Chapter 6

Organic matter and trace element rich sapropels and black shales: A geochemical comparison

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Abstract - A distinct Pliocene eastern Mediterranean sapropel (i-282) recovered from three Ocean Drilling Program (ODP) Leg 160 sites, has been investigated for its organic and inorganic composition. This sapropel is characterized by high organic carbon (C_{org}) and trace element contents, and the presence of isorenieratene derivatives. The latter indicates that the base of the photic zone was sulphidic during formation of the sapropel. Combined with evidence of bottom water anoxia (preservation of laminae, high redox-sensitive trace element contents, and the abundance and isotopic composition of pyrite) this leads to the tentative conclusion that almost the entire water column may have been euxinic. This anoxia resulted from high productivity and not from stagnation, because an approximation of the trace element budget during sapropel formation shows that water exchange with the western Mediterranean is needed. Entire water column euxinia has been suggested earlier for several black shales. With regard to the depositional environment and the C_{org} content, however, only the Caenomanian/ Turonian Boundary Event (CTBE) black shales appear to be comparable to this sapropel. The proposed trace element removal mechanism of scavenging and (co)precipitation in an anoxic water column, is thought to be similar for both types of deposits. The ultimate trace element source for the sapropel, however, is seawater, whereas it is hydrothermal and fluvial input for the CTBE black shale (because of the larger temporal and spatial distribution of that event). Nonetheless, the C_{org}-rich eastern Mediterranean Pliocene sapropel discussed here may be considered to be a younger analogue of CTBE black shales. As the type euxinic basin, the Black Sea is a contemporaneous analogue, which has, however, low sedimentary C_{org} and trace element contents because of local conditions.

Introduction

Organic matter rich marine sediments (sapropels) in the eastern Mediterranean have been reported as possible younger analogues, or precursors, of C_{org}-rich black shales *[Calvert, 1983; Thomson et al., 1995]*. The commonly used definition of a (marine) sapropel is: 'a discrete layer, greater than 1 cm in thickness, set in open marine pelagic conditions and containing greater than 2% C_{org} by weight' *[Kidd et al., 1978]*. The term black shale is less precisely defined and is applied to any fine-grained, dark-coloured sediment (usually rich in organic matter). Thus, sapropels can be considered a specific subclass of black shales, although it is as yet unknown in how far these deposits have been formed under comparable conditions.

Two mechanisms have been proposed to explain C_{org} enrichment in both sapropels and black shales: (1) increased production of marine and/or enhanced input of terrestrial organic matter, and (2) improved preservation of organic matter (because of an anoxic water column, expanded oxygen minimum zone, or higher sedimentation rates). However, the proposed formation models for sapropels and black shales differ in time control, basin physiography, and scale of the events. It has been demonstrated that the cyclic occurrence of Mediterranean sapropels between organic matter poor, bioturbated sediments correlates to variations in the eccentricity of the Earth's orbit and the obliquity and precession of the Earth's axis *[Rossignol-Strick, 1983; Langereis and Hilgen, 1991; Lourens et al., 1996a]*. At Mediterranean latitudes, the precession has the largest effects on climate. Since one precession cycle lasts 21,000 years on average, that is also the presumed duration of one sapropel-homogeneous cycle. Cyclicity in black shales has also been reported *[Arthur et al., 1990; De Boer, 1991; Wetzel, 1991; Wignall, 1994]*, but a precise time control on the formation of those sediments is often lacking *[Wignall, 1994]*. Black shales have been found in environments ranging from open marine to shallow shelves, whereas Mediterranean sapropels were formed in a satellite basin separated from the open marine environment by a shallow sill (the Strait of Gibraltar). In fact, most sapropels only occur in the eastern Mediterranean, which in its turn is separated by shallow sills from the western Mediterranean (Strait of Sicily) and the Black Sea (Bosporus). Such a setting is more sensitive to inhibition of circulation and water column stratification than an open marine setting. Finally, eastern Mediterranean sapropel formation occurred in a relatively small area, whereas some black shales are thought to have formed in extensive parts of the Atlantic and the equatorial Pacific during so-called oceanic anoxic events (OAEs *[Arthur et al., 1990]*). Alternative models for black shale formation do not invoke OAEs, but only increased productivity *[Pedersen and Calvert, 1990]*.

Contradictory to the suggestion implied by using the term OAE, it is not generally believed that the whole ocean was anoxic, but rather that an extended oxygen minimum zone caused increased organic matter preservation *[Wignall, 1994]*. However, recent evidence, based on the presence of molecular fossils derived from isorenieratene, suggests that the southern North Atlantic Ocean was completely anoxic during the formation of the Caenomanian/Turonian Boundary Event (CTBE) black shales *[Sinninghe Damsté and Köster, 1998]*.

Isorenieratene is a pigment exclusively biosynthesized by the brown-coloured strain of photosynthetic green sulphur bacteria (Chlorobiaceae). These bacteria require sunlight and hydrogen sulphide and are, therefore, restricted to a very specific habitat at the chemocline in the photic zone of euxinic basins. Isorenieratene and its dia- and catagenetically formed derivatives have also been encountered in other black shales *[Koopmans et al., 1996]*, and in the water column and Unit I and II sapropels of the Black Sea *[Repeta et al., 1989; Repeta, 1993; Sinnighe Damsté et al., 1993]*. In this paper, data are presented from eastern Mediterranean sapropels that also contain such molecular fossils.

Black shales are often enriched not only in organic matter but also in trace elements like Co, Cr, Cu, Mo, Ni, V, and Zn *[e.g. Vine and Tourtelot, 1970; Brumsack, 1980]*. These elements usually show a strong positive correlation with organic matter and/or sulphides. Their enrichment in the sediment is thought to be the result of accumulation in organic tissues, (co)precipitation with sulphides under anoxic conditions, or (post-depositionally) by diagenetic processes. Although sapropels may also be enriched in these elements, their contents reported thus far are generally not as high as those of some black shales *[Calvert, 1983; Pruysers et al., 1991; Thomson et al., 1995; Nijenhuis et al., 1996 (Chapter 2)]*. In contrast, the Pliocene eastern Mediterranean sapropels of this study do have very high C_{org} and trace element contents.

