20.74	4.02
4H-5, 94	**T5**	**32.44**	**1.62**	**0.094**	**17.26**	**–24.77**	**2.55**
4H-5, 95	**T5**	**32.45**	**1.79**	**0.107**	**16.77**	**–24.54**	**2.12**
4H-5, 96	**T5**	**32.46**	**1.64**	**0.105**	**15.62**	**–24.33**	**2.64**
4H-5, 97	**T5**	**32.47**	**1.46**			**–25.39**	
4H-5, 98	**T5**	**32.48**	**1.10**	**0.064**	**17.18**	**–25.65**	**4.51**
4H-5, 99	**T5**	**32.49**	**0.97**	**0.064**	**15.21**	**–25.65**	**4.45**
4H-5, 100	**T5**	**32.50**	**1.32**	**0.074**	**17.82**		**3.32**
4H-5, 101	**T5**	**32.51**	**1.81**	**0.123**	**14.73**	**–24.30**	**1.99**
4H-5, 102	**T5**	**32.52**	**2.21**	**0.123**	**17.93**	**–23.89**	**2.1**
4H-5, 103	**T5**	**32.53**	**2.14**	**0.119**	**18.02**	**–24.84**	**2.09**
4H-5, 104	**T5**	**32.54**	**1.95**	**0.104**	**18.73**	**–24.40**	**1.99**
4H-5, 105	**T5**	**32.55**	**1.74**	**0.092**	**18.95**	**–24.14**	**2.35**
4H-5, 106	**T5**	**32.56**	**1.53**	**0.088**	**17.34**	**–24.64**	**2.45**
4H-5, 107	**T5**	**32.57**	**1.98**	**0.113**	**17.53**	**–24.38**	**2.24**
4H-5, 108	**T5**	**32.58**	**2.16**	**0.094**	**23.01**	**–24.55**	**1.94**
4H-5, 109	**T5**	**32.59**	**2.06**	**0.097**	**21.24**	**–24.63**	**1.84**
4H-5, 110	**T5**	**32.60**	**1.68**	**0.108**	**15.53**	**–24.53**	**1.4**
4H-5, 111	**T5**	**32.61**	**1.82**	**0.114**	**15.95**	**–24.38**	
4H-5, 112	**T5**	**32.62**	**1.89**	**0.114**	**16.62**	**–24.52**	**2.22**
4H-5, 113	**T5**	**32.63**	**1.92**	**0.103**	**18.62**	**–25.25**	**2.76**
4H-5, 114	T5	32.64	0.84	0.050	16.83	–25.52	4.82
4H-5, 115	T5	32.65		0.040			5.15
4H-5, 116	T5	32.66	0.68	0.038	17.79	–26.25	5.4
4H-5, 117	T5	32.67	0.70	0.032	21.82	–26.56	5.29
4H-5, 118	T5	32.68	0.53	0.033	16.10	–26.68	5.33
4H-5, 123	T5	32.73	0.45	0.030	14.98	–25.92	5.5
4H-5, 128	T5	32.78	0.30	0.015	19.81	–27.78	5.43
4H-5, 133	T5	32.83	0.27	0.011	24.16	–26.63	5.53
4H-5, 138	T5	32.88	0.25	0.009	27.76	–26.65	5.35
4H-5, 143	T5	32.93		0.019			5.39
4H-5, 148	T5	32.98	0.31	0.025	12.52	–25.42	5.68
4H-6, 3	T5	33.03	0.33	0.020	16.60	–26.88	5.66
4H-6, 8	T5	33.08	0.41	0.028	14.67	–25.56	5.91
4H-6, 13	T5	33.13	0.37	0.027	13.54	–25.51	5.6

Note: Bold = sapropel intervals.

a statistically significant difference (single-factor ANOVA, $p < 0.05$).

Virtually all samples at both sites contained less ^{13}C than the eastern Mediterranean samples analyzed by Fontugne and Calvert (1992), which had a mean $\delta^{13}C$ of –18.8 ± 1.07‰ for nonsapropels and –21.0 ± 0.82‰ for sapropels. Furthermore, at Sites 969 and 974, $\delta^{13}C$ generally increased during sapropel intervals, whereas in sediments studied by Fontugne and Calvert (1992), $\delta^{13}C$ decreased during sapropel intervals.

Intersite Comparisons

A comparison of Sites 974, 969, and MD 84641 reveals a consistent east–west $\delta^{13}C$ gradient and spatially inconsistent trends in $\delta^{15}N$ and percent organic carbon. Table 4 presents average values of these parameters from the three sites, and Tables 5 and 6 show east–west $\delta^{13}C$ and $\delta^{15}N$ gradients including data from other sites.

One-way ANOVAs were performed to determine the statistical significance of isotope differences between Sites 969 and 974. The $\delta^{13}C$ of organic matter was significantly lower at Site 974 than at Site 969 for both sapropel intervals ($p < 0.05$, $F = 32.7$) and background intervals ($p < 0.05$, $F = 13.5$). However, $\Delta\delta^{13}C$ was essentially the same in both cores ($p = 0.81$; $F = 0.06$).

