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Early diagenesis of organic matter in recent Black Sea sediments: characterization and source assessment

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Abstract—The organic matter in 9 recent (not more than 250 years old) and 'organic-rich' sediments from the southern Black Sea shelf and upper slope have been characterized semi-quantitatively by Pyrolysis/Gas Chromatography/Mass Spectrometry (PY/GC/MS) and ^{13}C Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance (CPMAS-NMR) spectrometry. The organic matter of 7 of the studied sediments was found to be ligno-carbohydrate with a proteinaceous component, one sediment appeared to contain oxidized coal dust and one contained thiophenes in association with pyrite. The ligno component is derived from grasses and soft wood lignin. Material entrapped in an anoxic environment contained the highest proportions of carbohydrate and protein. All the samples had suffered diagenesis as is generally shown by the attachment of carboxyl groups and the removal of methoxyl groups. The evidence suggests that diagenesis occurred whilst the particles traversed the oxic water column. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

The nature of the organic material in recent Black Sea sediments is determined by the relative contributions from marine phytoplankton, riverine input, phytobenthos and zoobenthos (Shimkus and Trimonis, 1974; Trimonis, 1974; Hay, 1988; Hay *et al.*, 1989; Hay and Honjo, 1989). The uppermost layer of the sea floor, termed Unit I, deposited since the late Pleistocene/Holocene, is the repository for modern sediments (Ross and Degens, 1974) and the rate of sedimentation along the southern coast, north of Anatolia, is currently high due to the abundant supply of material from rivers.

The surficial sediment has been found to have a different organic composition to the dissolved or particulate material in the water column (Wakeham *et al.*, 1991; Wakeham and Beier, 1992). It is the comparatively rare, larger particles which contribute to the vertical flux of organic matter, whereas the more abundant and smaller particles are recirculated. In this sense diagenesis (that is, the microbial, biochemical transformation of potentially sedimenting material) starts in the water column. Diagenesis is especially evident in the 'fluff layer' immediately above the sediment and it appears complete at a depth of about 50 cm below the sediment surface (Cowie and Hedges, 1991). One can distinguish 5 previous types of analysis of Black Sea sediments, namely, (i) visual inspection and optical and electron microscopy to describe the presence of (partially) fossilised plankton and faecal pellets (e.g. Pilskaln, 1991); (ii) elemental composition (e.g. Cowie, 1990; Cowie and Hedges, 1991); (iii) infrared spectrometry (Huc *et al.*, 1978; KBr disc technique) to characterize the humic material and the kerogen in 3 deep sea cores —

perhaps, the best previous description of the kerogen in Black Sea sediments though there was no study of surficial matter; (iv) studies of the constituents of acid soluble sediment (Mopper *et al.*, 1978) and of bitumen, including elegant studies of biomarkers by gas chromatography/mass spectrometry (GC/MS), (Simoneit, 1974, 1978; Wakeham *et al.*, 1991, Wakeham and Beier, 1992); and (v) study of the compounds, especially of the alkanes and alkenes, generated by pyrolysis/gas chromatography/mass spectrometry (PY/GC/MS) of the insoluble kerogen present in a sapropel and a diatomaceous ooze obtained from deep ocean cores (van de Meent *et al.*, 1980).

The above studies have dealt mainly with deeper sediments and to a much lesser extent with surficial sediments and then, generally, with only the small fraction of the soluble bitumen. Consequently, one is still unable to portray the structural characteristics of the bulk of the organic matter in surficial sediments and there is uncertainty both about the origin of the organic sediment and of the effects of diagenesis. The present investigation is an attempt to provide this missing information by the use of 13C cross polarization, magic angle spinning nuclear magnetic resonance (13C-CPMAS-NMR) and PY/GC/MS.

13C NMR spectra furnish at least a semiquantitative 'average structure' of complex, amorphous, solid organic mixtures and PY/GC/MS generates a complementary, and again semiquantitative, description of the individual structures present in such materials. Both these well-established techniques are recognized for their value in describing materials such as humic acids and kerogen (van de Meent *et al.*, 1980; Hatcher *et al.*, 1983; Wilson *et al.*, 1983). Each technique has its particular difficulties and it is necessary that their results should confirm each other. Here, both techniques have been applied to 9 surface sediments from the coastal shelf of the southern Black Sea. These sediments were selected from a suite previously described by Yucesoy and Ergin (1992).

MATERIALS AND METHODS

The top 5cm of the sediment surface were sampled by a Dietz Lafonde grab sampler during the 1988–1989 cruises of the R/V Bilim in the southern Black Sea. Of the 47 surface sediment samples, 9, possessing relatively high organic C contents, were chosen for this study. The sampling stations are shown in Fig. 1 and partially described in Table 1. After visual inspection, the samples were subjected to grain size analysis. 30g of each wet sample were then dried at 50°C and hand ground to a particle diameter of less than 0.125mm. The total organic C content of each dried, ground sample was determined by oxidation with acidified $K_2Cr_2O_7$ and back titration with ferrous ammonium sulphate, essentially as described by Gaudette *et al.* (1974). The amount of CO_3 in each dried, ground sediment was determined by treating 1g samples with 10% HCl and determining the CO_2 evolved.