In this paper the possible sources of trace elements in sapropels and black shales will be discussed in order to compare their respective modes of formation.

Material and methods

The sapropel selected for this study is i-282 in the Mediterranean Precession Related Cycle (MPRC) coding, which is equivalent to cycle 107 of the Rossello Composite section *[Langereis and Hilgen, 1995]*. It has been dated by astronomical tuning at 2.943 Ma, Upper Pliocene (Piacenzian) *[Lourens et al., 1996a]*. It is identified unambiguously in Sites 964, 967 and 969 of ODP Leg 160 *[pers. comm. L. Lourens, 1997]*. This sapropel is compared with i-292 (corresponding to cycle 102 in the Rossello Composite), dated at 3.058 Ma *[Lourens et al., 1996a]*. The intervals studied are listed in Table 6.1, the site locations are shown in Fig. 5.1.

Table 6.1   *Specification of the studied intervals. Cycle coding after Lourens et al., 1996a.*

Leg	Hole	Core	Section	Interval studied (cm)	Sapropel interval (cm)	Depth of section top (mbsf)	Abbreviation	Cycle coding
160	964D	10H	1	90-132.5	103-110	80.1	964D10/1	i-282
160	967C	8 H	4	95-151	114-130	66.5	967C8/4	i-282
160	969E	6H	6	19-52	26-40	50.4	969E6/6	i-282
160	964E	6H	5/6	128-045	5-13	82.0	964E6/5	i-292
160	966C	5H	3/4	135-025	147-016	41.0	966C5/3	i-292

| 160 | 967C | 8H | 6 | 26-68 | 37-58 | 74.0 | 967C8/6 | i-292 |

Slices with a thickness of 0.5 to 2 cm were cut from the split cores, using Teflon cutters. The slices were freeze-dried, after which subsamples were taken. These samples were crushed and homogenized in an agate mortar, and subsequently used for all geochemical analyses. After removal of inorganic carbon with 1M HCl, C_{org} contents were measured with a Fisons NA 1500 NCS analyser. For trace element analyses, a 250 mg sample was digested in 10 ml of a 6.5 : 2.5 : 1 mixture of $HClO_4$(60%), HNO_3(65%) and H_2O, and 10 ml HF (40%) at 90°C. After evaporation to dryness on a sand bath at 190°C, the residue was dissolved in 50 ml 1M HCl. The resulting solutions were analysed with a Perkin Elmer Optima 3000 inductively coupled plasma atomic emission spectrometer (ICP-AES) for Mo, V, Cu, Co, Ni, Zn and Cr. As, Se and Sb were measured in the same solutions with a Perkin Elmer 3100 hydride atomic absorption spectrometer (AAS); Cd with a Perkin Elmer 4100 ZL ZGFAAS (AAS with Zeeman correction).

Precision of the analyses is better than 5%, except for the determination of Se and Sb, for which it is better than 10% for sediments that contain >1 ppm of each element. Accuracy was checked with international (SO1, SO3) and house (MMM91) standards and is also better than 5% for each element except As (+9%), Co (-9%) and Zn (-9%). Detection limits for trace elements are reported in Table 6.2.

Selected subsamples were ultrasonically extracted using 8 ml of methanol (MeOH)(4x), 8 ml of dichloromethane (DCM) (4x) and 8 ml of DCM (4x). Elemental sulphur was removed from the combined extracts by stirring with activated copper (24 hours). The obtained extractable organic matter was separated into an apolar and a polar fraction on an activated Al_2O_3 column. An aliquot of the apolar fraction, obtained by elution with four column-volumes of hexane:DCM (9:1 v/v), was further separated by argentation thin layer chromatography, using hexane as developer *[Bosch et al., 1998]*. Four fractions were isolated. The polar fractions, obtained by elution of the column with four column-volumes of DCM:MeOH (1:1 v/v), were desulphurized by Raney nickel *[Sinnighe Damsté et al., 1988]*. Fractions obtained were analysed by gas chromatography (GC), GC/mass spectrometry (GC/MS) and isotope ratio monitoring GC/MS (irm-GC/MS) *[Bosch et al., 1998]*.

Results

C_{org} contents in the sapropels are very high (up to 27%), and trace element contents are up to several orders of magnitude higher than in average shales. The highest concentrations of C_{org} and trace elements are reached within the sapropels, but in several cases elevated trace element contents also occur in adjacent non-sapropel intervals. Numeric data are reported in Table 6.2; results for 969E6/6 are shown graphically (Fig. 6.1) and are representative of the other sites except for Zn, which is not enriched in sapropel 964D10/1 (Table 6.2).

For an extensive report on the organic geochemical results we refer to *Bosch et al. [1998]*. Here we report that the apolar fraction of sample 160-969E-6H-6, 34-35, contains abundant novel aromatic compounds, which were identified as being diagenetically derived from

isorenieratene *[Bosch et al., 1998]*. $\delta^{13}C$ values of these compounds as determined by irm-GC/MS

Table 6.2   *Detection limits of the equipment used for trace element analyses. Average and maximum (in brackets) contents of C_{org} (%) and trace elements (ppm) in the sapropels and homogeneous intervals of this study. ID: presence of isorenieratene derivatives (++ abundant; +trace; - not detected).*