The difference in $\delta^{15}N$ between Sites 969 and 974 was highly significant for both background ($p < 0.05$, $F = 40.9$) and sapropel ($p < 0.05$, $F = 27.8$) sediments, with Site 974 averaging 1.8‰ heavier than Site 969. However, $\Delta\delta^{15}N$ was virtually identical ($p = 0.99$, $F < 0.001$) between the two sites, with an average value of about –3‰.

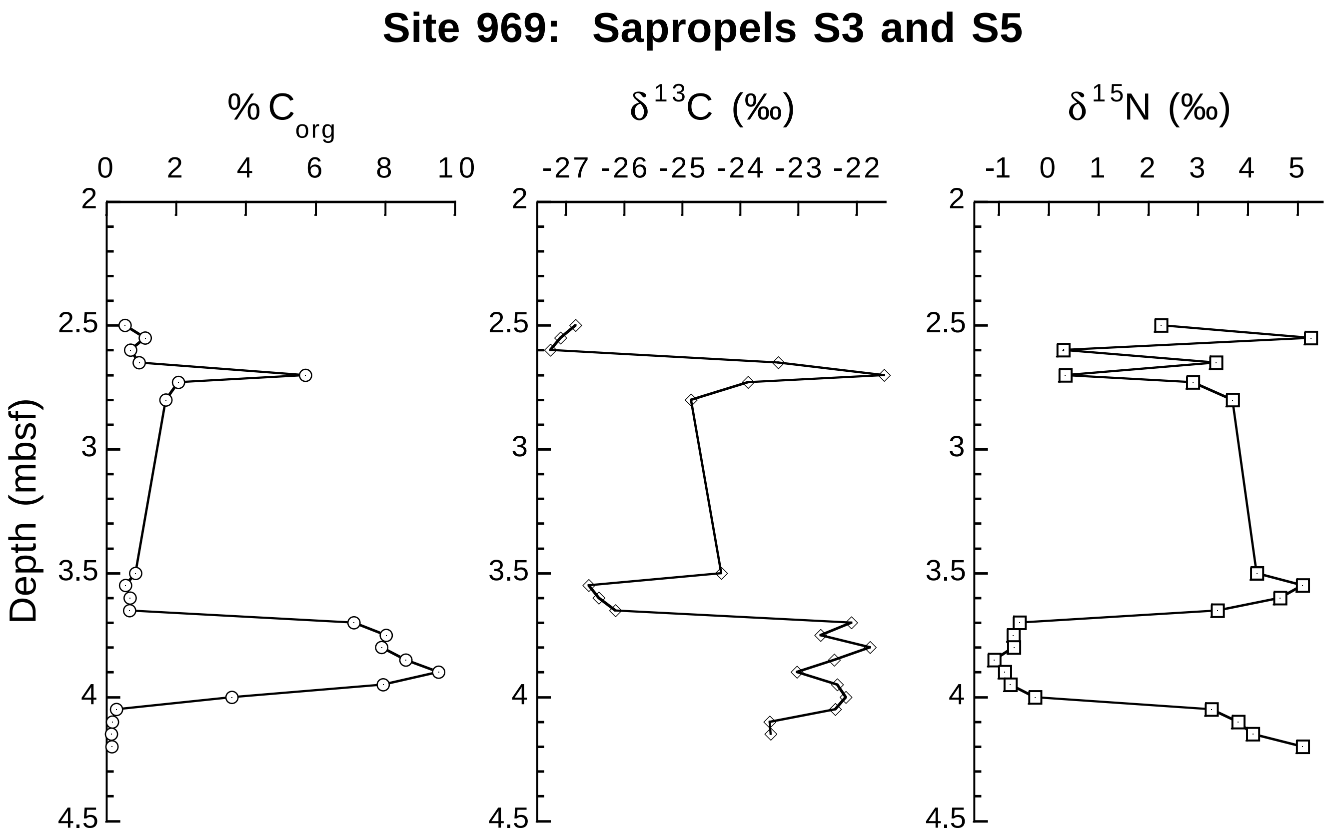

Figure 1. Isotopic and compositional trends for Site 969, sapropels S3 and S5.