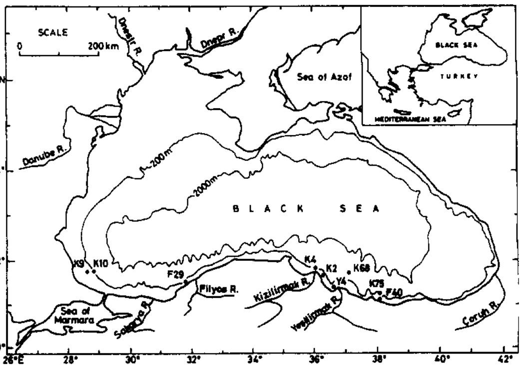

Fig. 1. Map of the Black Sea showing the locations of the surface sediments.

Small quantities of sample were digested with concentrated HCl and HF in order to remove inorganic material before spectrometry. ^{13}C CPMAS-NMR spectrometry was performed with a Brucker MSL 300 NMR spectrometer and a 7.05 Tesla magnet. A 7mm diameter, double air bearing, magic angle probe was used at room temperature. The Al_2O_3 rotor holding the sample was spun at approximately 4.5kHz. A TOSS (total suppression of spinning sidebands) sequence with 180°C pulses of about 8.7 μs duration was used to produce quantitative spectra. Spectra of sediments were compared with those of powdered lignin, powdered cellulose and mixtures of the two in known proportions.

PY/GC/MS analyses were performed using an integrated system consisting of a CDS Pyroprobe 1000 heated filament pyrolyser (Chemical Data System, Oxford, PA, USA) and a Varian 3400 gas chromatograph coupled to a Saturn II ion-trap mass spectrometer (Varian Analytical Instruments, Walnut Creek, CA, USA). A J and W Scientific DB5 capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness) was operated under a temperature programme running from 50 to 300°C at 5°C/min, the initial temperature being held for 2 mins. Samples (0.5–2.0 mg) were pyrolysed in duplicate in a quartz sample holder at 700°C for 20 s. The PY/GC interface was kept at 200°C and the injector at 250°C. The injection mode was split (1:50 split ratio). The He carrier gas had a flow rate of 1.5 ml/min. Electron impact of 70 eV generated mass spectra (1 scan/s) from 40 to 450 da. Compound identification was based on GC/MS comparison with authentic standards, on the search of the NIST 92 mass spectral library and of other published collections of PY/GC/MS data from similar samples (Hempling and Schulten, 1990; Ralph and Hatfield, 1991; Chiavari *et al.*, 1994). Peak quantification was expressed as a relative % of the total pyrogram.

RESULTS AND DISCUSSION

Sediment characteristics. As shown in Table 1, the majority of the surface sediment samples (top 5cm of sea floor and not more than 250 years old) were composed principally (97–99%) of fine-grained mud (particles less than 0.063mm in diameter). The term 'mud' used here refers to a mixture of sediment with varying proportions of clay- (less than 0.002mm diameter) and silt-sized (0.002–0.063mm diameter) materials. Exceptions occurred at 2 stations, F40 and F29 where sediments were sandy mud and gravelly mud, respectively, and thus contained relatively higher proportions of sandy (grains of 0.063–2 mm diameter; 17 and 9%, respectively) and gravelly (grains of greater than 2 mm diameter; 1 and 17%,

Table 1. Characteristics of the sediment samples studied from the southern Black Sea margin (Yucesoy and Ergin, 1992)

Sample	Water depth (m)	Total organic carbon (%)	Total carbonate (% $CaCO_3$)	Sediment type (%Mud)	Depositional environment
K9	80	1.30	4	mud (97%)	oxic to suboxic
K10	212	2.23	5	mud (99%)	anoxic
F29	79	1.25	9	gravelly mud (74%)	anoxic
K4	8	0.69	5	mud (99%)	oxic
K2	116	0.83	5	mud (99%)	suboxic
Y4	100	0.81	6	mud (99%)	oxic
K68	445	2.60	11	mud (99%)	anoxic
F40	63	3.09	1	sandy mud (82%)	oxic
K75	330	1.35	4	mud (98%)	anoxic

respectively) materials. Total CO_3 contents (%$CaCO_3$; Table 1) of the sediment samples were usually low and, with the exception of sediments F29, K68 and F40 which possessed 9%, 11% and 1% CO_3, respectively, varied over a narrow range (4–6%). The CO_3 percentages of the samples were generally associated with the presence of biogenic shells and the skeletal remains of several marine organisms. The total organic C contents of the sediments varied between 0.69 and 3.09% (Table 1) and were loosely correlated (r = 0.507) with the mud contents of the samples.

