The experimental analysis on the Late Quaternary deposits of the Black Sea

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Abstract − Holocene sediments taken from the south-eastern and western Black Sea have been investigated in relation to their geochemical, sedimentological and mineralogical characteristics. Their textures are characterized by their low amount of sand, upward-increasing silt and downward-increasing clay contents. While the terrigenous materials transported from Anatolian volcanic-based sources and European alluvial sediments form the shore deposits, the deep-sea sediments mainly consist of the marine biological production. The highest amount of organic carbon was deposited following the formation of anoxic conditions at the bottom until the beginning of the still continuing carbonate-rich coccolith *(Emiliania huxleyi)* deposition. The high metal concentrations are associated with fine-grained sediments, some with organic material. The metal concentration is diluted by high organic carbon and carbonate contents within the depositional sequences. While the abundance of illite in the western Black Sea describes the deltaic depositions, the downward decreasing smectite/illite ratio along the core, off the south-eastern shelf, indicates the downward increasing precipitation during the deposition. The variation in the sedimentation pattern and sedimented material is believed to be the response of the biochemical environment in the sea to the changing geological, biological and chemical conditions in and around the Black Sea during the last climatic changes. © 2001 Ifremer/CNRS/IRD/Éditions scientifiques et médicales Elsevier SAS

Résumé − Analyse de sédiments holocènes de la Mer Noire. Cette étude présente les caractéristiques géochimiques, sédimentologiques et minéralogiques de sédiments holocènes récoltés dans les parties sud-est et ouest de la Mer Noire. Leur texture présente une quantité faible de sable et des contenus en vase croissant vers le haut et en argile croissant vers le bas. Tandis que les matériaux terrigènes sont issus de sources volcaniques de l'Anatolie et des sédiments alluviaux issus des dépôts littoraux, les sédiments profonds sont principalement d'origine biologique marine. La plus grande partie du carbone organique a été déposée après l'apparition de conditions anoxiques au fond, et jusqu'au commencement du dépôt riche en coccolithes *(Emiliania huxleyi)* qui perdure. Les concentrations élevées en métal sont associées à des sédiments fins, quelques-uns avec du matériel organique. La concentration en métal est diluée par les contenus élevés en carbone organique et en carbonates au sein des séquences déposées. Alors que l'abondance d'illite dans la partie ouest de la mer Noire souligne la déposition deltaïque, la décroissance en profondeur du rapport smectite/illite le long de la carotte, à l'extérieur de la plate-forme sud-est, indique la précipitation croissante avec la profondeur durant le dépôt. La variation de la sédimentation et du matériel sédimenté est une réponse de l'environnement biochimique marin aux conditions géologiques, biologiques et chimiques changeantes au sein et autour de la mer Noire durant les dernières évolutions climatiques. © 2001 Ifremer/CNRS/IRD/Éditions scientifiques et médicales Elsevier SAS

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1. INTRODUCTION

The Black Sea is a semi-enclosed marine basin with an area of 432 000 km^2, a volume of 534 000 km^3, and a maximum depth of 2230 m. It is situated between the folded Alpine Belts of the Pontic Mountains to the south and the Caucasus and Crimea ranges to the north. It is almost in a state of isolation excluding the connection to Mediterranean through the Aegean Sea and Sea of Marmara, which has a sill depth of 30 m at the entrance of Bosphorus Strait.

The Black Sea basin has four main physiographic regions: 1) a continental shelf which is quite wide on the west of the Crimean Peninsula due to the high river inputs, and is very narrow along the mountainous coast of Turkey, eastern Russia, and south of the Crimean Peninsula; 2) a basin slope which is either steep and highly dissected by submarine canyons such as off most of the Turkish and part of the Russian coasts, or relatively smooth as found off Rumania and Bulgaria; 3) a basin apron divided into two unequal parts by the Danube fan; 4) a flat abyssal plain better developed in the eastern part of the Black Sea with a greater incidence of turbidity current deposits (Ross et al., 1970).

In the Black Sea, type and distribution of the sediments is highly dependent on the lithogenic and biogenic fluxes changing with climate, geological source, organic productivity and environmental conditions in the sea (Shimkus and Trimonis, 1974). The basin sedimentary structures are determined by banding, bedding, laminations, grading, slumping, brecciation, and bioturbation (Stoffers and Müller, 1978). The sedimentation pattern in the near-shore zone of the Black Sea is governed by surface and longshore bottom currents and wave actions, whereas in the deep basins it is controlled by an isolated cyclonic current system and bottom morphology (Degens et al., 1978). In contrast with the wide, large rivers of the north and north-west, the southern area has been drained by numerous small but extremely erosive rivers. Although these Turkish rivers have a total drainage area nine times smaller, they carry approximately 27.77 millions t $year^{-1}$ of detritus compared with 117.32 millions t $year^{-1}$ for the others (Hay, 1994).

Over the last 10 000 years three main sedimentary units were deposited in the Black Sea: Still continuing carbonate rich top unit 1 deposition started about 3000 years ago. Between 7000–3000 years BP organic rich unit 2 deposition was formed as a result of increasing plankton production brought on by the upward displacement of deep nutrient-rich water by the incursion of denser Mediterranean water into the deep basin after a sea level rise (Damste Sinninghe et al., 1993). The unit 1 coccolith rich and unit 2 sapropel rich sediments are deposited as varve structures where the varves are light and dark coloured thin layers alternated with each other as a result of seasonal variation in the supply of sediments and organisms (Reineck and Singh, 1975). At the bottom there exist unit 3, which was deposited when the Black Sea was a fresh water lake.

The Black Sea basin's oceanography is strongly affected by fresh water inputs from rivers, strait flows, atmospheric forcing, thermohaline factors, and bottom topography. Today, about 87% of the water volume of the Black Sea is anoxic (Özsoy and Ünlüata, 1997). The O_2/H_2S interface, having a mean depth of 200 m, has a slightly curved shape, with its highest point near the centre of the Black Sea and its deepest point at the shelf (Degens and Stoffers, 1980). The salinity of surface waters (17.5–19) is lower than the deep water region (22) (Oğuz et al., 1990) due to the high river input and high precipitation exceeding evaporation. Primary productivity of the Black Sea gives two peaks in a year, with a major bloom principally composed of diatoms in early spring, followed by a secondary bloom mainly comprising coccolithophorides in autumn (Sorokin, 1983). A basin scale cyclonic boundary current (referred to as the 'rim current' by Oğuz et al., 1993) is the main feature of the Black Sea general circulation.

2. SAMPLING AND ANALYTICAL METHODS

Five gravity cores were collected by the Turkish Petroleum Company and British Petroleum during a 1992 cruise in the Black Sea, using a 14.8 cm diameter, 7 m gravity core sampler. The box core BC36 was taken by Dokuz Eylül University again from the south-eastern Black Sea and the other box cores, S2, S8 and S11 were collected from the Danube Delta by RV *Poseidon* in 1994 (*figure 1*). The original length of the cores, locations and water depths are given in *table I*. In total 333 sub-samples were taken from different parts of each core for sedimentological, geochemical and mineralogical analyses (*table I*). The distribution of coccolith and sapropel varves between turbiditic deposits were used to define the stratigraphic layers.