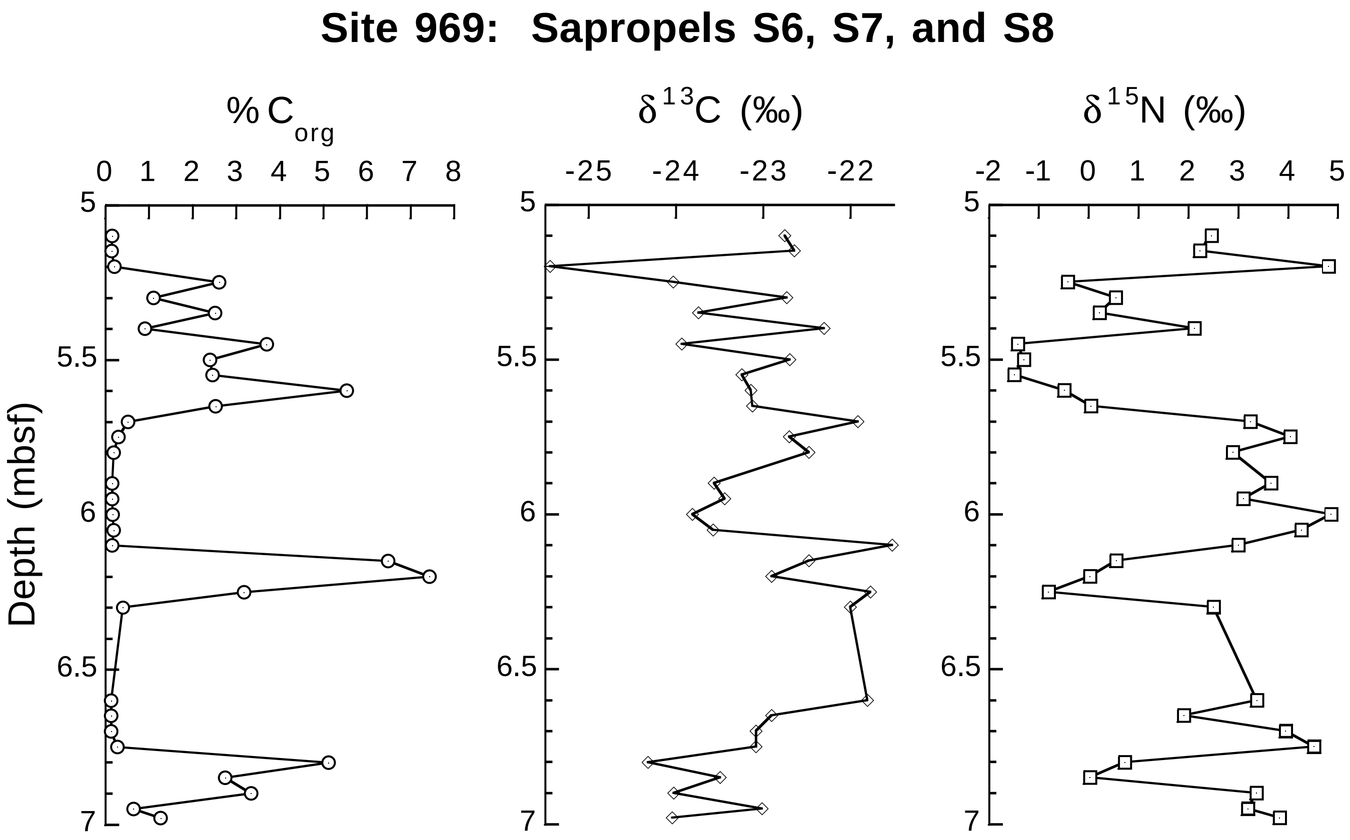

Figure 2. Isotopic and compositional trends for Site 969, sapropels S6, S7, and S8.