Table 1 also shows contemporary, redox-related bottom characteristics at the sampling sites of the sediments (Yucesoy and Ergin, 1992). Sediment samples taken from stations K10, F29, K68, and K75 are considered to be anoxic since, at these sampling sites, the dissolved O_2 concentrations diminished to zero at or above the sediment–water interface though it is possible that at some sites the interface was oxic at various times in the past (Cowie and Hedges, 1991). In contrast, sediment samples from the shallow water stations F40, Y4, and K4 may be regarded as oxic since the sediment–water interface lay far above the O_2 minimum. The other sediment samples represent varying oxic to suboxic to anoxic conditions (Table 1) and here, again, the oxicity may sometimes have changed.

NMR Spectra of samples K2, K4, K9, K10, K68, F40 and Y4. Figure 2 shows 3 typical ^{13}C CPMAS TOSS NMR spectra namely, samples (a) K2, (b) F40 and (c) F29. Experimental errors of 1ppm in the chemical shifts and ± 0.1 in the chemical shift ratios listed in Table 2, were determined by comparing the very similar — nearly superimposable — spectra from samples K2 and F40. Comparison with spectra of reference materials shows that all the spectra can be interpreted as mixtures of lignin and cellulose modified by diagenesis, the presence of lignin structures indicating the deposition of terrigenous material.

Usually, the spectrum of pure cellulose, with major peaks at 72 and 105ppm and minor peaks at 65 and 89ppm, is readily distinguished from the spectra of lignins with peaks at 32, 55, 71, 105, 111, 131, 147 and 172ppm (Alberts *et al.*, 1991; Fraga *et al.*, 1991). In the present investigation the distinction is less straightforward (see Fig. 2d, a synthetic mixture of Kraft lignin with cellulose). The low resolution, inherent in the NMR spectra of solids, renders the cellulose peaks at 65 and 89ppm difficult to pick out and the relative

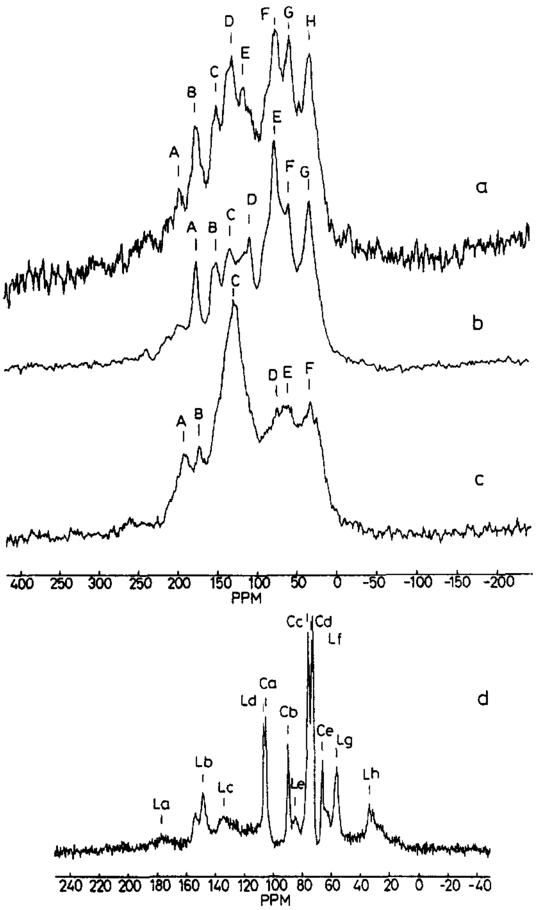

Fig. 2. 13C CPMAS TOSS NMR spectra: a) sediment K2, b) sediment F40, c) sediment F29, d) synthetic mixture: 50% (by weight) Kraft lignin + 50% cellulose (Lignin peaks = L; Cellulose peaks = C). Note the chemical shifts (ppm). a) A = 195.3, B = 147.5, C = 127.1, D = 124.2, E = 112.3, F = 72.1, G = 55.1, H = 29.0. b) A = 172.6, B = 140.0, C = 129.9, D = 104.8, E = 72.4, F = 55.7 G = 30.1. c) A = 192.2, B = 172.9, C = 128.3, D = 73.5, E = 59.2, F = 31.9. d) Ca = 104.8, Cb = 89.5, Cc = 75.6, Cd = 73.1, Ce = 65.7; La = 176.7Lb = 148.5, Lc = 135.8, Ld = 106.4, Le = 84.7, Lf = 72.0, Lg = 56.7, Lh = 33.3.

heights of the lignin peaks vary from sample to sample. Semi-quantitative comparison of the NMR spectra of the samples has therefore been attempted in Table 2 in terms of 4 absorption ratios (peak heights were considered, areas yielding no more information in spite of their slightly better accuracy):