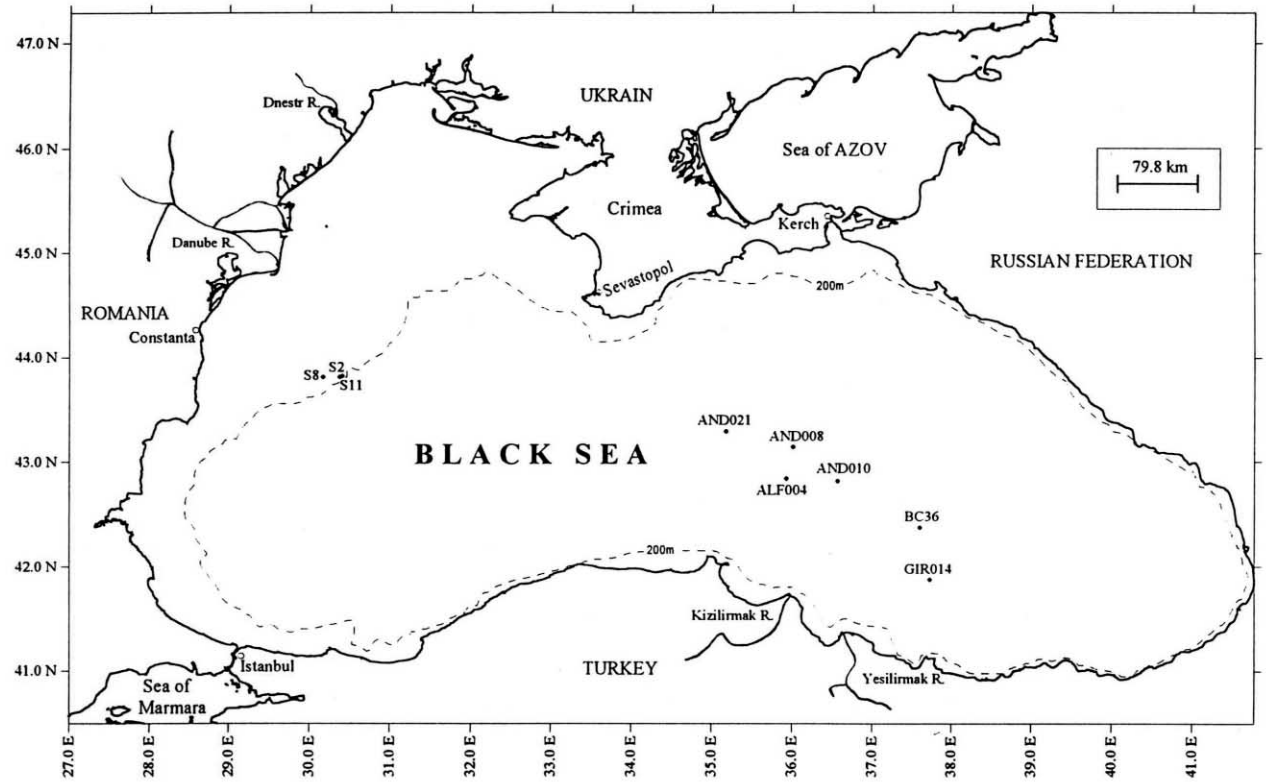

Figure 1. Locations of the cores.

Generally, the distribution of grain sizes in sediment is grouped into four categories, as gravel (> 2 mm), sand (2 to 0.063 mm), silt (63 to 2 μm) and clay (< 2 μm). In this study grain-size analysis was performed by using the wet sieving and pipetting methods according to the standard procedures outlined by Folk (1974). The gravel and sand sized materials, which were previously separated from the bulk samples were analysed under the binocular microscope to identify the terrigenous and biogenic materials within this fraction.

Table I. Sampled core lengths, water depths, locations and number of sub-samples taken from each core.

Core name	Length (m)	Water depth (m)	Latitude (N, degree)	Longitude (E, degree)	Sample number*	Sample number**
ALF004	4.0	2195	42.845	35.931	16 (16)	76
AND008	4.1	2199	43.145	36.012	20 (20)	–
AND010	3.7	2170	42.818	36.562	19 (19)	–
AND021	4.0	2218	43.295	35.181	21 (21)	–
GIR014	4.3	1945	41.872	37.726	24 (24)	136
BC36	0.41	2038	42.374	37.600	5 (5)	–
S2	0.32	150	43.817	30.374	5 (5)	–
S8	0.30	150	43.816	30.167	6 (6)	–
S11	0.25	300	43.940	30.504	– (5)	–

* Number of samples used for mineralogical and petrographical (in parenthesis) analysis, total: 116 (121); ** number of samples used to determine the heavy metal contents of the sediments, total: 212; all 333 samples are used for textural analysis and to determine the C_{org} and $CaCO_3$ content of the sediments.

For chemical analysis, about 10 g of oven dried subsamples were grounded by using an agath mortar and pestle, down to an approximate grain size of less than 0.063 mm in diameter. The $CaCO_3$ content of sediment can be estimated by measuring the volume of the CO_2 produced on treating a known weight of sediment with excess HCl. During this study, a gasometer system modified from Schiebler Calcimeter (Ediger, 1991) is used. For the organic carbon determination a modified Lichterfelder wet oxidation method described by Schlichting and Blume (1966) is used. The quantitative measurement of total carbon, total nitrogen and total hydrogen is based on the complete and instantaneous oxidation of the sample by high temperature flush combustion, using a Carlo Erba EA–1108 Model CHN Analyzer. The concentration of Co, Cr, Cu, Fe, Mn, Ni and Zn were determined by AAS after digestion with $HF–HNO_3$ mixture (Förstner and Wittmann, 1979).

To fix the basal spacing between the clay mineral layers to a known value, the clay sized sub-samples, which were already extracted from the whole samples, were saturated with 1N $MgCl_2{\cdot}6H_2O$ solution as explained by Jackson (1973). X-ray analyses of clay minerals were then carried out using a Phillips X-ray diffractometer under the following conditions: copper-α radiation, line source, nickel filter, 40 kV/30 mA, 10 beam slit and 0.1 detection slit. Under the same conditions whole sub-samples were also analysed to identify the petrographic properties of the sediment.

3. RESULTS AND DISCUSSION

3.1. Core description and their internal structure

Five different long gravity cores, ALF004, AND008, AND010, AND021 and GIR014, and four short box cores, BC36, S2, S8, S11 were used to describe the sedimentological and environmental processes in the Black Sea (*figures 2 and 3*). Whereas the box cores only consist of the most recent deposited part of unit 1, the gravity cores includes all different Holocene sedimentary units of the Black Sea which are mainly the terrigenous rich fine-grained, homogenous mud layers and silty deposits (turbidites), i.e., neoeuxinian deposits (unit 3), believed to represent re-deposition of basin-margin sediments which is a very low-energy process of emplacement (Lyons, 1991); organic-rich micro-laminated sapropel varve layers, i.e., old Black Sea deposits (unit 2); and recent carbonate-rich coccolith varve deposits (unit 1) from the bottom to the top (Arkhangelskiy and Strakhov, 1938). Inorganic precipitate aragonite layer observed in these cores, indicating the alternation of sea from fully oxic fresh water lake to anoxic marine environment due to the rising sea level in a tropical climate (Kukal, 1971).

Among gravity cores, GIR014 consists only of the unit 3 turbidites of massive to coarsely banded, greenish-grey to olive-grey clay, except for 13.5 cm totally sapropel varve layers (unit 2) at the top. The presence of distinct dark and light sand or mud layers along the unit 3, in pre-sapropel time, is maybe a reflection of the periodically changing conditions close to the sediment/water interface in the Early Holocene (Sarayev et al., 1986). The light coloured sedimentation of unit 3 is an indicator of in situ oxidising conditions, because while the anoxicity increases, due to the deposition of organic matter, sediment colour becomes darker. Also yellow and grey different turbidite layers observed along unit 3 reflect the different minerals present. Absence of unit 1 and the top layer of unit 2 on the core GIR014 can be explained by the location of this core where the bottom morphology and long shore deep currents may have caused erosion of the sediments.

The box cores S2, S8 and S11 taken from the Danube Delta, consist of recent sediments. While S2 and S8 are wholly shelly mud with 1.5% organic carbon content in average, S11 consists of only coccolith varve deposits with 5% organic carbon content in average. This difference might be the result of still existing oxic conditions at the 150 m water depth at which S2 and S8 cores were taken (Brewer, 1971), and is also due to the relatively steep slope at this location. Well-preserved laminations throughout the S11 core, indicate the prevailing anoxic bottom waters at 300 m. Since there exist anoxic bottom conditions lacking strong bottom currents and are therefore no bottom-dwelling organisms, the structure of the sediment tends to be preserved. Therefore along the entire S11 core, generally there is a noticeable distinction between the light/dark pairs of coccolith varves, which are in fact a product of seasonal contrast in composition (Ross et al., 1978).