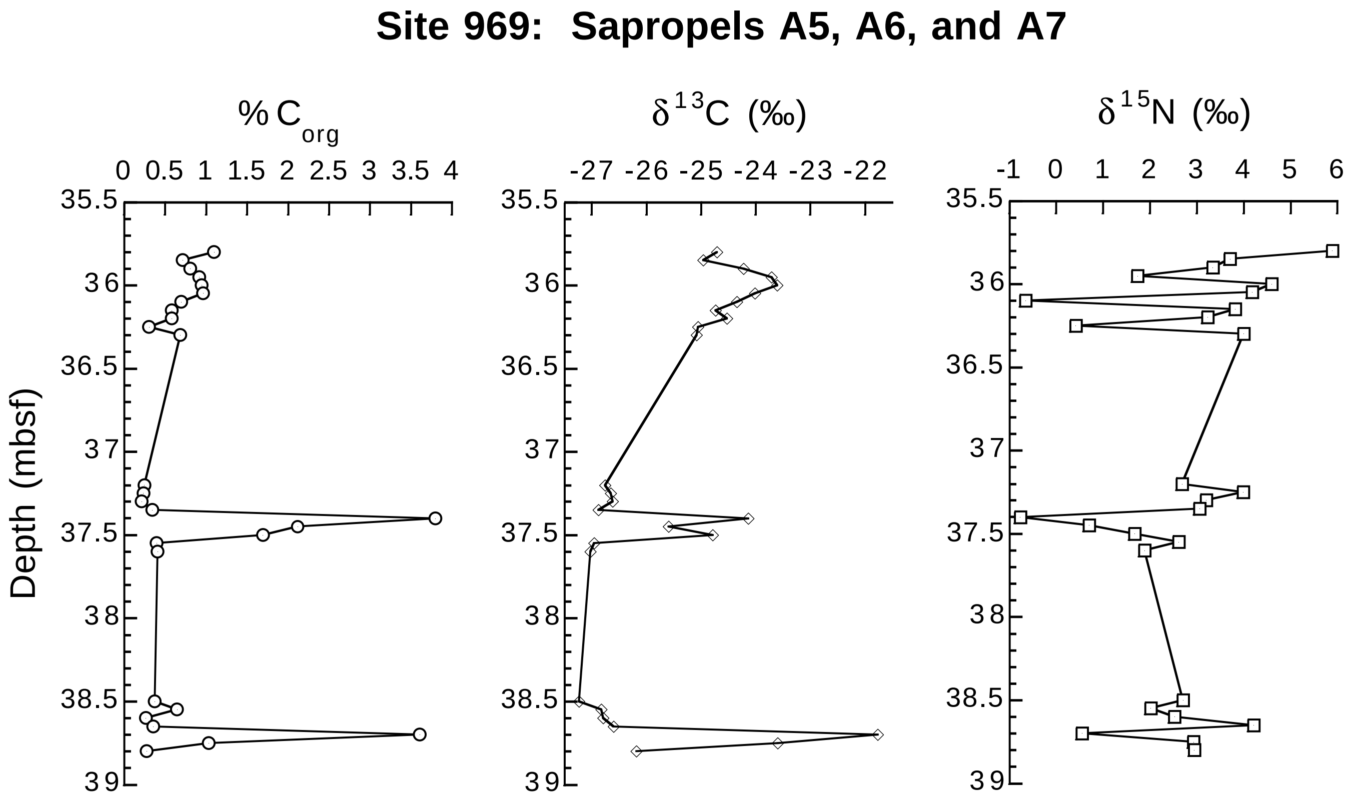

Figure 3. Isotopic and compositional trends for Site 969, sapropels A5, A6, and A7.

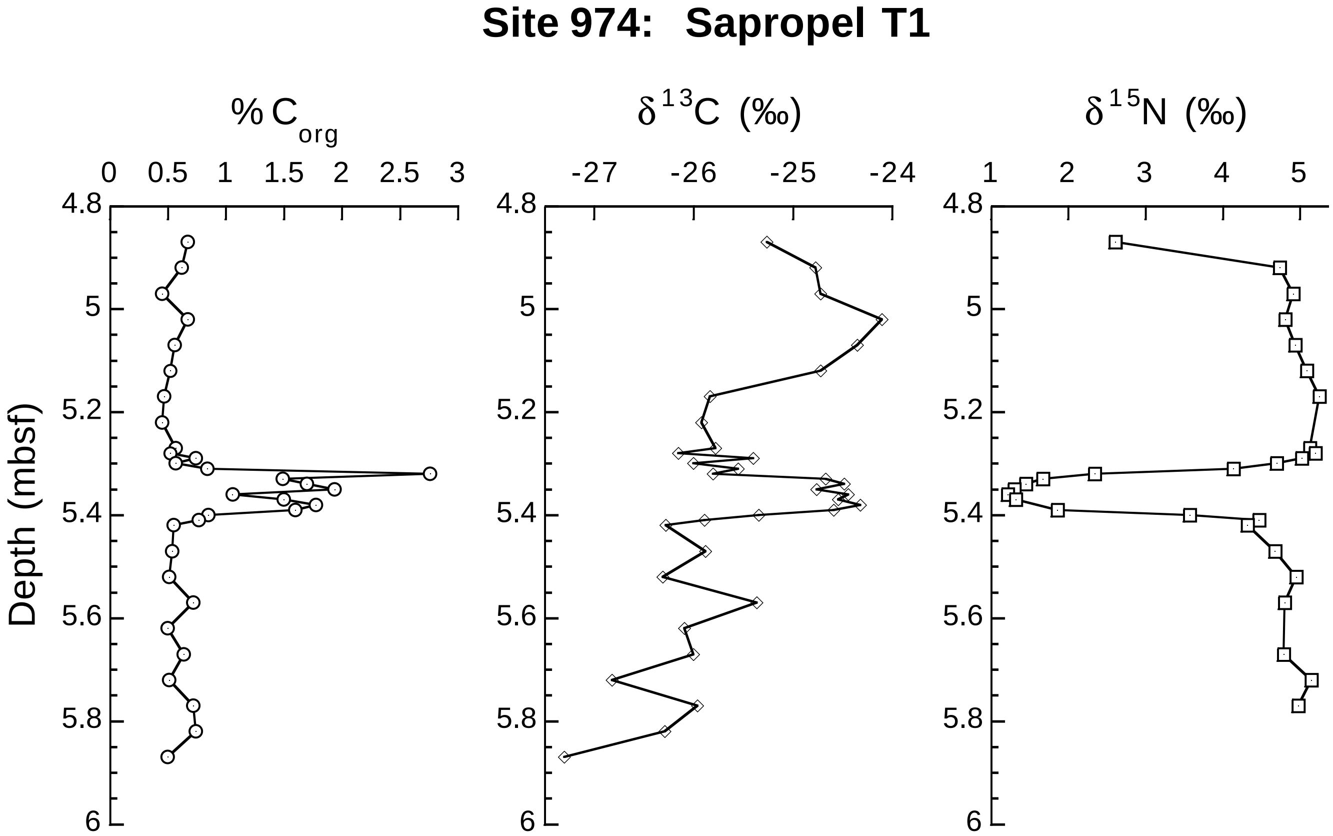

Figure 4. Isotopic and compositional trends for Site 974, sapropel T1.