(1) Ratio 1—absorption at 72ppm/absorption at 105ppm

(2) Ratio 2—absorption at 72ppm/absorption at 126–131ppm

(3) Ratio 3—absorption at 172ppm/absorption at 126–131ppm

(4) Ratio 4—absorption at 55ppm/absorption at 126–131ppm

An indication of the relative amounts of cellulose and lignin is provided by ratio 1, a value of 1.95 being typical of cellulose and lignin in samples of sugar-cane bagasse, silver birch and a 3:1 mixture of pure cellulose with Kraft lignin (Araujo, 1990). Ratio 2 between absorptions attributable to C atoms in cellulose (72 and 105ppm) and aromatic C — roughly proportional to lignin concentration — (126–131ppm) also indicates the relative amounts of cellulose and lignin. Ratio 3 is an indication of the degree of oxidation, the absorption at about 172ppm being characteristic of C atoms in carboxylic acid groups on aromatic rings. Finally, ratio 4 is approximately proportional to the number of methoxyl groups (at 55ppm) on each aromatic ring and hence it is another measure of the severity of diagenesis, low numbers indicating biochemical attack.

Table 2 shows that only sample K68 gave relatively high values of ratios 1 and 2, with a ratio 1 similar to the value of 1.95 ± 0.1 mentioned above as typical of an approximately 3:1 cellulose/lignin mixture. The lower ratio 1 values of the other samples suggest that, with the exception of sample K68, a component of the absorption at 105ppm was due to C atoms in lignin. These data suggest that sample K68 was derived from material which was either little affected by diagenesis or else contained relatively high proportions of cellulose.

Ratio 3 was fairly constant (0.8 ± 0.1) for all samples with the exception of K10 and perhaps K68 where more oxidation had occurred. The presence of carboxyl groups indicates that what have been referred to as lignin structures have started to metamorphose towards lignite (peat?). Consistent with this, one observes that generally the aromatic peak in these spectra is centered near 129ppm as in lignites; only in sample K68 was the lignin value, 131ppm, observed. One recalls that all the sediments were young and that K10 and K68 which had the highest values of ratio 3 (largest numbers of carboxyl groups per aromatic C) were found in an anoxic environment. The generation of carboxyl groups seems therefore to have taken place — rather efficaciously — in the water column.

Finally, considering ratio 4 for samples K9, K10 and K68, Table 2 suggests that sample K9 had relatively few methoxyl groups and relatively little cellulose, consistent with the sample being the most affected by diagenesis.

Sample K10 apparently possessed the most methoxyl groups of these sediments and a high proportion of carboxyl groups. However, the proportion of cellulose was modest. One speculates, therefore, that this sample was derived from a deposition of terrigenous vegetation containing an above average proportion of lignin. This had become oxidised but, unlike the other samples, had been transformed no further than this and had lost few, if any at all, of its methoxyl groups.

Comparison with sample K10 suggests methoxyl groups to have been lost from sample K68. The NMR spectrum suggests, therefore, that in this respect the sample was more affected by diagenesis than sample K10 but that the original deposition was of material containing a higher proportion of cellulose. Interestingly, K68, the deepest of the sediments to have been examined, is now preserved in an anoxic environment thus providing evidence for our contention that most of the diagenesis we have observed occurred whilst the particles were sedimenting through the oxic layer of the water column.

The NMR spectra of the other samples can be described in a similar way, the spectra were more 'average', so to speak, but rather few samples have been examined. Only samples K9, F40 and just possibly K68 contained significant proportions of long alkyl chains, as shown by spiky NMR absorption near 29ppm. Such alkyl chains were probably due to algal/microbial membrane detritus or possibly to the fatty acids examined by previous workers (Simoneit, 1974, 1978; Wakeham *et al.*, 1991; Wakeham and Beier, 1992). Long alkyl chains being characteristic of liptinites (Snape *et al.*, 1979; Davis *et al.*, 1988), only in samples K9, F40 and K68 can subsequent metamorphosis generate liptinites; presumably the other samples would eventually metamorphose to vitrinites.

Table 2. Comparison of NMR spectra of surface sediment samples from the southern Black Sea margin

Ratio	Sample							
	F40	K2	K4	K9	K10	K68	Y4	F29
1	1.52	1.68	1.40	1.47	1.66	1.88	1.53	1.20
2	1.91	1.86	1.40	1.09	1.68	2.83	1.57	0.54
3	0.81	0.75	0.85	0.73	1.38	0.97	0.76	0.33
4	1.40	1.25	1.13	1.04	1.85	1.37	1.15	0.47