	I.D.	C-org (%)	As (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Mo (ppm)	Ni (ppm)	Sb (ppm)	Se (ppm)	V (ppm)	Zn (ppm)
detection limit			0.2	0.03	3.3	3.3	3.3	3.3	3.3	0.4	0.2	3.3	6.7
964D10/1	+												
sapropel		15.3 (25.3)	112 (297)	34 (65)	76 (147)	182 (265)	264 (388)	195 (392)	317 (727)	26 (37)	29 (44)	1317 (2235)	115 (142)
homogeneous		0.1	20	0.3	12	54	47	13	36	3	0.2	99	120
967C8/4	+												
sapropel		8.4 (15.4)	58 (88)	3 (8)	48 (75)	77 (96)	110 (138)	202 (410)	183 (251)	8 (17)	22 (38)	555 (884)	90 (114)
homogeneous		0.1	22	0.1	19	46	48	32	51	2	0.4	99	55
969E6/6	++												
sapropel		17.7 (27.3)	41 (62)	31 (88)	37 (66)	168 (197)	207 (334)	407 (728)	299 (382)	9 (14)	24 (36)	1937 (3575)	163 (181)
homogeneous		0.2	13	0.1	14	96	53	16	80	2	1	99	135
964E6/5	+												
sapropel		12.0 (24.2)	n.d.[1]	22 (55)	112 (206)	245 (414)	265 (378)	151 (363)	280 (379)	n.d.[1]	n.d.[1]	923 (2061)	121 (161)
homogeneous		0.1	n.d.[1]	0.1	19	45	47	6	40	n.d.[1]	n.d.[1]	75	43
966C5/3	-												
sapropel		6.0 (11.6)	n.d.[1]	1 (3)	22 (46)	47 (61)	74 (137)	133 (295)	101 (159)	n.d.[1]	n.d.[1]	340 (797)	57 (86)
homogeneous		0.3	n.d.[1]	0.1	10	38	31	7	37	n.d.[1]	n.d.[1]	84	42
967C8/6	+												
sapropel		13.2 (20.3)	n.d.[1]	8 (18)	35 (59)	76 (90)	135 (177)	224 (515)	174 (327)	n.d.[1]	n.d.[1]	918 (1630)	98 (144)
homogeneous		0.2	n.d.[1]	0.2	17	57	51	13	49	n.d.[1]	n.d.[1]	126	58

[1] n.d.: no data

Table 6.3 *Average and maximum (in brackets) contents of C_{org} (%) and trace elements (in ppm) and the presence or absence of isorenieratene derivatives (I.D.) for sapropels i-282 (this study), S1 [Calvert, 1983], S1-S7 [Pruysers et al., 1991], from the Black Sea [Brumsack, 1989] and Faneromeni (Crete; Nijenhuis et al., 1996 (Chapter 2)), and black shales from the CTBE [Arthur et al., 1990; Thurow et al., 1988], the Monterey Formation [Piper and Isaacs, 1995a], the Kimmeridge Clay [Tribovillard et al., 1994] and the Posidonia Shale [Brumsack, 1991].*

	sapropel i-282	sapropel S1(DSDP Leg 13)	sapropels S1-S7	Unit I/II Black Sea sapropels	Miocene sapropels Faneromeni	CTBE ODP Leg 103	CTBE ODP Site 641A	Monterey Formation	Kimmeridge Clay	Posidonia Shale
C_{org}	13.1 (27.3)	6.1 (20.2)	2.5 (4.7)	6.4 (14)	1.6 (3)	9.3	8.5 (35.6)	6.2 (17.3)	4.4 (35)	9.2 (18.3)
As	70 (297)	7 (128)	(40)	25 (49)	7 (11)	35	126 (210)	10 (24)	n.d.[1]	28 (57)
Cd	23 (88)	n.d.[1].	n.d.[1]	1 (2)	0.4 (0.7)	14	54 (197)	7 (32)	4 (14)	3 (5)
Co	54 (147)	n.d.[1]	21 (34)	27 (51)	12 (14)	38	468 (600)	8 (15)	21 (26)	22 (64)
Cr	142 (265)	n.d.[1]	117 (158)	70 (105)	182 (225)	122	141 (430)	146 (570)	118 (146)	60 (140)
Cu	194 (388)	129 (404)	58 (122)	87 (175)	38 (55)	190	353 (921)	51 (177)	76 (104)	73 (159)
Mo	268 (728)	73 (228)	(85)	80 (185)	8 (30)	163	1950 (5050)	26 (101)	81 (220)	33 (125)
Ni	266 (727)	130 (261)	139 (195)	96 (150)	219 (289)	145	464 (870)	130 (373)	127 (230)	109 (285)
Sb	14 (37)	n.d.[1]	(5)	n.d.[1]	0.9 (2)	16	35 (118)	4 (12)	n.d.[1]	n.d.[1]
Se	25 (44)	n.d.[1]	n.d.[1]	n.d.[1]	1.2 (3)	n.d.[1]	n.d.[1]	15 (56)	n.d.[1]	n.d.[1]
V	1270 (3575)	n.d.[1]	142 (401)	173 (415)	79 (170)	647	968 (3627)	204 (564)	249 (437)	178 (305)
Zn	123 (181)	117 (274)	70 (107)	83 (108)	80 (93)	1273	6866 (17170)	146 (460)	170 (628)	235 (695)
I.D.	yes	no	no	yes[2]	n.d.[1]	yes[3]	no[3]	no[4]	yes[5]	yes[6]

[1] n.d.: no data   [2] *Repeta, [1993]; Sinninghe Damsté et al. [1993]*   [3] *Sinnighe Damsté and Köster [1998]*

[4] *Schouten [1995]*   [5] *Van Kaam-Peters et al. [1997]*   [6] *Van Kaam-Peters [1997]*