The thicker coccolith varve layers of western Black Sea can be explained by the near-shore maximum of primary

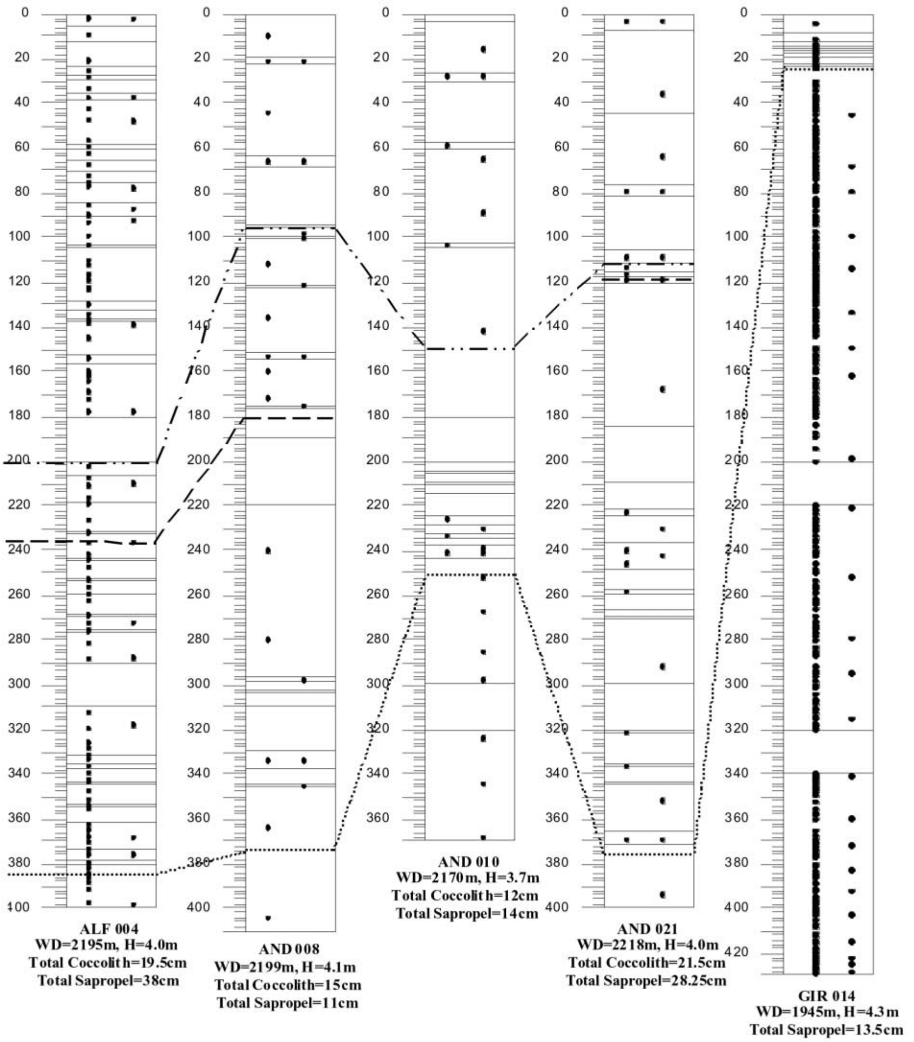

Figure 2. Schematic representation of deep Black Sea cores and sampling locations.

production that is clearly related to the abundant supply of mineral nutrients from the Danube and other rivers. Turbiditic deposition is widespread in areas at the base of a steep continental slope such as off Turkey's coast where the sedimentation rate is the relatively high (> 30 cm per 1000 years) due to its topographic features (Çağatay et al., 1987). Starting from the final and permanent invasion of *E. huxleyi*, upward decreases in the thickness of unit 1 coccolith varve layers and in terrigenous input are observed, suggesting the *E. huxleyi* blooms becoming less intense and getting drier climatic conditions around the Black Sea. Along all the cores, the distinction in varve layers implies a remarkable homogeneity in production, accumulation and preservation of biogenic material over

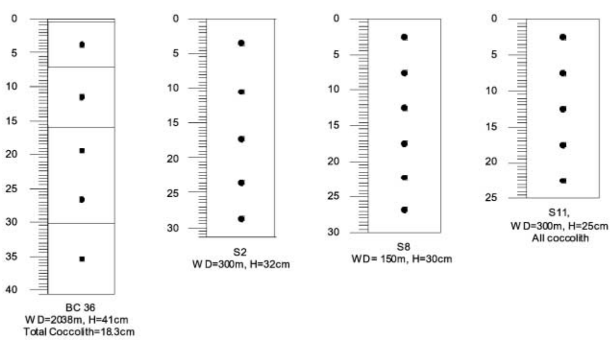

Figure 3. Schematic representation of box Black Sea cores and sampling locations.

much of the Black Sea during unit 1 and unit 2 depositions. The first time and short period invasion of *E. huxleyi* (transition zone) marks a fundamental change in depositional conditions from finely-laminated sapropel varves to laminated more calcareous coccolith varves, indicating that the surface water salinity had increased to at least 11 which is the threshold for production of *E. huxleyi* (Bukry, 1974), due to changing climatic conditions and consequently changing river discharge.

3.2. Sediment texture

Both particle size distribution and composition of the sediments are either a controlling factor in most sedimentological and geochemical processes or intimate reflections of the influence of provenance, tectonism and climate. In general, sediments from the south-eastern part of the Black Sea, particularly off the mouths of major rivers, Kizilirmak and Yesilirmak, and those from relatively deeper waters are characterised by their high mud (silt and clay) content coinciding with the prevailing cyclonic circulation in this region (Shimkus and Trimonis, 1974). The coarse fraction of deep Black Sea sediment does not contain gravel, and it is only composed of sand size material. According to experimental results, the sand fraction along the cores of the south-eastern Black Sea has an average of 0.5% in unit 1, of 1.0% in unit 2 turbiditic layers and reaches to 1.7% along unit 3 (*tables II and III*). Rarely observed higher values of the sand concentration (up to 25.6%), mostly along ALF and GIR cores are well representative of graded turbiditic deposition. Since sand content decreases towards the top of the core and the content of fine-sized particles increases, it can be concluded that the sedimentation process in the Black Sea was governed mainly by the decreasing energy of the transporting turbidity currents (Berner, 1974; Jipa, 1974). Silt fraction along the ALF, AND, GIR and BC cores slightly decrease with increasing depth. While along unit 1 turbidites it has an average of 57%, it is 55.7% along the unit 2 and along the unit 3 the average is 41.1% (*tables II and III*). Silt fraction in unit 1 coccolith layers have an average of 67.8%. The approximately 2.5 μm diametered *E. huxleyi* coccolith (Fagerbakke et al., 1994) is the main reason for the high silt content of unit 1. As the opposite of the silt data, the clay material percentages increases with the increasing depth of the core off Turkey's shore resulting a distinct decrease in silt/clay ratio. With this oppositely changing clay and silt data, the silt/clay ratio decreases to a value less than 1% in unit 3, while it was about 1.67% in unit 1 (*table II*).

Since S cores are located on the delta front of shelf region, coarse grain material fraction, which indicates a high energy environment, is higher than that of the other cores. Along these cores, while the coarse material fraction increases to 10.1% average in homogeneous mud deposits, it does not vary much in coccolith layers ranging between 0.5–1.3% (*table II*). The content of the coarse fraction is again gravel-free and in this part of the Black Sea is composed mostly of shell fragments. The silt fraction in recently deposited sediments of the western Black Sea shelf averages 33.6% (*table II*). This value in coccolith varve layers increases approximately two times as being 63.5% (*table II*). As the opposite, the average of clay fraction is 56.2% in mud deposits and 35.6% in coccolith varves (*table II*). From the results, it can be concluded that the composition of material becomes finer going from shelf to the deeper parts of the Black Sea because of the changing energy conditions in these parts of the sea, and from top to the bottom of the cores related to the variations in hydrological and biological processes due to the changes in the sea level and/or to the supply and rates of the fluvial sediments. Comparing with the recent sediments of the western and south-eastern Black Sea, the silty material is the characteristic of the south-eastern part while the finer grains dominates the western part. The darkening of sediment colour from the unit 3 to the upper units, also indicates the passage to the finer grain material from coarser ones, since finer material exists in darker colour.