NMR Spectrum of sample F29. This spectrum (Fig. 2c) is similar to that of a lignite and the ratios shown in Table 2 differ significantly from those of the other samples. There is a marked aromatic peak near 128ppm and one estimates about 60% of the C atoms in the sample to have been aromatic. There appears to be a significant proportion of aliphatic ethers in this sediment absorbing around 66ppm but some of this absorption could be due to incomplete elimination of 'spinning sidebands'. Many of the methylene and methyl groups had chemical shifts around 25 and 20ppm suggesting them to be adjacent to aromatic rings (Snape *et al.*, 1979). There is little evidence of chains of methylene groups and, in contrast to many lignite spectra, which do show the paraffin spike near 28–29ppm (Axelson, 1985; Davis *et al.*, 1988), this material is vitrinite not liptinite. The peak around 173ppm is due to carboxyl groups attached to aromatic rings. Absorption at 192ppm could have been due to aromatic aldehydes and ketones produced by oxidation (Wehrli and Wirthlin, 1976) but could also be due to incomplete elimination of 'spinning sidebands'. In fact this sample was obtained directly to the north of the Zonguldak coal basin where bituminous coal is mined and it may be assumed that this was the source of the organic material in sediment F29. Indeed, a coal preparation plant associated with the mining generates a black plume by discharging its residues directly into the sea. The carboxyl groups and the consequent relatively low aromaticity observed in the sample probably resulted from the oxidation of bituminous coal in sea water. Whereas coals are notoriously easy to oxidise, the reaction does not normally proceed as far as producing carboxyl groups at sea temperatures. Moreover, the sediment was found in an anoxic environment (Table 1). The observation of a lignite-like NMR spectrum therefore supports diagenesis in the oxic water column. The NMR spectrum of sample K75 consisted of a noisy, unresolved hump of absorption between chemical shifts of 0 and 250ppm possibly due to the presence of pyrite in the sample.

Finally, it should be noted that although the ratios 1–4 may be quantitative, it remains possible that in such complicated organic material as these sediments, some carbon atoms may not have contributed to the NMR spectra (Love *et al.*, 1993).

Pyrolysis/Gas Chromatography/Mass Spectrometry of the samples. PY/GC/MS of samples K4, K9, K10, K68, K75, F29, F40 and Y4 generated a total of about 80 compounds having identifiable mass spectra. PY/GC/MS of all sediments except K75 generated pyrograms which were qualitatively similar and consisted of 5 groups of compounds; those derived from lignin, carbohydrates, N heterocyclic aromatics, simple aliphatics and substituted benzenes. A typical pyrogram is shown in Fig. 3. Peaks eluting before scan 120 are omitted because they are the most volatile pyrolysis fragments, such as low molecular weight alcohols, acetic acid and acetic anhydride, which are difficult to separate and, in any case, are of little diagnostic value. The wealth of pyrolysates whose mass spectra indicated their derivation from lignins and carbohydrates provides independent confirmation of the interpretation of the NMR spectra. Table 3 lists the relative percentages of compounds generated from lignin. Vinyl phenol, detected amongst the products from 5 of the sediments, has been postulated to arise from pyrolysis of grasses (Hruza *et al.*, 1974; Evans *et al.*, 1984). The other compounds in Table 3 are taken to be characteristic of pyrolysis products from softwood lignin (Meuzelaar *et al.*, 1982) which appears to be the major source of lignin in these contemporary sediments.

Sediment K75 was unique in that more than 95% of the pyrogram was due to peaks from S, (**S8**, S7 and S6). This is consistent with the significant content of pyrite present. Nevertheless, this sediment contains more than 1% organic C (Table 1) and a significant number of peaks due to organic material were present in the pyrogram. These peaks, with benzonitrile (+phenol) as the largest (~12% of the organic pyrolysate), represented a different 'mix' of compounds to those obtained from the other sediments. Sample K75 was the only sediment to give significant traces of thiophenes on pyrolysis. Thiophene derivatives could be the pyrolysis products of organic compounds from the sediments, although their genesis as products of inter- and intramolecular reactions

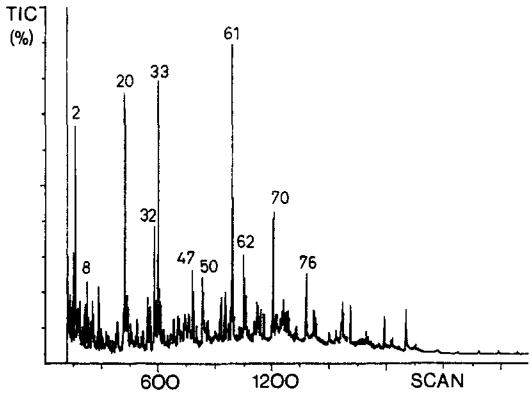

Fig. 3. Typical pyrogram obtained from a sediment (sample K10). Pyrolysis and GC conditions as stated in text.

#	scan	mm	name
2	154	92	toluene
8	216	98	(3H)-2 furaldehyde
20	419	94	phenol
32	580	108	4-methylphenol
33	598	124	guaiacol
47	780	138	4-methylguaiacol
50	833	120	4-vinylphenol
61	988	150	4-vinylguaiacol
62	1049	154	2,6-dimethoxyphenol (syringol)
70	1206	164	trans-isoeugenol
76	1379	180	4-vinylsyringol

(A table of all 80 compounds identified from the sediments is available.)