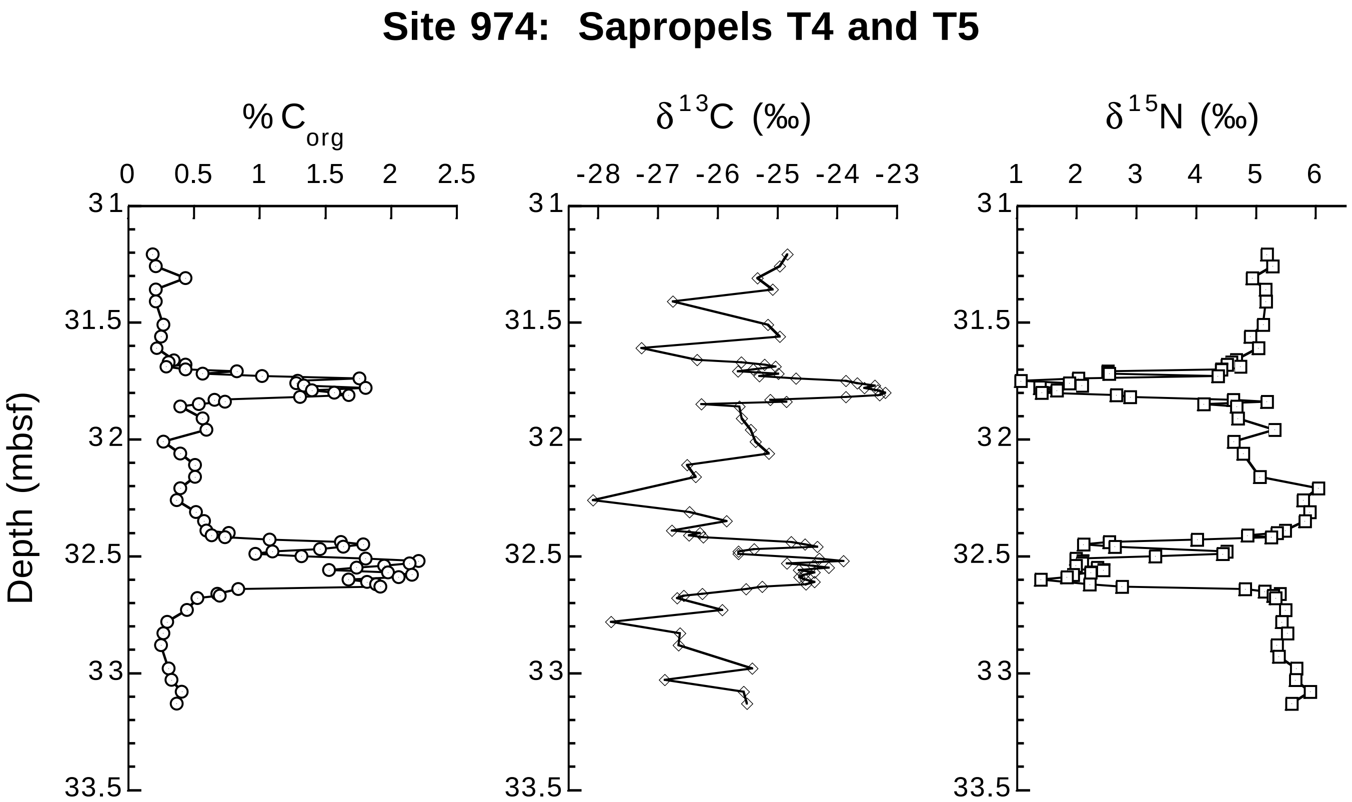

Figure 5. Isotopic and compositional trends for Site 974, sapropels T4 and T5.

Table 4. Averages of isotopic and percent organic carbon data for two eastern Mediterranean and one western Mediterranean site.

Parameter		Site MD 84861 32°E 33°N (Near mouth of Nile)	Site 969 25°E 34°N (Mediterranean Ridge)	Site 974 12°E 40°N (Tyrrhenian Sea)
C_{org} (%)	Nonsapropel	0.3	0.5	0.5
	Sapropel	2 to 4.5 (avg = 2.5)	3 to 9 (avg = 4.7)	1.6
	Enrichment Factor	~ 8	~ 10	~ 3
$\delta^{13}C$ (‰)	Nonsapropel	–18.8	–24.7	–25.8
	Sapropel	–21.0	–23.1	–24.5
	$\Delta\delta^{13}C$	–2.2	+1.6	+1.3
$\delta^{15}N$ (‰)	Nonsapropel	+6.0	+3.5	+5.0
	Sapropel	+1 to+2	+0.2	+2.2
	$\Delta\delta^{15}N$	~ –4	–3.3	–2.8

Note: Data for site MD 84641 are from Fontugne and Calvert (1992) and Calvert et al. (1992) and are approximate.

Table 5. Values of $\delta^{13}C$ of organic matter in late Pleistocene sapropels from the eastern Mediterranean and Tyrrhenian Seas.