were +8‰ enriched relative to algal derived organic compounds measured in the same sample, confirming their origin from isorenieratene derived from photosynthetic green sulphur bacteria. The presence of isorenieratane among the released hydrocarbons after desulphurization of the polar fraction was confirmed by coelution with an authentic standard. Identical isorenieratene derivatives were also found in individual samples of the other sapropels (Table 6.2). Because of the lower amounts of these compounds, $\delta^{13}C$ analyses were not performed on those samples, but the very specific biological source of isorenieratene indicates that photosynthetic green sulphur bacteria are in these cases also the most probable
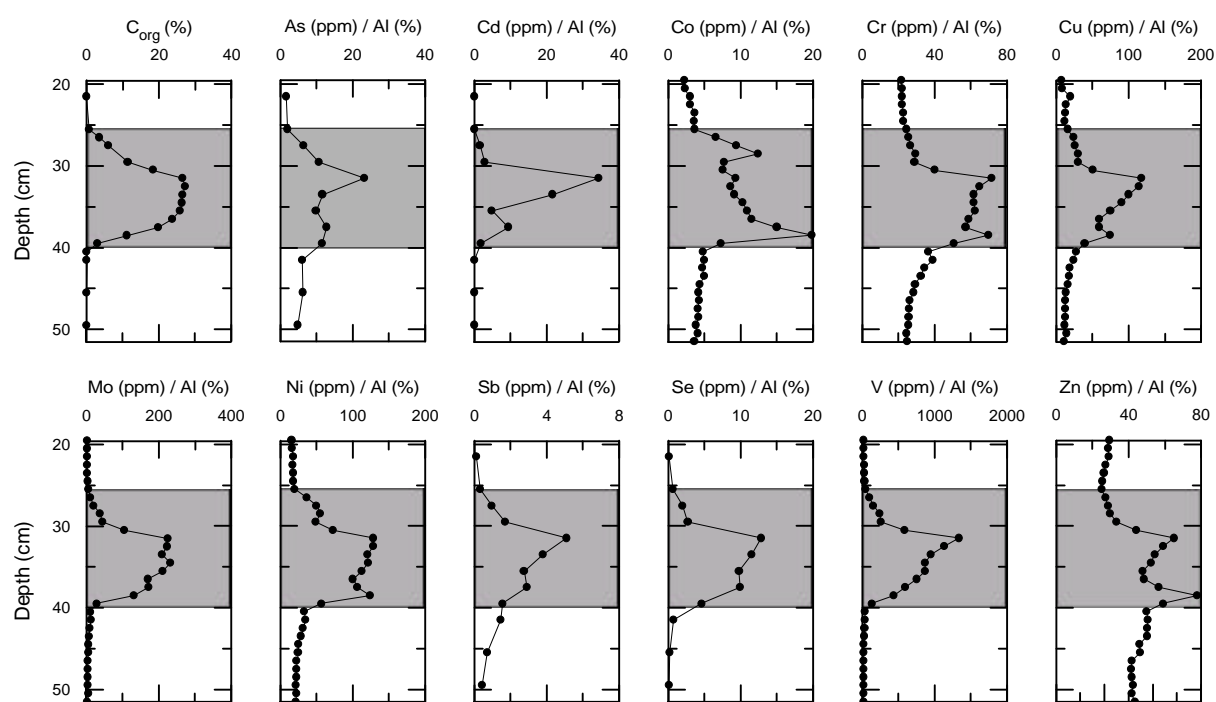

Figure 6.1   *C_{org} and trace element contents of interval 969E6/6. Sapropel indicated by shading.*

origin.

Discussion

The distribution patterns of trace elements and C_{org} are comparable to those previously reported for Mediterranean sapropels *[e.g. Calvert 1983; Pruysers et al., 1991; Nijenhuis et al., 1996 (Chapter 2)]*. Average and maximum C_{org} and trace element contents of the sapropels of this study, however, are considerably higher than ever reported before (Table 6.3). Furthermore, the occurrence of intact isorenieratene in sapropels has been reported only once before for a Mediterranean (Pleistocene) sapropel *[Tibbets, 1980]*. The presence of isorenieratene and its derivatives in the Pliocene eastern Mediterranean sapropels of this study point to sulphidic conditions at the base of the photic zone *[Bosch et al., 1998]*. Bottom water anoxia is indicated by the presence of laminae in the sapropels (absence of benthic life) and the abundance and

isotopic composition of pyrite *[Passier and De Lange, 1998]*. Consequently, during the formation of these sapropels, a large part of the water column, or even all of it except the upper part of the photic zone, must have been euxinic. These specific water column conditions may have resulted in more effective scavenging and (co)precipitation of redox-sensitive and chalcophilic trace elements, resulting in the observed high contents in the sapropels. In the following we will approximate the trace element budget of the eastern Mediterranean during the formation of these Pliocene sapropels, in order to derive the ultimate trace element sources.

Possible trace element sources

The enrichment of trace elements in marine sediments may, in general, originate from six sources:

(1) super- and subjacent sediments, through diagenesis

(2) suboxic shelf and slope sediments

(3) hydrothermal input

(4) aeolian input

(5) fluvial runoff

(6) seawater.

The relative importance of these sources may be assessed by evaluating the trace element budget of the eastern Mediterranean during formation of the i-282 sapropel. The accompanying calculations will be simplified by taking the average composition and thickness of the sapropel at the three sites. These sites form a transect and are, therefore, thought to be representative for the whole of the eastern Mediterranean (Fig. 5.1). In our calculations we will assume that ⅚ of the eastern Mediterranean seafloor has been covered with this sapropel (excluding near-coastal areas), and that there are no significant effects of a 'burn-down front' *[Thomson et al., 1995; Van Santvoort et al., 1996]*. The formation time of Pliocene sapropels is estimated to be between 3,000 and 6,000 years *[Wehausen and Brumsack, 1998]*.

(1) Super- and subjacent sediments, through diagenesis - Sapropels are deposited under anoxic-sulphidic conditions whereas the underlying sediments are suboxic *[Passier et al., 1996; Passier and De Lange, 1998]*. Sapropels may, therefore, act as sinks for chalcophilic elements (which coprecipitate with sulphides) and certain redox-sensitive elements (which are immobilized under anoxic conditions) that are mobilized in the suboxic parts of the sediment *[Thomson et al., 1995]*.

Assuming that trace element maxima in the sediment are only caused by diagenesis, we can calculate the initial concentration by redistributing the total trace element amount equally over the sapropels and homogeneous intervals. Such calculations for cycle i-282 result in very high hypothetical contents (Table 6.4, in bold) comparable to the average or even maximum contents reported for *sapropels* by previous studies (cf. Table 6.3). If these hypothetical contents of cycle i-282 are compared with values obtained by the same method for other sapropels in the same cores (same site for 964), we find distinct differences for most elements, whereas we would expect similar contents if diagenesis were the only cause of the

enrichment. These comparisons show that diagenesis can be ruled out as the single source of the trace element excess in the sapropel.