Table 3. Sediment pyrolysis: Relative percentages of compounds from lignin

	Relative yields (% of total pyrogram)						
	F40	K4	K9	K10	K68	Y4	F29
Compound*							
4-vinylphenol (120)	1.9	1.8	5.2	4.2	1.8	-	—
guaiacol (124)	4.8	7.1	6.0	7.2	1.4	9.3	3.9
4-vinylguaiacol (150)	7.0	6.9	7.5	9.6	1.2	10.3	—
vanillin (152)	1.1	1.5	1.3	1.4	-	1.2	—
syringol (154)	1.2	1.8	1.5	2.9	-	2.5	—
4-vinylsyringol (180)	1.8	1.1	1.5	3.0	-	2.5	—
eugenol (164)	1.4	-	1.1	1.1	-	1.0	—
trans-isoeugenol (164)	5.0	2.5	3.7	5.0	0.8	3.9	—

* = molecular mass in parentheses.

between S and organic compounds within the pyrolyser cannot be ruled out in principle. The presence of pyrite in an anoxic sediment involves bacterial action associated, of course, with the consumption of organic material (Berner, 1974; Jannasch *et al.*, 1974; Strizhov *et al.*, 1990) and this is what appears to have happened here.

It is evident from Table 3 that sediments K68 and F29 gave lower concentrations of lignin pyrolysates than the other sediments. This observation corroborates the NMR results which indicated K68 to possess the highest proportion of cellulose to lignin (Ratio 2, Table 2) and the aromatic component of the organic material of F29 to be derived from high rank coal which had already metamorphosed beyond the lignite stage.

Table 4 lists the relative proportions of the major pyrolysis compounds that were generated from cellulose in the sediments. Most of these were derivatives of furan, cyclopentene or pyranone, established by previous work as characteristic of cellulose (e.g. Shafizadeh, 1982; Hayes *et al.*, 1989; Ralph and Hatfield, 1991; Galletti and Bocchini, 1995). As opposed to the relatively easy identification of lignin-derived pyrolysis products, i.e. phenolics with very diagnostic mass spectra, the identification of cellulose markers is much less straightforward. Cellulose pyrolysis produces a large number of carbohydrate isomers as the result of unpredictable dehydration and their mass spectra are poor, with few or no molecular ions and a fragmentation pattern which is not diagnostic. For the identification of such material, this investigation relied heavily on the literature (e.g. Ralph and Hatfield, 1991). Cellulose, which the NMR spectra indicate to have been present in the sediments, generally yields levoglucosan-derivatives under pyrolysis (Shafizadeh and Fu, 1973; Shafizadeh, 1982). However, the absence of levoglucosan, as the pyrograms seem to indicate, is not *per se* indicative of the absence of polysaccharides but rather suggests that the original macromolecule may have undergone microbial degradation, as the result, for instance, of humification. The PY/GC/MS conditions used in the present work detected levoglucosan derivatives when other samples containing materials of different composition were analysed (Terron *et al.*, 1993) Under such circumstances, furan-derivatives become useful markers for the presence of polysaccharides (Hayes *et al.*, 1989; Galletti and Bocchini, 1995). It should be recalled that inorganics were removed from the present sediments by treatment with HCl and HF. These strong acids undoubtedly hydrolyse polysaccharides such as cellulose and the resulting sugars may have dissolved in the aqueous solution. This is indeed the major shortcoming of the present investigation which has to be overcome in future work.

Table 5 lists the relative yields (ratios) of pyrolysates from cellulose and lignin material. As one would expect from the previous discussion, the results from sediment F29 were anomalous. If the origin of the predominant organic material in F29 was bituminous coal from the Zonguldak basin, the abundant cellulose pyrolysates obviously had a different source (Table 4). The pyrolysis products from the other sediments, (Tables 2 and 3) were qualitatively similar and consistent with the description of the NMR spectra of their organic substrates as being lignocellulosic material which had suffered diagenesis. In agreement with the NMR spectra (Table 2, Ratio 2), the relative yields of pyrolysis products indicate the deepest anoxic sediment, K68, to have contained the highest proportion of cellulose to lignin (Table 5, Ratios A–D). Indeed, inspection shows the relative yields of pyrolysis products in these sediments as expressed by Ratio D in Table 5 to be loosely correlated with the proportions of carbohydrates to lignin indicated by the NMR spectra (Ratio 2 of Table 2).