Site	Longitude	S1	S3	S4	S5	S6	S7	S8	S9	S10	Reference
Site 974	12°8′E						–24.7				This study
DED 8708	13°34′E			–22.4	–22.1		–23.2	–21.4	–22.3	–21.6	M. Paterne (unpubl. data, 1990)
DI 10103/8K	20°40′E		–21.3								Sutherland et al. (1984)
TR 83-7	25°59′E					–22.7	–22.3				Ten Haven et al. (1987)
TR 83-30	28°37′E	–22.6									Ten Haven et al. (1987)
Site 969	29°52′E	–23.6	–22.7		–22.3	–23.3	–22.4	–23.9			This study
MD 84639	32°42′E	–21.2									Fontugne and Calvert (1992)
MD 84642	32°34′E	–21.2	–19.7	–21.0	–22.0	–21.6					Fontugne and Calvert (1992)
MD 84641	32°34′E	–20.8	–19.8	–20.6	–20.6	–22.4	–20.8	–22.2	–20.6	–20.8	Fontugne and Calvert (1992)
MD 84629	33°45′E	–20.9									Fontugne and Calvert (1992)

Note: ODP Site 974 has not been correlated stratigraphically with the other sites, so it is unclear to which eastern basin sapropel, if any, the value given corresponds. Table constructed after Fontugne and Calvert (1992).

Table 6. Values of $\delta^{15}N$ of organic matter in late Pleistocene sapropels from the eastern Mediterranean and Tyrrhenian Sea.

Site	Longitude	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	Reference
Site 974	12°8′E								+1.6			This Study
Site 964	17°45′E		+1.6	–0.2	+0.4							Sachs (1996)
Site 969	29°52′E	+0.8		+1.6		–0.7	–0.7	–0.1	+0.4			This Study
Site 969	29°52′E					–0.7	–0.2	+0.2				Sachs (1996)
MD 84641	32°34′E	+2.3		+2.7	+2.5	+0.5	+1.4	+0.4	+2.2	+2.8	+1.5	Calvert et al. (1992)

Note: ODP Site 974 has not been correlated stratigraphically with the other sites, so it is unclear to which eastern basin sapropel, if any, the value given corresponds. Averages for core MD 84641 are approximate.

Table 7. Framework for interpreting the observed compositional and isotopic trends at Sites 969 and 974.

Mechanism for sapropel formation	Predicted signature in sapropels	Existing evidence for and against this mechanism
Influx of terrigenous organic material	Negative $\delta^{13}C_{org}$ excursion ($\delta^{13}C$ of terrestrial $C_{org} \approx -27$‰)	+Plant debris, terrestrial biomarkers, & high C/N found in selected Eastern Mediterranean cores and sapropels (Deroo et al., 1978; Sigl et al., 1978).
	Unchanged $\delta^{13}C_{carbonate}$	+Negative $\delta^{13}C$ and $\delta^{15}N$ excursions in sapropels (Calvert et al., 1992).
	Negative $\delta^{15}N$ excursion ($\delta^{15}N$ of terrestrial PON ≈ 0‰)	– $\delta^{13}C_{sap}$ has marine signature of –20‰ to –23‰ (Fontugne and Calvert, 1992).
	Increased C/N ratio	– No positive $\delta^{13}C$ gradient away from Nile.
Influx of terrigenous nutrients and DIC, resulting in enhanced surface productivity	Negative $\delta^{13}C_{org}$ and $\delta^{13}C_{carbonate}$ excursions (lighter and more abundant DIC)	+Negative $\delta^{13}C_{org}$,$\delta^{13}C_{carbonate}$, and $\delta^{15}N$ excursions in sapropels (Calvert et al., 1992).
	Negative $\delta^{15}N$ excursion (more abundant & possibly lighter nitrate)	+Oxygen isotope and other evidence for freshwater flooding during sapropel formation.
	No elevated C/N ratio	+Light $\delta^{13}C$ of *G. ruber* carbonate at many eastern and western Mediterranean sites (Vergnaud-Grazzini et al., 1986 and Thunell et al., 1990).
Upwelling-supplied increase in surface nutrients and DIC, resulting in enhanced surface productivity	Heavier $\delta^{13}C$ (production increases more than $CO_{2(aq)}$)	+Negative $\delta^{13}C$ and $\delta^{15}N$ excursions in sapropels (Calvert et al., 1992).
	Lighter $\delta^{13}C_{carbonate}$	+Freshwater flooding likely triggered estuarine circulation and E. Med. upwelling.
	Lighter $\delta^{15}N$ (more nitrate)	+Light $\delta^{13}C$ of *G. ruber* carbonate at many eastern and western Mediterranean sites (Vergnaud-Grazzini et al., 1986 and Thunell et al., 1990).
	Diatom bloom (upwelled waters are Si-rich)	±Localized high diatom and silicoflagellate abundance in E. Med. sapropels (Sutherland et al., 1984).
Deep-water anoxia and enhanced preservation	Heavier $\delta^{13}C$ (diagenetic effect on C is lessened)	+$\delta^{15}N_{sap, chlorin} \approx \delta^{15}N_{modern\ plankton}$, suggesting $\delta^{15}N$ excursions in sapropels are a diagenetic signal (Sachs, 1996).
	Lighter $\delta^{15}N$ (diagenetic effect on N is lessened)	+Freshwater flooding likely triggered estuarine circulation and Eastern Mediterranean anoxia.
	Possibly unchanged $\delta^{13}C_{carbonate}$	

The contrast in organic carbon content between sapropel layers and nonsapropel layers was more dramatic at Site 969 (enrichment factor ≈10) than at Site 974 (enrichment factor ≈3) ($p < 0.05$, $F = 5.7$).