3.3. Petrography and mineral composition of the sediment samples

For the petrographical interpretations of the primary minerals, the observation of the sand sub-samples under the binocular microscope and X-ray diffraction of whole sub-samples are referenced.

Quartz, feldspars and mainly mica (muscovite and biotite) minerals were the most abundant minerals everywhere along the cores. Throughout the cores, the low values of quartz distribution are stable with small exceptions. The degradation of the crystalline structure of quartz may be attributed to the masking effect of excess organic matter in unit 1 and unit 2. Quartz and feldspar

Table II. Sedimentological and geochemical parameters.

	Coccolith		Sapropel	Turbidites					Shelf mud deposits
Parameters	Unit1	Shelf		Unit1	Transition zone	Unit2	Unit3	Total	
Sand	0.0–0.4	0.5–1.3	–	0.0–3.5	0.0–2.1	0.0–15.9	0.0–25.6	0.0–25.6	7.5–16.1
	0.2 (0.2)	0.8 (0.3)	–	0.5 (0.8)	0.4 (0.7)	1.0 (3.2)	1.7 (2.9)	1.5 (2.8)	10.1 (2.5)
Silt	56.0–75.4	57.8–68.5	–	16.6–81.6	47.8–74.4	22.3–84.0	0.2–78.0	0.2–84.0	30.1–38.2
	67.8 (5.9)	63.5 (3.8)	–	57.0 (13.0)	58.9 (8.4)	55.7 (15.4)	41.1 (17.9)	44.3 (18.2)	33.6 (2.4)
Clay	24.4–43.9	30.4–40.9	–	12.3–83.3	23.5–52.2	10.9–77.5	21.7–99.3	10.9–99.3	51.4–61.4
	32.0 (5.9)	35.6 (3.8)	–	42.3 (13.7)	40.7 (9.0)	43.3 (16.7)	57.2 (17.2)	54.1 (17.7)	56.2 (3.0)
Silt/Clay	1.27–3.09	1.41–2.26	–	0.20–6.64	0.92–3.17	0.29–6.70	0.00–3.60	0.0–6.7	0.50–0.73
	2.21 (0.55)	1.81 (0.30)	–	1.67 (1.24)	1.58 (0.71)	1.78 (1.53)	0.88 (0.59)	1.05 (0.86)	0.60 (0.07)
C_{org}	1.96–6.46	4.82–5.47	7.36–14.72	1.27–2.55	1.08–1.86	1.48–3.90	0.42–2.96	0.42–3.90	1.18–2.40
	4.52 (1.32)	5.22 (0.27)	10.82 (2.14)	1.88 (0.42)	1.49 (0.27)	2.21 (0.70)	1.35 (0.66)	1.63 (0.68)	1.51 (0.35)
$CaCO_3$	19.82–74.16	36.18–44.03	2.22–15.03	11.85–18.04	9.77–14.51	6.60–15.30	6.49–29.54	6.49–29.54	13.13–18.26
	51.89 (16.57)	40.46 (3.36)	7.87 (4.06)	15.27 (2.01)	12.63 (1.70)	11.60 (2.85)	15.31 (5.87)	14.37 (4.71)	15.66 (1.97)
Total carbon	3.776–12.981	8.451–9.745	7.885–25.157	2.296–3.844	1.855–2.508	2.313–3.919	1.315–4.292	1.315–4.292	2.967–3.512
	9.547 (2.520)	9.264 (0.511)	14.827 (4.987)	2.825 (0.506)	2.273 (0.262)	2.751 (0.442)	2.507 (0.805)	2.591 (0.668)	3.267 (0.176)
Total nitrogen	0.075–0.422	0.300–0.338	0.463–1.696	0.030–0.105	0.032–0.050	0.043–0.172	0.000–0.116	0.000–0.172	0.034–0.044
	0.278 (0.095)	0.315 (0.018)	0.954 (0.319)	0.057 (0.024)	0.043 (0.006)	0.086 (0.035)	0.040 (0.026)	0.052 (0.031)	0.037 (0.003)
Total hydrogen	0.527–1.299	0.774–0.899	0.420–3.888	0.439–0.892	0.633–0.849	0.545–1.165	0.295–0878	0.295–1.164	0.318–0.403
	0.828 (0.190)	0.844 (0.054)	2.379 (1.056)	0.676 (0.128)	0.732 (0.083)	0.751 (0.162)	0.639 (0.135)	0.676 (0.139)	0.370 (0.027)

Values are ranges, means and standard deviations (in parenthesis) along different sedimentary units (%).

Table III. Ranges of trace metal concentrations in different sedimentary units.

Metals	Coccolith	Sapropel	Turbidites			
			Unit1	Unit2	Unit3	All
Co	0.016–0.027	0.020–0.041	0.018–0.033	0.018–0.036	0.002–0.036	0.002–0.036
Cr	0.095–0.262	0.064–0.105	0.200–0.353	0.160–0.348	0.081–0.474	0.081–0.474
Cu	0.031–0.045	0.090–0.149	0.026–0.055	0.028– 0.085	0.019–0.062	0.019–0.085
Fe	28.84–40.28	22.81–41.54	36.60–52.38	37.05–49.13	22.47–62.24	22.47–62.24
Mn	0.453–0.574	0.272–0.934	0.549–0.707	0.329–1.424	0.401–1.827	0.329–1.827
Ni	0.084–0.136	0.104–0.174	0.126–0.235	0.080–0.217	0.072–0.255	0.072–0.255
Zn	0.056–0.078	0.077–0.104	0.060–0.095	0.062–0.126	0.046–0.127	0.046–0.127

Values are in mg g^{-1}.

have an inverse relation in all samples, resulting the low quartz/feldspar ratio, which is related to petrography of the source areas (Ross et al., 1978). For example, in the coccolith varve samples, quartz is almost absent and feldspars reach their maximum. While the feldspars are dominant along unit 1, the chlorite slightly increases towards unit 3. Although along the top units the abundance of minerals shows a visible difference, they are all equal in unit 3.

Other abundant minerals identified mostly in the upper layers of the deposition are pyrite (FeS_2) and anhydrite. There is a significant relation between the increasing pyrite (FeS_2) and increasing organic carbon contents and this is related to the prevailing sulfidic conditions in the sediments (Berner, 1981; Raiswell, 1986). The high amounts of anhydrite should be formed at a low temperature from the saline solution after the cores taken. Since primary precipitation of anhydrite from seawater is improbable, it is nearly always a secondary mineral produced by the decomposition of pyrite at the surface (Deer et al., 1974).

In the western shelf samples of S2 and S8, which are all homogeneous mud deposits, the abundant mineral seems to be chlorite, followed by the same abundances of feldspars, quartz and some pyrite. Along the core S11 the most common mineral is feldspar with some garnet minerals.

The overall high smectite content in the southern Black Sea is related to the presence of volcanic rocks, which are widely distributed on the Turkish mainland (Müller and Stoffers, 1974). The smectite/illite (*S/I*) ratio of the deep sea cores AND008 and AND021 is about half of that of the others (*figure 4*), proving that the decrease in the *S/I* suggests increasing distances from the land based sources or their riverine input (Ergin et al., 1999). Lower *S/I* ratios of the samples of the Danube Delta are due to the high suspension of transported illite contents of the Danube (Stoffers and Müller, 1978).

Unit 1 clay minerals predominantly consist of smectite and illite with higher *S/I* ratios than the other units along the deep sea cores (*figure 4*). Smectite generally, shows an upward increase from the base towards the surface of the cores, which is often associated with downward increasing illite contents. Decreasing *S/I* ratios in unit 2 also indicate the changes in the paleo-climate, as a transition from a warmer climate to the present climatic conditions. Increasing smectite in the surface of the cores denotes slightly increasing alkaline, Ca and Mg rich conditions (Deer et al., 1974) as in the Black Sea.