Pyrrole, pyridine, indole and methyl pyrroles and pyridines were evolved by pyrolysis of all the sediments except K75. Table 5 includes the ratios of pyrrole and indole to guaiacol. Two sources may be postulated for these N heterocyclics; heterocyclic material released by the pyrolysis of lignin and pyrolysates from protein. Usually not more than a few % of the aromatics obtained by the pyrolysis of

Table 4. Sediment pyrolysis: Relative percentages of compounds from carbohydrates

	Relative yields (% of total pyrogram)						
	F40	K4	K9	K10	K68	Y4	F29
Compound*							
2-furaldehyde (96)	4.3	2.8	2.2	1.1	2.6	2.4	4.1
(3H)-2-furaldehyde (98)	1.1	1.0	1.3	1.5	1.4	1.0	1.0
dihydrofuraldehyde (98)	—	—	—	—	—	—	1.6
2 methylcyclopentene-1-one (96)	1.4	1.4	1.3	1.0	2.0	1.3	1.7
2-acetylfuran (110)	—	—	—	—	0.9	—	1.9
2,3-dihydro-5-methyl-furan-2-one (98)	0.8	1.0	—	—	—	1.2	4.6
5-methyl-2-furaldehyde (110)	2.4	1.9	1.5	1.0	2.3	1.9	2.8
2-hydroxy-3-methyl-cyclopentene-1-one(112)	3.1	2.0	2.0	1.3	2.4	2.6	5.6
2,3-dimethylcyclo-pentene-1-one (110)	—	—	—	—	—	—	0.9
N,N-dimethyldihydro-pyranone (126)	—	—	—	—	—	—	0.6
N,N'-dimethyldihydro-pyranone (126)	1.1	—	—	—	1.3	0.7	2.1

* = molecular mass in parentheses.

coaly materials are N heterocycles, whereas it is well established that the pyrolysis of proteins generates pyrroles, pyridines and indoles; though the total pyrolysis yield of volatiles from proteinaceous materials is significantly less than that of lignin-containing materials (Chiavari *et al.*, 1993). Table 5 indicates the ratios of heterocyclics and cellulose pyrolysates to lignin monomers to be of similar orders of magnitude. This suggests the proportion of heterocyclics to be too high to have been derived solely from lignin structures; most heterocyclics must have formed from proteins. This is particularly the case for sediment K68 which has the largest proportion of both proteins and carbohydrates (Tables 2 and 5). This sediment also contains the largest % of CO_3 (11%) suggesting the protein and carbohydrate may have originated from marine organisms whose shells and skeletons are part of the CO_3. Minor components of the pyrolysates consist of simple alkylated benzenes, alkanes, a few alkenes, phenol and vinylbenzene.

General implications. Tables 2–5 provide the most detailed description of the bulk of the organic material in surface sediments from the Black Sea along the coast of Turkey. The average organic C content of the 49 sediments that were originally sampled from the southern coast was 1%. The 9 samples examined here contained 0.6–3.1% of organic C. The rate of sedimentation in the southern coastal region of the Black Sea is high, ~25cm per 1000 years (Ross *et al.*, 1970), nevertheless, it has been estimated that only between 0.7 and 2.1% of the organic C is preserved in the bottom sediments (Calvert *et al.*, 1991). This is not high compared to C accumulation rates in equivalent oxygenated environments (Mueller and Suess, 1979). Thus, it is pertinent to enquire whether more organics are buried in oxic or anoxic surface sediments.

In the Black Sea, as elsewhere in the world's oceans, most of the organic matter is recycled. Consistent with this and in agreement with the surmise of Calvert *et al.* (1987) that some of the fraction of Unit 1 in the deeper basin may be derived from terrigenous sources, the organic material in 7 of the 'organic-rich' sediments analysed here possessed a significant component of lignin, clearly of a terrigenous origin and non-degradable by marine biota. The terrigenous character of the sediments suggests that the relatively high organic content of sediments K75, F40 and K68 may be derived partly from high sediment loads from the extremely erosive rivers/streams discharging into the southeastern Black Sea (i.e., Yesilirmak River). The reasons for the accumulation of organic matter in sediments from stations K9 and K10 are not known but regionally favored hydrographic conditions together with riverine transport from the north (i.e., Danube River) might be responsible for part of the organic C contents in these samples.

Table 5. Sediment pyrolysis: Ratios of carbohydrates and nitrogen heterocycles to lignin

Sediment ratio	F40	K4	K9	K10	K68	Y4	F29
A	0.34	0.28	0.19	0.10	2.0	0.18	oo
B	0.61	0.40	0.29	0.11	2.2	0.23	oo
C	0.50	0.27	0.25	0.14	3.2	0.20	0.72
D	0.90	0.39	0.37	0.15	1.8	0.26	1.05
E	0.31	0.11	0.25	0.28	1.4	0.16	0.69
F	0.27	0.17	0.27	0.36	1.9	0.16	—

A = 5-methyl-2-furaldehyde:4-vinylguaiacol B = 2-furaldehyde:4-vinylguaiacol C = 5-methyl-2-furaldehyde:guaiacol D = 2-furaldehyde:guaiacol E = pyrrole:guaiacol F = indole:guaiacol.