DISCUSSION

Table 7 summarizes four proposed mechanisms for sapropel formation, the geochemical signatures associated with each mechanism, and the evidence for and against each proposed mechanism. Based on this information and on data collected in this study, we conclude that no single mechanism can explain all the sapropel-related isotopic trends in the Mediterranean Sea, or even those in the eastern basin of the Mediterranean. Instead, we believe that a combination of localized mechanisms, perhaps triggered by a single global or regional event, produced the observed trends.

Terrigenous Input Theories

The positive $\delta^{13}C$ excursions associated with sapropel formation at Sites 969 and 974 are inconsistent with the addition of significant amounts of either terrigenous organic matter or terrigenous DIC, both of which are isotopically lighter than marine organic carbon. Fontugne and Calvert (1992) cite terrigenous DIC input as a possible cause of the negative $\delta^{13}C$ excursion during sapropel formation near the mouth of the Nile (Site MD 84641), but data from Site 969 on the Mediterranean Rise constrain the spatial extent of this mechanism: most Site 969 sapropels are more enriched in ^{13}C than surrounding sediments, though a few (S1 and S6–S8) from the late Pleistocene have roughly the same isotopic composition as surrounding sediment or are depleted by up to 1‰. This variability could reflect the changing intensity of the Nile floods from sapropel to sapropel, and thus the changing extent of their oceanographic influence. The larger, positive $\delta^{13}C$ excursions (up to 4.4‰) from the early Pleistocene suggest that terrigenous input from the Nile did not reach the Mediterranean Ridge at this time.

The lack of a positive $\delta^{13}C$ gradient away from the mouth of the Nile is also inconsistent with a widespread influence of terrestrial input. Although $\delta^{13}C$ would be expected to increase as the importance of the isotopically light terrestrial source decreased, sediment $\delta^{13}C$ actually decreases west of the Nile (Table 5).

Upwelling

During glacial sea-level drawdown, the sill at Gibraltar would have become very shallow (<200 m deep), thus restricting deep-water flow from the Mediterranean to the Atlantic. Consequently, deep waters would have been enriched in isotopically light carbon and nitrogen, as well as other remineralization products, such as silica and phosphate. During the transition to interglacial conditions, eastern Mediterranean upwelling (driven by westward surface flow and estuarine circulation) could bring this water to the surface, creating high-nutrient conditions, an isotopically lighter DIC pool, and, since increases in productivity caused by upwelled nutrients could outstrip the supply of upwelled DIC, a heavier $\delta^{13}C_{POC}$ pool. Bidigare et al. (1997) observed these patterns in the Peru upwelling zone, where $\delta^{13}C_{DIC}$ is 1‰ lighter, but $\delta^{13}C_{POC}$ is 4‰ heavier than at less productive Pacific sites.

These predictions match the $\delta^{13}C_{DIC}$ patterns found in the eastern Mediterranean (Vergnaud-Grazzini et al., 1986) and the Tyrrhenian Sea (Thunell et al., 1990) and are also consistent with the negative $\delta^{15}N$ excursions associated with the sapropels. Three additional lines of empirical evidence suggest that upwelling and enhanced productivity contributed to sapropel formation. First, Boyle and Lea (1989) found a five-fold increase in Cd/Ca ratios in the most recent sapropel, suggesting an enrichment in surface-water phosphate concentration at that time. Second, Calvert (1983) noted that barium is twice as abundant in five eastern Mediterranean sapropels as in the associated marls, and subsequent work demonstrates that the barium concentration in foraminifers correlates positively with silica abundance and with primary productivity rates (Boyle and Lea, 1989; Bishop, 1988). Finally, the high diatom concentrations found in sapropel S5 at four sites south and east of Crete suggests that upwelling of silica-rich waters might have occurred in this region (Schrader and Matherne, 1981). This upwelling could explain the isotope trends at Site 969, which lies within the estimated range of the diatom enrichment.

Assuming an estuarine-type circulation during episodes of sapropel formation, surface currents in the Eastern Mediterranean would flow westward and upwelling at Site 969 would not affect Site MD 84641, which shows an isotope excursion in the opposite direction. Instead, the negative $\delta^{13}C$ excursion at Site MD 84641 could reflect local terrigenous input of DIC or organic matter.