The well developed crystals of the smectite suggest the proximity to sources (Ergin et al., 1999). So the crystallinity of smectite usually decreases from the shelf to offshore. On the western coast, since the shelf is longer than the south-eastern shelf, the crystallinities of the smectite peaks in this region are similar to those of south-eastern samples. The smectite content with higher crystallinity has only an increase between the 50–150 cm layers of GIR014, supporting the results that will be concluded from the geochemical and sedimentological analysis of the samples in this interval.

Illite is the predominant mineral determined in all samples. Its concentration along the deep sea cores is rising downwards, but in any case is less than that of S cores. The high abundances of illite in western shelf samples is most probably due to the locations of the cores being close to the Danube delta (Stoffers and Müller, 1978). Chlorite and illite are indicative of weak weathering intensities. Levels relatively rich in chlorite,

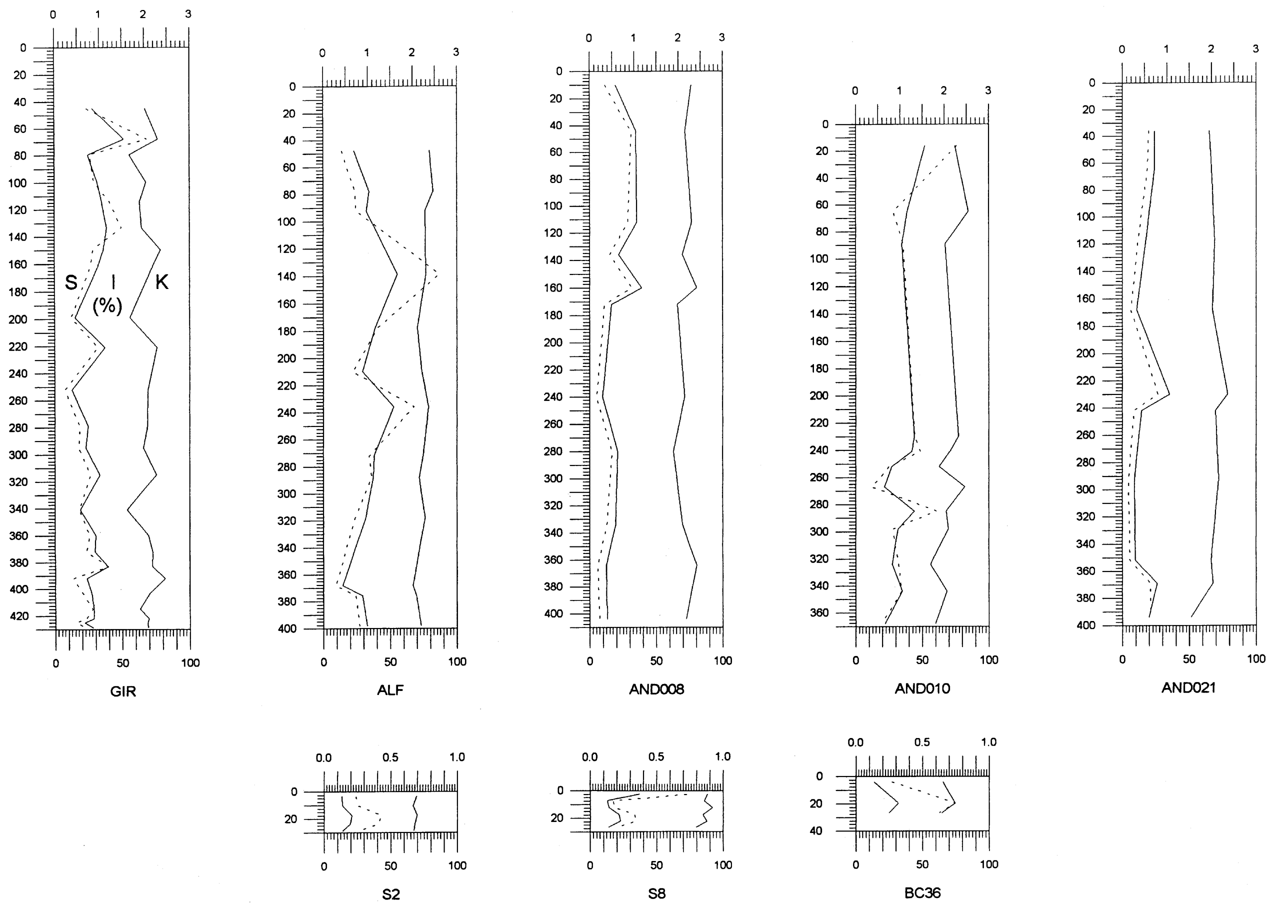

Figure 4. Smectite (*S*), illite (*I*) and kaolinite (*K*) percentages ($S + I + K = 100\%$) along the cores with bottom *X*-axis, *S/I* ratios along the cores (dashed line) with top *X*-axis.

illite as well as quartz in whole sample are interpreted as corresponding to relatively dry periods, while more humid periods lead to more intensive weathering and consequently to the dominance of clay minerals more advanced to the relative stability state, such as kaolinite, smectite is taken to indicate a climate with contrasting seasons and pronounced dry season (Singer, 1984). Grain size data indicates that illite is associated with clay size minerals while smectite is with silt.

The majority of chlorite in the kaolinite-chlorite mutual peak is verified by the second experiment carried out after heating the samples. The source of high quantities of chlorite off Turkey's coast is mainly the sediment load of the Kizilirmak River (Çağatay et al., 1987).

The visual examination of sub-samples reflect the highly terrigenous character of the Black Sea sediments (Calvert and Batchelor, 1978). The main terrigenous inputs reflecting the environmental conditions are wood particles, plant remains and seed particles. Except for the western shelf cores, plant remains are deposited throughout the deep Black Sea cores. The identification of them may give the climatic and environmental conditions. For example, the pollen amount increasing in the unit 2 sediment samples indicates the enlargement in the forest area, and consequently suggests higher precipitation in the drainage basin of rivers (Emery and Hunt, 1974). And the observed coal particles in the transition zone sediment samples of AND021 and AND008 cores, may have been left from a previous drier climatic period, which is confirmed by the first invasion of *E. huxleyi*. On the shelf areas there are contributions of shell fragments to the carbonate content in addition to the calcareous rock particles determined along all the cores. The main con-

Table IV. Average heavy metal concentrations of different types of rocks and sediments of Black Sea.

Rocks and sediments	Co	Cr	Cu	Fe	Mn	Ni	Zn	Reference
Igneous, rock average	0.0250	0.100	0.055	50.0	0.950	0.075	0.070	Turekian and Wedepohl, 1961
Limestone, average	0.0001	0.011	0.004	3.80	1.100	0.020	0.020	Turekian and Wedepohl, 1961
Sandstone, average	0.0003	0.035	0.005	9.80	0.050	0.002	0.016	Turekian and Wedepohl, 1961
Shale, average	0.0200	0.100	0.050	47.0	0.850	0.080	0.090	Krauskopf, 1985
Southern Black Sea, surface sediments, average	0.0110	0.110	0.049	32.8	0.570	0.077	0.087	Yücesoy and Ergin, 1992
Entire Black Sea, average	0.0260	0.143	0.038	38.6	0.818	0.082	0.098	Hirst, 1974
Southern Black Sea, core sediments, average	0.0220	0.093	0.036	35.2	0.722	0.051	–	Çağatay et al., 1987
Southern Black Sea, surface sediments, average	0.0230	0.093	0.033	–	0.571	0.048	–	Çağatay et al., 1987
Coccoliths, average	0.0213	0.159	0.038	35.22	0.536	0.110	0.069	this study
Sapropels, average	0.0279	0.087	0.121	31.92	0.506	0.131	0.087	this study
Turbidites, average	0.0216	0.194	0.041	43.99	0.781	0.129	0.080	this study
Unit1 turbidites, average	0.0230	0.240	0.041	45.84	0.635	0.170	0.080	this study
Unit2 turbidites, average	0.0243	0.202	0.044	45.00	0.775	0.136	0.084	this study
Unit3 turbidites, average	0.0208	0.184	0.040	43.78	0.803	0.120	0.079	this study

Values are in mg g^{-1}.

stituents of these shells are generally foraminifers, gastropods, ostracods and pelecipods. The reason for the abundance of foraminifers in this region is the high production resulting from the high nutrient input from the Danube River. At the bottom of the unit 2, at the boundary between unit 2 and unit 3, a thin aragonite layer was observed. The anoxic depositions are also characterised by preserved vertebrate remains (Lyons, 1991). For example, in coccolith layers of BC36, the fish *Syngnathus Schmidti* (Black Sea pelagic pipefish) (Popov, 1928) is quite abundant.