Table 6.4 *Contents (in ppm) obtained by equally distributing trace element contents over the entire intervals 964D10/1, 964E6/5, 967C8/4, 967C8/6, 969E6/1 (160-969E-6H-1, 110-150 combined with 160-969E-6H-2, 0-20) and 969E6/6. Values for cycle i-282 are in bold. n.d.: no data*

Interval	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Mo (ppm)	Ni (ppm)	V (ppm)	Zn (ppm)
964D10/1	**9**	**23**	**75**	**82**	**41**	**83**	**299**	**119**
964E6/5	2	29	68	72	27	68	173	52
967C8/4	**1**	**27**	**54**	**64**	**92**	**84**	**213**	**64**
967C8/6	4	26	66	93	116	110	512	77
969E6/1	n.d.	53	72	68	37	126	241	53
969E6/6	**n.d.**	**23**	**127**	**119**	**182**	**173**	**879**	**147**

(2) (Sub-)oxic shelf and slope sediments - Trace elements are mobilized in suboxic sediments and may subsequently escape to the water column. In the case of eastern Mediterranean sapropel formation, this may lead to a transfer of trace elements from the (sub-)oxic shelf and slope sediments to the seawater, and subsequently to anoxic sapropel sediments in the deeper parts of the basin. Recycling of trace elements is linked to the iron and manganese cycles, and is commonly thought to be an important mechanism in the Black Sea *[Kempe et al., 1991]*. However, there are virtually no quantitative data on the amount of trace elements mobilized and the related fluxes out of the sediment. Still, we would like to quantify the potential of this source. We, therefore, have assumed that the maximum trace element quantity that can be mobilized is the amount present in the upper half metre of sediment in 30% of the eastern Mediterranean surface area. The actual maximum quantity is probably lower, since not all of the trace elements present in those sediments will be mobilized, and because 30% of the surface area is most likely an overestimate. Still, for Cd (1%), Mo (9%), Se (3%) and V (16%), only a small fraction of the excess trace element quantity in the sapropel can be supplied under these assumptions. However, for some other trace elements, this maximum amount is a higher fraction of the total sapropel trace element quantity, and, therefore, this mechanism could be important, if the flux out of the (sub-)oxic sediments is high enough. We have used data from *Shaw et al. [1990]* to quantify fluxes out of (sub-)oxic sediments and to calculate the fraction of the trace element amount in the sapropel that can be supplied in this way during the maximum assumed sapropel formation period of 6,000 years (Table 6.5). Although there are considerable uncertainties in the flux estimates, and in their applicability to the Mediterranean region, these data suggest that trace element mobilization from (sub-)oxic shelf and slope sediments could potentially be a significant source for Co, Cr and Zn.

(3) Hydrothermal input - The cyclic occurrence of sapropels in the Mediterranean region is not likely to be caused by hydrothermal venting, but the total amount of trace elements available

Table 6.5 *Results of calculations for establishing the possible sources of the trace elements in sapropels i-282 and i-292 with a composition that is the average of the three sites, a thickness of 12 cm (16 cm for i-292), and a dry density of 1.8 gr/cm³, covering ɓ of the eastern Mediterranean (total surface area: 1.66 million km²). Values for homogeneous intervals have been calculated in the same way.*

Column 1:   *Excess trace element content of the sapropel (the average content of the sapropel minus the average content of the homogeneous interval).*

Column 2:   *The total excess trace element quantity of the sapropel over ɓ of the eastern Mediterranean.*

Column 3:   *The fraction of the trace element amount that may be supplied by mobilization from (sub-)oxic shelf and slope sediments in 6,000 years. Based on suboxic flux ranges estimated from Shaw et al. [1990]; values in brackets are based on our assumed maximum (see text) because no flux data were available. Lowest values based on 10% (sub-)oxic sediments and lowest flux estimate; highest values based on 30% (sub-)oxic sediment and highest flux estimate. Numbers used (element, flux coefficient (10^{-6} cm/s), lower flux (nM/cm), higher flux): Co (5, 5,10), Cr (7, 18, 60), Cu (4, 15, 20), Mo (6, 200, 400), Ni (5, 33, 50), V (6, 87, 800).*

Column 4:   *The trace element content of the C_{org} present in the sapropel assuming that all (excess) trace elements are fixed to organic matter.*

Column 5:   *The trace element content of marine organic matter (converted to C_{org} by multiplication with 2.5, assuming that the dry matter of marine organisms contains 40% C_{org} [Brumsack, 1980; Arthur et al., 1990].*

Column 6:   *Trace element concentration of seawater [Broecker and Peng, 1982; Bruland, 1983].*

Column 7:   *Trace element concentration of river water [Broecker and Peng, 1982; Martin and Whitfield, 1983; Brumsack, 1989].*

Column 8:   *The total trace element amount present in the eastern Mediterranean (EM) with a composition of column 6.*

Column 9:   *The excess trace element quantity present in the sapropel expressed in multiples of the amount present in the eastern Mediterranean (EM).*

Column 10:   *The period of river water input needed to supply the excess amount of trace elements present in the sapropel to the Mediterranean, based on a river composition as in column 7, and 1.5 times the present-day riverine input of 514 km³/yr plus 400 km³/yr from the Black Sea [Lacombe and Tchernia, 1972]. The trace elements already present in the eastern Mediterranean have been deducted from the sapropel total; trace element fixation in the western Mediterranean is neglected.*

Column 11:   *The period of seawater exchange with the western Mediterranean needed to supply the excess trace element content of the sapropel. The trace elements already present in the*

Mediterranean have been deducted from the sapropel total. The water input from the western Mediterranean is 39,800 km^3/yr [Béthoux, 1980].