Westward surface flow would carry upwelled nutrients across the Ionian Sea and possibly into the western Mediterranean and the Tyrrhenian Sea. Although this scenario is generally consistent with isotope trends at Site 974, it presents two problems. First, nutrients in the upwelled water parcel would be consumed as they moved the substantial distance westward toward the Tyrrhenian Sea, which should lead to a smaller nitrogen isotopic depletion in sapropels at Site 974; in fact, the observed $\Delta\delta^{13}C$ and $\Delta\delta^{15}N$ are not significantly different for the two sites. Second, this interpretation assumes that the Tyrrhenian Sea sapropels formed contemporaneously with those in the eastern Mediterranean, but no correlation has yet been demonstrated. Alternatively, a separate upwelling system in the western Mediterranean could independently explain the isotope shifts at Site 974.

Enhanced Preservation

Sachs (1996) found negative $\delta^{15}N$ excursions in six eastern Mediterranean sapropels, consistent with our findings and those of Calvert et al. (1992), but he disputed the interpretation of Calvert et al. that these excursions reflect increases in primary productivity. Instead, Sachs argued that they represent a diagenetic signal and that surface ocean processes did not change significantly during episodes of sapropel formation. According to this argument, diagenesis leads to a 2‰ to 8‰ enrichment in ^{15}N of sediments relative to sinking particles and a roughly 0.5 to 2.5‰ depletion in ^{13}C (Sachs, 1996, and references therein; Fontugne and Calvert, 1992, and references therein; McArthur et al., 1992). Thus, the higher $\delta^{15}N$ values in nonsapropel sediments resulted from diagenetic alteration of organic matter while the lower $\delta^{15}N$ values within sapropels indicate a decrease in diagenesis during periods of anoxia and enhanced preservation or organic matter.

Although isotope data from Sites 969 and 974 are consistent with this scenario, many of Sachs's assumptions are open to challenge. For example, Altabet (1988) and Saino and Hattori (1987) have found that most alteration in $\delta^{15}N$ of sinking particulate organic matter occurs in the upper few hundred meters of the water column, and thus would occur regardless of deep-water oxygen concentrations. François et al. (1992) argue that diagenesis has only a minor influence on the $\delta^{15}N$ of sedimentary organic matter. Furthermore, Sachs' argument relies on the assumption that virtually no diagenesis occurred under anoxic conditions (or, at least, no diagenesis that affected the isotope record), but post-depositional breakdown is known to continue in anoxic sediments, albeit at a slower rate (Pedersen and Calvert, 1990). Sachs' scenario is also inconsistent with the considerable evidence supporting altered surface ocean processes during sapropel formation.

If deep-water anoxia has a small diagenetic effect on isotope ratios (as most studies suggest), then our data set provides little information about whether deep-water anoxia occurred during sapropel formation. However, enhanced preservation is not inconsistent with the observed isotopic trends, and circumstantial evidence appears to support some role for enhanced preservation. For example, in an estuarine circulation regime (hypothesized to occur during sapropel formation), the eastern Mediterranean would contain less oxygen than the western basin since altered deep Atlantic water would progressively lose its oxygen as it flowed eastward. This scenario is consistent with the smaller enrichments in organic carbon in the Tyrrhenian Sea sapropels relative to those in the eastern Mediterranean. In addition, deep-water oxygen depletion occurs whenever an increased downward flux of organic carbon is not offset by increased deep-water oxygen supply, thus suggesting that any mechanisms that generate sapropels through increased surface productivity would have the secondary effect of facilitating deep-water anoxia (Emeis et al., 1991) and enhanced preservation of organic matter.

CONCLUSIONS AND DIRECTIONS FOR FURTHER RESEARCH

The positive $\delta^{13}C$ excursions in sapropels at Sites 969 and 974 allow us to rule out terrigenous nutrients and terrigenous organic matter as basinwide factors in sapropel formation. The available nitrogen and carbon isotope data are consistent with sapropel formation through either enhanced preservation in the sediments or increases in surface productivity through upwelling. Although Sites 969 and 974 display very similar properties, a better knowledge of the temporal relationship between the sapropels at these sites will be required to distinguish between sapropel formation mechanisms involving a single, Mediterranean-wide event and those involving separate eastern and western events.

Our inability to identify a single mechanism for sapropel formation at all three sites does not mean that these sapropels are unrelated. On the contrary, all the mechanisms examined here could have been triggered by freshwater flooding, possibly caused by African monsoonal rains and (for interglacial sapropels) by glacial meltwater or Black Sea overflow. For example, in an estuarine circulation regime, basin-wide anoxia would be consistent with regional upwelling and localized freshwater influx in the eastern Levantine Basin, producing a negative $\delta^{13}C$ shift at Site MD 84641 and a positive $\delta^{13}C$ shift at the other two sites.

These conclusions reveal two important gaps in knowledge. First, stratigraphic correlation between eastern and western Mediterranean sediments is necessary to constrain the spatial extent of sapropel forming events in the two basins. Second, additional work on the isotopic effects of diagenesis, and the use of additional biomarkers to compare organic matter in sapropels, nonsapropel sediments, and modern-day plankton, may help to distinguish between upwelling and enhanced preservation as mechanisms for sapropel formation.

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