3.4. Geochemical properties of the Black Sea sediments

The variations in geochemical parameters in the Black Sea sediments documents the responsiveness of the geochemical conditions in the basin to environmental and climatic changes. The range and average values of these parameters in each unit are given in *tables II, III and IV*.

In general $CaCO_3$ percentage in turbidite layers of a core vary between 6.49 and 29.54% with an average of 14.37% in the south-eastern Black Sea (*tables II and III*). The equal carbonate contents of unit 1 and unit 3 turbiditic deposits may indicate the constant environmental conditions on the Black Sea mainland since the post-glacial sea level rise. The lower carbonate concentration in unit 2 can be explained by the decrease in coarser material in this unit since terrigenous carbonate rock particles are abundant in coarser sedimentary fractions. Microscopic studies supported that in the Black Sea not only the biogenic calcareous remains, which are mainly composed of coccoliths of *E. huxleyi*, are a source of carbonate but also the terrigenous calcareous rock materials transported to the sea by the rivers. The carbonate percentages of unit 1 coccolith varve layers are 51.89% and 40.46% in both parts of the Black Sea, as the south-eastern and western respectively (*table II*). The relatively low carbonate value in the shelf cores can be explained by the dilution effect of the high amounts of terrigenous carbonate-free material transported by Danube river. Since the high concentration of organic matter and carbonates in the sediments can be described by the slow rate of accumulation in the halistatic areas, such a dilution effect is strongest along the periphery of the basin where the production of phytoplankton is high (Strakhov, 1954). The carbonate analysis indicates that the intensity of marine carbonate production during deposition of unit 1 was nearly six times greater than the production during the deposition of unit 2.

The organic carbon (C_{org}) concentration of deep Black Sea sediment changes between 0–15% according to the core locations, anoxicity of the marine environment, terrigenous input to the sea and the level of the primary productivity (*table II*). In unit 3 sediments which were deposited when the Black Sea was a fresh water lake, the C_{org} concentration is as low as 1.35% in average (*table*

II). After this period starting from the Mediterranean water inflow to the Black Sea, organic matter preservation began due to arising anoxicity. While the concentration of C_{org} in turbiditic layers of unit 2 has a small increase to 2.21%, C_{org} content of sapropel varve deposits reach 10.82% on average (*table II*). The increase in concentration of C_{org} of turbiditic sediments in unit 2 relative to that in unit 3 indicates that approximately 50% of the sedimented organic matter was also mineralised after deposition before establishment of anoxic bottom conditions. In addition to sapropels, the other main constituents of organic matter accumulated in unit 2 are abundant terrigenous wood and plant remains. Concentration of C_{org} in coccolith varve deposits of western shelf and the deep Black Sea cores are 5.22 and 4.52% respectively (*table II*). The low organic carbon values of unit 1 probably are due to the photosynthetic production of coccoliths and relatively higher bulk sedimentation rate whereas the high organic carbon values of unit 2 probably resulted from high marine production of organic matter and low inorganic sedimentation rate under anoxic conditions (Shimkus and Trimonis, 1974). Total carbon (*TC*), total hydrogen (*TH*), and total nitrogen (*TN*) values, all act together (*tables II and III*), increasing and decreasing in the same units. The ranges especially of *TC* and *TN* clearly represent the boundary between the units (*table II*). They are maxima in unit 2 sapropels due to the high organic carbon content (14.827%, 0.954% and 2.379% in averages *TC*, *TN*, and *TH* respectively) and lowest in unit 3 turbidites, as expected due to oxicity and the non preservation of the organic matter in the Black Sea (2.507%, 0.040% and 0.639% in averages *TC*, *TN*, and *TH* respectively) (*table II*).

The heavy metal concentrations were measured along ALF004 and GIR014 cores. The results were discussed assuming that they both together are a core representing all different depositions. Unit 1 and unit 2 were discussed regarding ALF004 and unit 3 was discussed according to the results of GIR sample analyses. All the average metal concentrations in each unit and in different type of sediments are given in *table IV*. The properties of metals along the deep Black Sea cores are explained below in order of abundance.

3.4.1. Iron

Fe(III) ion concentration in the Late Quaternary sediments of south-eastern Black Sea, changes between 22.47-62.24 mg g^{-1} (*table III*). In coccolith and sapropel varve layers the concentration of iron decreases since their ion capture capability is lower than the sedimentary minerals and thus increasing C_{org} and carbonate concentrations dilute the concentration of Fe(III). There is an abrupt decrease in Fe(III) concentration between 50–150 cm depth in GIR014 which totally represents the turbiditic sedimentation of unit 3. It is the exact place where carbonate content and also sand fraction, which is a less promising size for retaining metals, have their highest values. The abrupt changes in geochemical, sedimentological and also mineralogical parameters in this depth interval may indicate the changes started with the Mediterranean water inflow and continue till the establishment of anoxic bottom water.

3.4.2. Manganese

The concentration of Mn in Late Holocene sediments of the Black Sea, is significantly correlated with sedimentary units (*table III*). The average concentration of Mn decreases from 0.803 to 0.635 mg g^{-1} whilst going up to the surface (*table IV*). Elevated Mn content of unit 3 indicates deposition of manganese as MnO through an oxic water column, whereas relatively low Mn contents of other units imply anoxic bottom waters during their deposition. The high and quite similar Mn values with respect to coccolith and sapropel samples in turbiditic sediments shows that the major part of Mn is supplied from land and from the same source (*table IV*).

3.4.3. Chromium

The concentration of chromium changes from 0.081 to 0.474 mg g^{-1} increasing towards the upper layers in turbidites with an average of 0.194 mg g^{-1} (*tables III and IV*). The decrease in the range of abundance of Cr in coccolith and sapropel varve layers indicate that both organic and inorganic carbon and Cr concentrations are inversely proportional, i.e., increasing amount of carbon dilutes also the Cr concentration. There is no significant relation with grain size and Cr content (*figures 5 and 6*).

3.4.4. Nickel

Ni concentration of turbidites along the Black Sea cores decreases towards the bottom from 0.170 mg g^{-1} to 0.120 mg g^{-1} on average (*table IV*). In coccolith and sapropel depositions, the averages decrease to 0.110 and 0.131 mg g^{-1} respectively because of the dilution effect of Ni-free carbonate and organic matter (*table IV*). The general source of Ni is material derived from ultramafic/