The two 'solid state' techniques used here, pyrolysis/gas chromatography/mass spectrometry and ^{13}C CPMAS NMR spectrometry, have complemented each other in providing a semiquantitative description of the organic matter present in the 9 coastal-shelf sediments. With two exceptions, the organic material consisted of partially fossilised, (soft-wood) lignocellulose together with a small component of partially preserved protein. Of the two exceptions, one contained coaly material, probably originating from the nearby Zonguldak coal basin and the other, an anoxic sediment, was rich in pyrite. The formation of the pyrite was accompanied by an unusual organic matter diagenesis which yields a unique pyrolysate containing mainly phenol and some thiophene derivatives. The reasons for the presence of pyrite in sample K75 are not clear though the southeastern Black Sea coast is relatively rich in metallic minerals.

One might expect the carbohydrate component of the ligno cellulose sediments to derive from cellulose associated with the grasses and soft-wood lignin implicated by the PY/GC/MS; however, the presence of proteinaceous material suggests the sediments may also contain a component from marine organisms (for example from faecal pellets, Pilskaln, 1991) and obviously some, at least, of the carbohydrate may also have had a marine origin. This is particularly true of sample K68, an anoxic sediment, containing a significant concentration of (marine) CO_3 and relatively large concentrations of both proteinaceous material and carbohydrate. Whereas studies of biomarkers in bitumen extracted from sediments in the deeper Black Sea have generally emphasised their terrigenous origin (e.g. Simoneit, 1974, 1978), Cowie and Hedges (1991) suggested that the organic material they analysed in surficial sediments in Sinop Bay had a common, predominantly marine origin. Mopper *et al.* (1978) investigated the composition of the amino acids and sugars they obtained by acid hydrolysis of Black Sea sediments and tried thereby to distinguish between marine and terrigenous sources for the organic material. They suggested that in sediments possessing relatively high % of organic C and yielding high glucose to ribose and sugar to amino acid ratios, terrigenous sources predominate. Only one surficial sediment was examined. Our own results on coastal sediments show little correlation between the % of organic C in the sediment and the composition as expressed by either NMR spectroscopy or by PY/GC/MS and lignin and proteinaceous material almost certainly derived from terrigenous and marine sources, respectively. We cannot ascribe the source of carbohydrate and in discussing the relative proportions of the organic structures in these sediments it is necessary to consider the reactions which have occurred in the oxic water column.

It is well established that as diagenesis/catagenesis proceeds, cellulose and proteins are removed by oxidation and hydrolysis and lignin matures to lignite. The organic material characterised here has been part of the sediment for only up to 250 years and although partial fossilisation — notably carboxylation and demethoxylation of lignin structures — is evident, much carbohydrate and proteinaceous material was still present. One notes, in passing, that further maturation of the lignocarbohydrate structures examined here should generate material yielding similar infrared spectra to those Huc *et al.* (1978), observed from Black Sea kerogens.

No simple distinction could be made between oxic and anoxic sediments; thus, F40 and K2 gave nearly identical NMR spectra though the former was deposited in a much more oxic environment. Obviously as particulate organic material sinks through the oxic water, it suffers oxidation in the water column and such decay of organic matter will continue when the material settles onto an oxic surface sediment. When, however, the material descends through the oxic water into the anoxic zone and settles onto an anoxic sediment, then in the absence of specific S active bacilli oxidative diagenesis must cease. This description, given the uncertainties as to the precise composition of the original organic material and the length of time it has resided in the water column, is consistent with the analytical results. This provides a simple explanation of how larger proportions of carbohydrate and protein were preserved in the anoxic sample K68 than in the oxic K4 sample in only 8m depth.

CONCLUSIONS

The observations described here indicate that most of the particulate organic matter in oxic water of the Black Sea is recycled and only a small portion, resistant to complete biochemical oxidation, is sedimented. In this sense, most of the initial diagenesis of the contemporary near shore sediments occurs in the water column. Not unexpectedly, the major portion of the organic material in these contemporary sediments consists of partly diagenetically altered lignin — carbohydrate material containing some proteinaceous matter. The lignin component is derived both from grasses and soft wood lignin. Significant quantities of long chain alkanes were present in some sediments (K9, F40 and possibly K68). The sediments reflect the effects of diagenesis by the presence of carboxyl groups and the loss of methoxyl. The sediments were not more than about 250 years old and it seems that the diagenetic reactions occurred as the sediments traversed the oxic water layer of the Black Sea. This is entirely consistent with the nature of the larger scale, oxidative, biochemical recycling which occurs there (e.g. Didyk *et al.*, 1978; Khrustalev *et al.*, 1990). The sediments represent only a small proportion of the particulate organic C in the water column. One sediment derived from a localised discharge of coal particles and another contained pyrite, which affected their composition. 13C-CPMAS-NMR and PY/GC/

MS have produced complementary results. The major effect of an anoxic environment appears to be the preservation of structures formed by biochemical change in the oxic water column.

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