		1 Excess content (ppm)	2 Total excess (10^{12}g)	3 Shelf / slope fraction	4 Content in C$_{org}$ (ppm)	5 Content in C$_{org}$ marine organisms (ppm)	6 Seawater conc. (ppb)	7 River water conc. (ppb)	8 Total in EM (10^{12}g)	9 Seawater volume (#·EM)	10 Period river water input (kyr)	11 Period seawater input (kyr)
i-282	As	51	12	(77%)	371	12.5	1.7	1.7	4.34	3	3	0.1
	Cd	22	5	(1%)	159	30	0.08	0.02	0.2	26	188	1.7
	Co	39	10	4-28%	286	2.5	0.001	0.2	0.003	3779	35	253
	Cr	88	21	9-91%	638	5	0.21	1	0.543	40	15	2.6
	Cu	150	37	3-12%	1091	27.5	0.25	1.5	0.637	58	18	3.8
	Mo	257	63	<9%	1868	5	10.6	0.5	27.03	2	52	0.089
	Ni	224	55	5-24%	1627	18.75	0.47	0.5	1.19	46	78	3
	Sb	12	3	(44%)	86	1.25	0.15	1	0.38	8	2	0.4
	Se	25	6	(3%)	179	2.5	0.14	0.2	0.35	17	21	1.1
	V	1206	296	<16%	8781	9	1.8	0.77	4.59	64	276	4.3
	Zn	21	5	(100%)	151	275	0.39	0.35	0.99	5	9	0.3
i-292	Cd	8	2	(3%)	74	30	0.08	0.02	0.2	12	81	0.7
	Co	26	8	5-32%	250	2.5	0.001	0.2	0.003	3238	30	217
	Cr	46	15	13-	445	5	0.21	1	0.54	27	10	1.8
	Cu	88	28	4-16%	845	27.5	0.25	1.5	0.64	44	13	2.9
	Mo	169	53	<11%	1614	5	10.6	0.5	27.03	2	39	0.065
	Ni	121	38	7-34%	1159	18.75	0.47	0.5	1.2	32	54	2.1
	V	603	191	4-24%	5777	9	1.8	0.77	4.59	42	176	2.7
	Zn	40	13	(100%)	382	275	0.39	0.35	0.99	13	24	0.8

will be higher in a geological period of increased hydrothermal activity, like the Cretaceous. This mechanism can be ruled out, however, since an element such as Zn, which is typically associated with hydrothermal activity *[James and Elderfield, 1996]*, is only slightly enriched in the sapropels, whereas non-hydrothermal elements, like Mo and V *[Björnsson et al., 1972]*, show strong enrichments.

(4) Aeolian input - Estimates for the contribution of wind-derived material in Mediterranean sediments are highly variable, so aeolian input is a potentially important trace element source. Yet in the orbital forcing model sapropels are formed during wet climatic conditions, when wind input is likely to be lower rather than higher. Evidence for lower wind-borne input during sapropel formation has been reported recently *[Foucault and Mélières, 1995; Wehausen and Brumsack, 1998]*.

(5) Fluvial runoff - The average trace element concentrations in river water are generally rather low (Table 6.5), and the water volumes supplied to oceans by rivers are relatively small. Consequently, a special setting and long periods of time are needed for river water to become the main source of trace elements in marine sediments.

Unfortunately, no reliable data for pristine (pre-anthropogenic) trace element input of rivers into the Mediterranean are available. Data from recent trace element studies are affected by anthropogenic contributions, whereas in older studies these elements have neither been sampled contamination-free, nor measured accurately enough. Therefore, data of the mean world river composition *[Broecker and Peng, 1982; Martin and Whitfield, 1983; Brumsack, 1989]* are used in the following calculations. Since climatic conditions during precession minima are more humid *[Rossignol-Strick, 1983; Rohling and Hilgen, 1991]*, river input into the Mediterranean is likely to be significantly higher during sapropel formation than at present. Furthermore, the sharp contrast in climate during precession minima (humid) and maxima (arid) may lead to a higher trace metal load of circum-Mediterranean rivers *[Wehausen and Brumsack, 1998]*.

Even if a 50% increase of the present-day fluviatile input (including the amount coming through the Bosporus from the Black Sea, which was a freshwater lake in the Pliocene), and the incorporation of all trace elements supplied by rivers into the sediment is assumed, long periods of fluviatile input into the Mediterranean are needed to supply the amount of trace elements present in the sapropel (Table 6.5, column 10). Except for As and Sb, these values are unrealistically high if we assume a sapropel formation time of 3,000-6,000 years. Even doubling the river flux or the trace metal concentration in the fluviatile input would not provide the amounts of trace metals that are actually found in the sapropel within a reasonable time period.

(6) Seawater - Based on mean seawater trace metal concentrations *[Broecker and Peng, 1982; Brumsack, 1989]*, we have calculated the amount of seawater that has to be stripped of its trace element content in order to explain the composition of the sapropel (Table 6.5, column 9). Less then fifty times the amount present in the eastern Mediterranean is sufficient for most elements. Based on the current water input ($40 \cdot 10^3$ km^3 yr^{-1}, *[Béthoux, 1980]*) of western Mediterranean surface water, this means that about 4,000 years of exchange with that basin are necessary (Table 6.5, column 11).

Vanadium is a key element for this calculation because its seawater concentration is known well (1.8 ppb; *[Bruland, 1983; Collier, 1984]*) and its river water concentration ranges from 0.5 to 1.0 ppb *[Shiller and Boyle, 1987]*, i.e. lower than in seawater. For the elements Cr, Cu, and Ni the time necessary for their accumulation is comparable to that of V. As, Mo, Sb and Zn can easily be supplied within the inferred sapropel formation time. This is not the case for Co, for which another source, e.g. suboxic shelf and slope sediments, has to be important. Still, seawater is the most likely source for the trace metal enrichments encountered in the sapropels.

As discussed earlier, a large part of the eastern Mediterranean water column may have been euxinic during the formation of the i-282 sapropel. Under such conditions, redox-sensitive and chalcophilic trace elements can be bound to organic matter (Cr, Mo, V, Cu, Zn), or (co)precipitated as sulphides (As, Cd, Co, Cu, Ni, Zn). Indeed, concentrations of Cd, Cu, Mo, Se, V and Zn have been reported to be considerably lower in anoxic than in oxic seawater *[Pilipchuk and Volkov, 1974; Collier, 1984; Jacobs and Emerson, 1985; Takayanagi and Wong, 1985]*. Through deposition of organic matter and sulphides, trace elements may be efficiently transferred from seawater to the sediment. This concept has often been proposed to explain trace element enrichments in sapropels *[Nijenhuis et al., 1996 (Chapter 2); Van der Weijden, 1993]*, and seems to be the most likely mechanism for the trace element enrichment in the Pliocene Mediterranean sapropel discussed here. The lack of a Zn enrichment in 964D10/1 and its relatively low enrichment at the other sites compared with recent sapropels and older black shales (Table 6.2, 3) is unexpected in this scenario, but might be explained by a relatively low supply of this element to the Mediterranean in the Pliocene. The strong hydrothermal input of Zn in the Cretaceous can account for its high enrichment in black shales of this period *[Arthur et al., 1990]*.