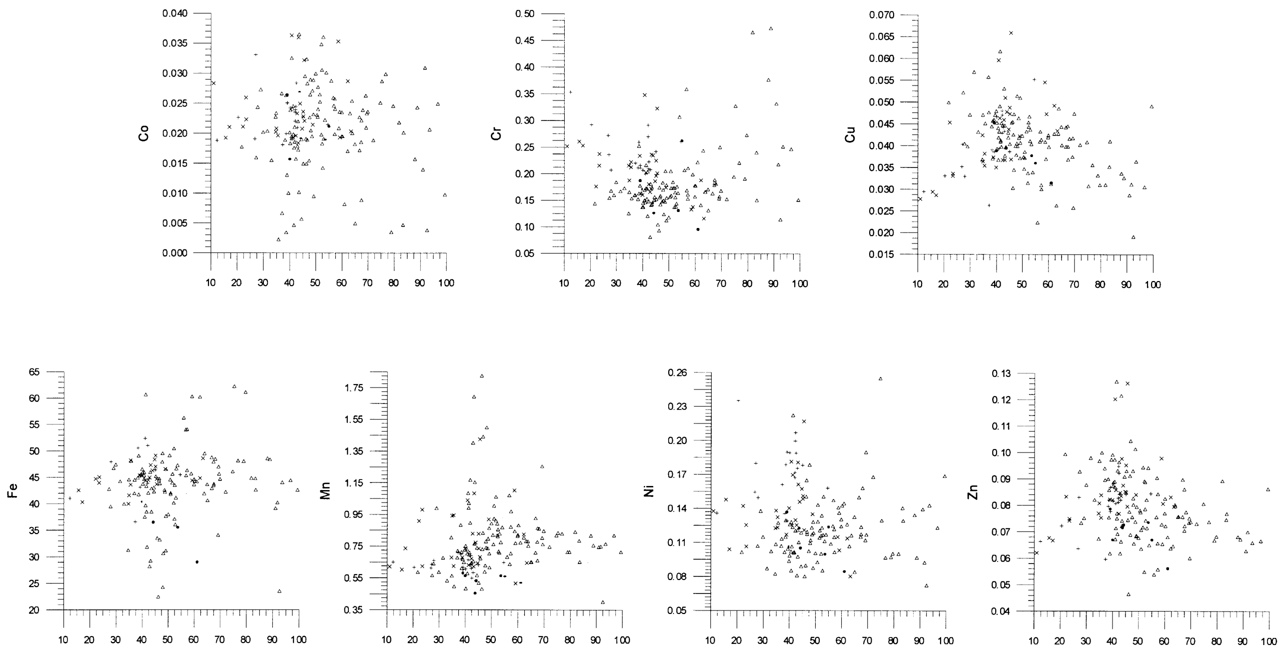

Figure 5. Changes in heavy metal distribution (mg g^{-1}) with respect to clay content (%) of the sediments; unit 1 (+), unit 2 (x), unit 3 (△) turbidites and coccoliths (·).

mafic rocks, carried by the Kizilirmak and Yesilirmak from the coastal hinterland.

3.4.5. *Zinc*

Zn contents of deep Black Sea sediments have an average of 0.080 mg g^{-1} along the core (*table IV*). The concentration of Zn decreases in coccolithic varve deposits whereas it increases in sapropels. This must be due to the change in carbonate contents of the samples. The dependence of Zn on grain size is similar to Cu as it is increasing in silt sized, carbonate free materials. This can be explained by the fact that fine-grained sediments tend to have relatively high metal contents, due in part to the high specific surface area of the smaller particles (*figures 5 and 6*); this enrichment is mainly due to surface adsorption and ionic attraction (Buckley and Cranston, 1991). Silt fractions unlike clay, are apparently much more favoured by the studies on heavy metal contents (Ergin, 1990).

3.4.6. *Copper*

The concentration of Cu changes between 0.019–0.062 mg g^{-1} with an average of 0.041 mg g^{-1} along turbidites and coccolith varves of deep Black Sea cores (*tables III and IV*). In sapropel varves the enrichment of Cu concentration (*table IV*) to 0.121 mg g^{-1} on average, supports the fact that in the reducing conditions of the Black Sea, Cu concentration is influenced by the organic matter (Volkov and Fomina, 1974). Comparing with the grain size, Cu content shows an increase with increasing silt size in GIR014 sub-samples (*figures 5 and 6*). The inverse relation in ALF004 core sub-samples is due to the increasing carbonate content of silt fraction and accordingly due to the dilution effect of carbonate. The dilution of Cu towards the upper part can also be explained by the decreasing marine productional deposition towards the bottom of the core. The important occurrences of Cu are from the drainage area of the Yesilirmak, which contain ophiolitic materials that are related to hydrothermal deposits.

3.4.7. *Cobalt*

Along the unit 3, the range of Co concentration is between 0.002 mg g^{-1} and 0.036 mg g^{-1} (*table III*), increasing with decreasing depth and not depending on grain size (*table IV, figures 5 and 6*). The concentration of Co in the anoxic deposition is slightly less than that in

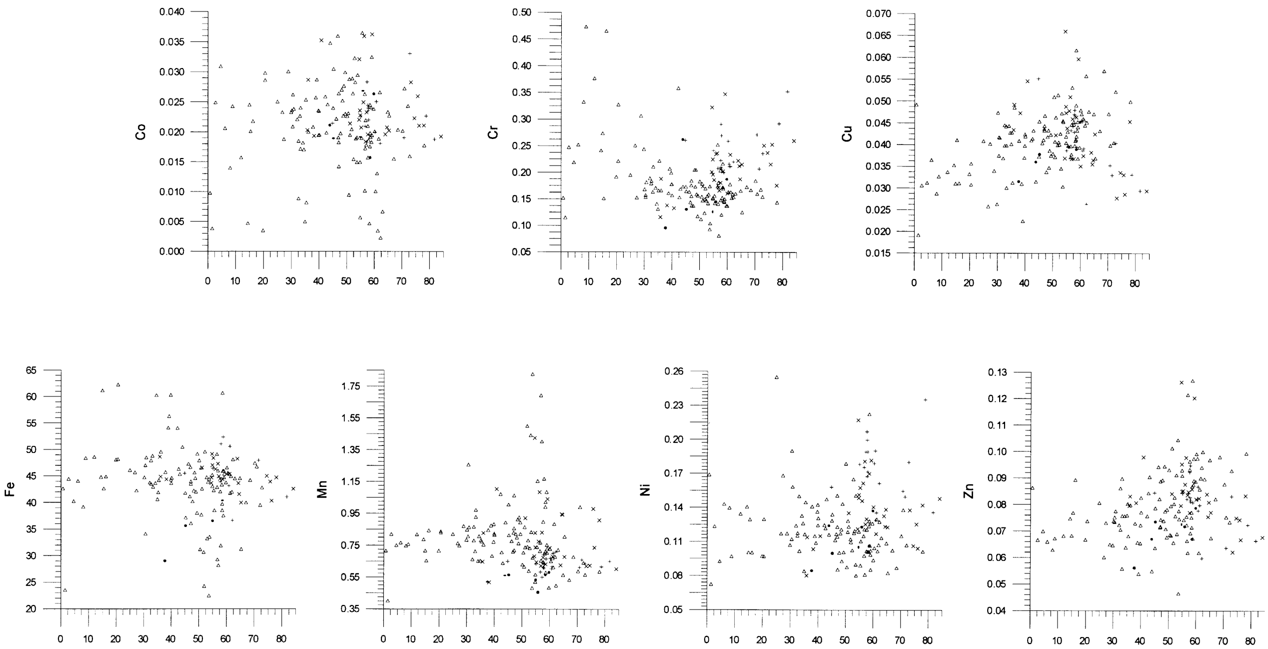

Figure 6. Changes in heavy metal distribution (mg g^{-1}) with respect to silt content (%) of the sediments; unit1 (+), unit2 (x), unit 3 (△) turbidites and coccoliths (·).

oxic depositions and approximately constant on average along both unit 1 and 2 (*table III*).

The heavy metal concentrations along the cores reflect the geological source rock on the mainland. Comparing average metal contents of samples to those of source rocks (*table IV*), mainly with ignious rock which is abundant all around the south-eastern Black Sea (Atalay, 1992), all the metals, Fe, Mn, Zn, Cu, Co, have constant amounts in turbiditic depositions of the three units, indicating the same source rock during the Late Holocene sedimentation. Upward enrichment of Cr and Ni can be explained as predominance of a river source caused by changes in precipitation in the drainage area of the rivers draining into the Black Sea or the change in the distribution of the terrigenous matter in the Black Sea (Hay et al., 1991). The source of the enriched metals are mainly the volcanics and ultramafics occurring on the north-eastern Black Sea coast. The plot of heavy metals against each other (*figure 7*) verify that trace elements can be concentrated in iron and manganese oxyhydroxides, as all Zn, Cu, Co, Cr, distributions are controlled by Fe and Mn, and Fe and Mn are associated together in samples. The quite positive behaviour of Cu and Zn indicates their mutual terrigenous sources.

4. CONCLUSIONS

Different gravity and box core samples taken from the south-eastern and western Black Sea were studied with respect to geochemical, sedimentological and mineralogical properties to explain sedimentation processes in this regions, to compare recent deep and shelf sedimentations and to obtain some information indicating the paleoenvironmental conditions of the Black Sea. The deep Black Sea gravity cores represent all the different sedimentary units, indicating the environmental changes during the last 10 000 years. The main change in deposition started with the saline Mediterranean water inflow into the Black Sea, followed by anoxic, increasing saline and also alkaline and a changing environment from lake to marine conditions resulting in different sedimentary units. The previous sedimentary deposits, unit 3, the neoeuxinian deposition, shows the properties of a fully oxic, fresh water lake with light coloured sediments. The

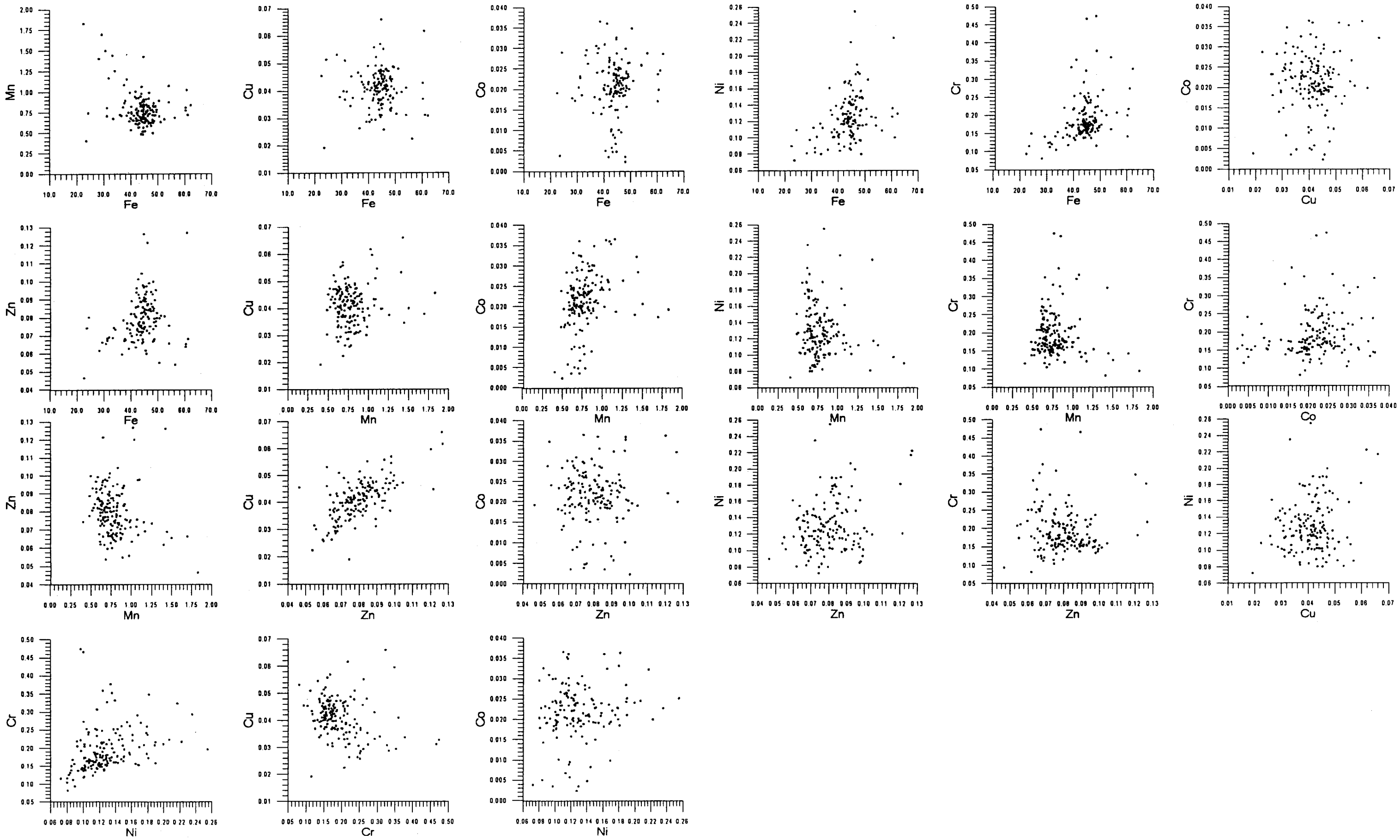

Figure 7. Changes in metals with respect to each other (all in mg g^{-1}).

unit is described by its relatively low organic carbon content, high terrigenous carbonate content in the coarse fraction together with graded bedded turbidites and coarser grain deposits with higher clay contents than other units. Deposition of unit 2 was synchronous with anoxic conditions developing at the bottom. Because of the anoxicity organic matter was better preserved during the deposition of this unit. The organic matter, sapropels (10.82% C_{org}), were deposited as annual varve couples with terrigenous material. unit 2 has very low amounts of sand sized material. Silt towards the surface of the core and clay increases with depth. The general upward increase in fine grained (silt and clay) and downward increase in coarse grained sediments within the cores are considered to reflect changes from high to low energy depositional conditions which lasted till the Late Holocene high stands of the sea level. The top unit 1 is the present/recent depositional layer. The main property of this unit is its high marine carbonate content (51.89% $CaCO_3$), due to the deposition of coccoliths of phytoplankton *E. huxleyi*. The unit is also deposited in the form of varves together with the terrigenous material. Unit 1 is low in organic carbon with abundant silt size material both due to the high production and deposition of the coccoliths of *E. huxleyi*. The recent sediments of the western shelf have the same properties as southeastern one, with lower amounts of carbonates (40.46% $CaCO_3$) and higher amounts of organic carbon contents due to the high amounts of terrigenous organic material transported by the Danube River. Heavy metal distributions along the deep Black Sea cores give information on the surrounding mineral sources and changes in supply rates. Results reveal that Late Holocene changes are due to the high organic or high carbonate contents of the sapropel and coccolith varve deposits, thus, their dilution affect on the metal concentration. Comparing the average metal content of the sediments with the average of surrounding rocks (especially ignious rocks analysed by Turekian and Wedepohl, 1961), only the high amount of Cr and Ni, increasing in turbiditic deposition towards the surface is significant. This difference suggests the enrichment of these metals in the region due to the change in the courses of the rivers as well as the abundant igneous rocks along the Black Sea coast. The climatic and environmental changes have a significant effect on the mineral types, which contribute to the lithogenic parts of the marine sediments. The results of the x-ray diffractions of the clay minerals denotes that illite is the abundant mineral in all sediment samples of the southern and western Black Sea. The decrease in illite with increasing smectite, as a result increasing *S/I* ratio from Neoeuxinian to recent deposits indicate the drying of climatic conditions since the Early Holocene. The high illite content of the western Black Sea results from the material carried by the Danube River from the European lowlands, whereas the smectite content in the southern Black Sea is related to the presence of volcanic rocks which are widely distributed on the Turkish mainland. The mutual peak of chlorite and kaolinite also exist as high as smectite in all samples. According to the petrographic analyses supported by the whole sample mineralogy (XRD), minerals such as quartz, pyrite and micas (biotite and muscovite) are determined to be the abundant minerals in sand sizes, followed by feldspars and chlorite in bulk samples. As preserved organic matter, pyrite formation also indicates the prevailing anoxic conditions. The main organic parts of the terrestrial input indicating the surrounding environmental conditions composed of the wood and plant remains, pollens and coal particles. The high amounts of plant-like materials also support the widespread forests on the mainland indicating more humid climatic conditions around the southern Black Sea coast during the unit 2 deposition. The high amounts of undissolved skeletal remains of organisms are abundant in the coccolith and sapropel varve deposits indicating the effect of the new depositional conditions. The distribution of these biogenic sediments are controlled by production, reduction and dilution in the marine environment.

The gravity cores that we used in this study were taken from TPAO and Dokuz Eylül University archives. We are grateful to all academic and technical staff of METU–Institute of Marine Sciences, and of the Soil Science Department of Çukurova University, Prof. Dr Alec F. Gaines and Prof. Dr Mustafa Ergin for their valuable assistance and guideness.

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