Because the concentration of trace elements in anoxic seawater is not zero, and because anoxia may have developed under stagnant conditions, when water exchange with the western Mediterranean was probably lower than at present, the calculated period of seawater exchange is too low. If the periods necessary to supply Co, Cr, Cu, Ni and V are higher than calculated, they may exceed the assumed sapropel formation period of 3,000-6,000 years. Therefore, circulation during sapropel formation was most likely not at a standstill. *Passier et al. [in press] (Chapter 5)* have shown, based on Ba contents of the sapropels, that the total amount of organic matter being produced during the formation of this Pliocene sapropel is high enough to reduce all oxygen supplied in the present circulation mode, leading to anoxia in the eastern Mediterranean. However, the concomitant high nutrient demand cannot be met by the present-day hydrography. There are three ways by which the nutrient availability can be increased: higher river influx, shoaling of the pycnocline into the photic zone, or circulation reversal.

There is no doubt that river input was higher during sapropel formation (see before). *Sarmiento et al. [1988]* have shown that 1.7 times the present river input into the eastern Mediterranean will supply enough phosphate to support a productivity that will lead to anoxia. Since the present-day eastern Mediterranean exports its nutrients with its bottom water to the western Mediterranean, this latter basin will subsequently also become anoxic. Anoxic

events, visualized by the occurrence of sapropels, are, however, more limited both in time and space in the western Mediterranean than in the eastern Mediterranean. The western Mediterranean can remain oxic if water exchange (and thus nutrient supply) at the Strait of Sicily is reduced by at least a factor of twelve *[Sarmiento et al., 1988]*. Such a decrease of seawater exchange at the Strait of Sicily would also drastically reduce the marine trace element input in the eastern Mediterranean. Thus, in such a stagnation scenario, a period longer than 3,000-6,000 years would be needed for supplying the observed sapropelic trace element content.

Shoaling of the pycnocline into the photic zone because of increased freshwater input will allow deep water nutrients to become available for primary productivity *[Rohling and Gieskes, 1989]*. However, this also invokes water column stratification and, therefore, stagnation.

Circulation reversal in the eastern Mediterranean from anti-estuarine during non-sapropel periods to estuarine during sapropelic periods would result from a decrease of surface water salinity due to increased riverine input [*e.g. Calvert, 1983; Buckley and Johnson, 1988; Thunell and Williams, 1989]*. In this case the eastern Mediterranean will change from a nutrient desert to a nutrient trap, utilizing nutrients from both the inflowing western Mediterranean deep water and the riverine input, while exporting nutrient-poor surface water to the western Mediterranean. In this case the eastern Mediterranean will inevitably become anoxic, while the western Mediterranean remains oxic *[Sarmiento et al., 1988]*. Furthermore, since there are no circulation restraints, trace elements will be supplied by the western Mediterranean deep water, which has higher concentrations than the surface waters flowing into the eastern Mediterranean in the other scenarios. Therefore, based on nutrient and trace element demands, and on the absence of widespread anoxic events in western Mediterranean Pliocene sediments, a circulation reversal in the eastern Mediterranean seems to be the most plausible scenario.

Summarizing, early diagenesis can only account for a small fraction of the trace element enrichment in the sapropels, in other words, the largest part of the signal is primary. The contribution by shallow shelf and slope sediments is difficult to quantify, but might be significant for the elements Co, Cr and Zn. Aeolian input and hydrothermal activity are not responsible for the trace element enrichments found in the sapropels. The trace element amounts in the sediments cannot be supplied by river water in a reasonable time period. Seawater can provide enough trace elements (except for Co), except if water exchange at the Strait of Sicily was more restricted than at present.

For comparison, these calculations were also applied to sapropel i-292 at sites 964, 966 and 967. Isorenieratene derivatives have been found in this sapropel, except at Site 966 (Table 6.2). Although the time intervals calculated (Table 6.5) are shorter for i-292 than they are for i-282, the result is essentially the same: rivers cannot supply the trace elements in a reasonable time period, and several thousands of years of seawater exchange with the western Mediterranean are necessary for most trace elements. The differences in calculated time intervals between i-282 and i-292 are likely to be caused by samples originating from different

sites. In particular, those from Site 969 with well-developed sapropels being used for i-282, whereas those from Site 966 with poorly developed sapropels were used for i-292.

Comparison with black shales

Some black shales are characterized by high C_{org} and trace element contents and the presence of isorenieratene derivatives, like the Pliocene sapropels of this study. In order to assess to what extent these deposits are equivalent, we will compare the geochemistry of these sapropels with that of black shales which are also rich in C_{org} and trace elements, which have been analysed for isorenieratene, and for which trace element sources and enrichment mechanism have been inferred in the literature (Table 6.3).

Organic matter and trace element contents - Although the maximum C_{org} content in black shales can be extremely high (up to 50-65% in certain thin oil shale horizons of the Kimmeridge Clay *[Van Kaam-Peters, 1997]*), the average and maximum C_{org} contents of the i-282 sapropel are similar to those reported for many Mesozoic and Caenozoic black shales (Table 6.3). The trace element content of the sapropel is, however, higher than that of most black shales listed in Table 6.3, with those from the CTBE as notable exceptions. The lower trace element and C_{org} content of the Monterey Formation may be explained by a moderate level of primary productivity and the absence of free H_2S in the water column; plankton is the only source for most trace elements *[Piper and Isaacs, 1995a]*. For the Posidonia and CTBE black shales and the Kimmeridge Clay, anoxic bottom water conditions have been inferred from trace element enrichment patterns *[Brumsack, 1980; 1991; Dypvik, 1984; Tribovillard et al., 1994]*. The Posidonia Shale formed in an epicontinental sea, therefore, after a marine trace element source, fluvial input was most important for the trace element enrichment in this black shale *[Brumsack, 1991]*. In the CTBE black shales, trace elements must be derived from seawater, rivers, and possibly hydrothermal (Zn) input *[Brumsack, 1980; Arthur et al., 1990]*. The Kimmeridge Clay formed on a continental shelf where circulation may have been reduced due to shallow sills *[Tribovillard et al., 1994]*. The ultimate trace element source has not been reported.

Isorenieratene - On the basis of trace element data it was concluded that strong anoxic conditions were important for the trace element enrichment in the Posidonia and CTBE black shales and in the Kimmeridge Clay. In all these black shales, isorenieratene derivatives have been found *[Van Kaam-Peters, 1997; Sinninghe Damsté and Köster, 1998]*. Despite extensive research this is not the case for the Monterey Formation *[Schouten, 1995]*, which is in agreement with the inferred lack of sulphate reduction in the water column during its formation. For the CTBE black shales in the southern part of the North Atlantic Ocean it was recently suggested *[Sinninghe Damsté and Köster, 1998]* that they were deposited under a water column that was sulphidic up into the photic zone. Thus, scavenging by sulphides could explain the high trace element contents, as suggested previously by *Brumsack and Thurow [1986]*.

In conclusion, photic zone anoxia and high trace element fixation rates are typical for some black shales. However, the black shales discussed in this paper differ from organic matter rich Pliocene sapropels by their shallower setting and different ultimate trace element sources.

The CTBE black shales are most similar to the i-282 sapropel in the sense that some of these are also found in abyssal sites and that trace elements are accumulated by scavenging by organic matter and sulphides in an anoxic water column. Still, the time scale of the anoxic events is quite different: several thousands of years for the sapropel versus 10^5 years or more for the CTBE. Because of this larger time scale and lateral distribution, seawater as a trace element reservoir is not large enough for the CTBE black shales and, therefore, fluvial and hydrothermal input dominate on a long term basis *[Arthur et al., 1990]*.

Water column anoxia is generally attributed to stagnant conditions. For Mediterranean sapropel formation this is not necessarily the case *[Sarmiento et al., 1988]* and in fact our trace element data suggest that these Pliocene sapropels may have been formed under conditions of ongoing circulation. This could have been the case in the southern North Atlantic Ocean during the formation of the CTBE black shale as well *[Sinninghe Damsté and Köster, 1998]*. The fact that the C_{org} and trace element contents are comparable, however, seems to be coincidental. The presence of isorenieratene derivatives does not always coincide with the highest trace element contents (Table 6.3). This has two important implications. First, although the presence of isorenieratene suggests that the water column was anoxic up into the photic zone, the absence of isorenieratene only indicates that the photic zone was not euxinic; it does not provide any information on the oxygen levels of the rest of the water column. In the case of the CTBE black shale at Site 641, characterized by very high trace element contents, it is likely that a large part of the water column was anoxic during its formation, but anoxia did not extend into the photic zone. Secondly, isorenieratene-derived compounds are not a prerequisite for high trace element contents. One reason for this is that it is unknown how long the water column has been anoxic. Isorenieratene derivatives may be found in a black shale or a sapropel even if sulphidic conditions lasted only a few years. Another reason is that the trace element amount that can be precipitated is strongly dependent on the duration of sapropel/black shale formation and the local setting: sedimentation rate, the amount of trace elements already present in the basin, the potential amount supplied by rivers, wind and hydrothermal vents and the importance of diagenesis.

The Black Sea: a modern analogue?
The largest contemporary euxinic basin, the Black Sea, may be considered as a modern analogue of Pliocene sapropels and CTBE black shales. This basin has been anoxic for more than 7,000 years and currently is sulphidic up into the photic zone *[Repeta et al., 1989]*. Isorenieratene and its derivatives are found in Black Sea sediments, indicating that similar conditions existed in the past *[Repeta, 1993; Sinninghe Damsté et al., 193]*. In this basin, trace metals are trapped during mixing of oxic surface water (which is a mixture of river water and eastern Mediterranean seawater) with anoxic deep water. The trace element contents of the Black Sea sediments, however, are not as high as those found in the eastern Mediterranean Pliocene sapropels and in CTBE Black Shales (Table 6.3). Still, the trace element extraction efficiency is very high, and the mechanism (scavenging by organic matter and sulphides in an

anoxic water column *[Brumsack, 1989]*) is the same as inferred for the Pliocene sapropels and the CTBE black shales. The trace element content in sediments of the Black Sea is lower because the exchange with the eastern Mediterranean at the Bosporus is restricted, which limits the trace element input from seawater into the basin, and because the sedimentation rate is rather high, diluting authigenic signals from trapping processes within the anoxic water column.

Conclusions

Some eastern Mediterranean Pliocene sapropels are characterized by exceptionally high C_{org} and trace element contents and the presence of isorenieratene derivatives. The trace element enrichment is thought to be the result of efficient scavenging by sulphides and organic matter in a euxinic water column. Because seawater is the ultimate trace element source, circulation must have been relatively vigorous during sapropel formation, and may have been reversed in the eastern Mediterranean.

A comparison of the sapropel with C_{org} and trace element enriched black shales shows that the latter are not always deposited in comparable environments, and often have lower trace element contents. The CTBE black shales are an exception, but were deposited over a longer time period and in a larger area than Mediterranean sapropels. As a result, fluvial and hydrothermal input are the ultimate trace element sources in this case. Still, because the inferred trace element removal mechanism in the CTBE black shale is similar to that in the sapropels, and because the water column was also sulphidic up into the photic zone during deposition of these sediments, sapropels can be considered younger analogues of these black shales.

The Black Sea is a smaller, contemporaneous analogue of both the CTBE black shale and the sapropels investigated, because it also has a sulphidic water column, and the same efficient trace element removal mechanism is operative. Sedimentary trace element contents are lower in this basin because of a limited supply and dilution due to the high sedimentation rates.