![USGS logo](science for a changing world)

Geochemical Characteristics of Holocene Laminated Sapropel (Unit II) and Underlying Lacustrine Unit III in the Black Sea

Open-File Report 2010–1323

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2011

Cover photograph: Taking a gravity core of Black Sea sediments.

Contents

Figures

Tables

Geochemical Characteristics of Holocene Laminated Sapropel (Unit II) and Underlying Lacustrine Unit III in the Black Sea

By Walter E. Dean[1] and Michael A. Arthur[2]

Abstract

Leg 1 of the 1988 *R/V Knorr* expeditions to the Black Sea recovered 90 gravity and box cores. The longest recovery by gravity cores was about 3 meters, with an average of about 2.5 meters, recovering all of the Holocene and upper Pleistocene sections in the Black Sea. During the latest Pleistocene glaciation, sea level dropped below the 35-meters-deep Bosporus outlet sill of the Black Sea. Therefore throughout most of its history the Black Sea was a lake, and most of its sediments are lacustrine.

The oldest sediments recovered (older than 8,000 calendar years) consist of massive to coarsely banded lacustrine calcareous clay designated as lithologic Unit III, generally containing less than 1 percent organic carbon (OC). The base of overlying Unit II marks the first incursion of Mediterranean seawater into the Black Sea, and the onset of bottom-water anoxia about 7,900 calendar years. Unit II contains as much as 15 percent OC in cores from the deepest part of the Black Sea (2,200 meters). The calcium carbonate ($CaCO_3$) remains of the coccolith *Emiliania huxleyi* form the distinctive white laminae of overlying Unit I.

The composition of Unit III and Unit II sediments are quite different, reflecting different terrigenous clastic sources and increased contributions from hydrogenous and biogenic components in anoxic Unit II sapropel. In Unit II, positive covariance between OC and three trace elements commonly concentrated in OC-rich sediments where sulfate reduction has occurred (molybdenum, nickel, and vanadium) and a nutrient (phosphorus) suggest a large marine source for these elements although nickel and vanadium also have a large terrigenous clastic source. The marine sources may be biogenic or hydrogenous. A large biogenic source is also suggested for copper and cobalt. Because abundant pyrite forms in the water column and sediments of the Black Sea, we expected to find a large hydrogenous iron component, but a strong covariance of iron with aluminum suggests that the dominant source of iron is from terrigenous clastic material. Most elements in lacustrine Unit III sediments have a strong covariance with Al indicating a very dominant terrigenous source. In Unit II, some elements, especially nickel, molybdenum, vanadium, and zinc, do not correlate with aluminum and have concentrations well above terrigenous clastic material, indicating a marine source.

---

[1]U.S. Geological Survey, MS 980 Federal Center, Denver, CO 80225.

[2]Department of Geosciences, Pennsylvania State University, University Park, PA 16802.

Introduction and Background

The Black Sea is a tectonically restricted basin with an area of about 423,000 square kilometers. Its only connection to the rest of the world ocean is through the Bosporus Strait, to the Sea of Marmara, and through the Dardanelles Strait to the Aegean Sea (fig. 1). The sill depth of the Bosporus is presently about 35 m (Scholten, 1974), and it is this sill that has effectively isolated the Black Sea and limited the influx of relatively warm, saline Mediterranean surface waters to the basin through the bottom waters of the Bosporus. The Black Sea has a positive water balance (Demaison and Moore, 1980), receiving 350 cubic kilometers of freshwater from a total drainage area of 2.2 million square meters including the Danube River drainage system to the west, the Dniester, Dnieper, Bug, Kuban, and Don Rivers to the north, and lesser amounts from rivers draining the Caucasus and Anatolian highlands to the east and south (Shimkus and Trimonis, 1974). Therefore, the Black Sea exports water of low salinity to the Mediterranean through the surface of the Bosporus. The bottom waters of the Black Sea are anoxic because of the strong vertical salinity stratification as a result of an excess of precipitation and river runoff over evaporation (Murray and others 1991). During the last Pleistocene glaciation, when sea level was below the sill at the Bosporus, freshwater could not exit, and the Black Sea was a large freshwater lake. The first influx of Mediterranean water into the Black Sea lake occurred about 7700 calendar years ago (cal. yr; 7.7 cal ka) (Jones and Gagnon, 1994; Arthur and Dean, 1998). Therefore, most of the Quaternary sediments on the bottom of the Black Sea are lacustrine.
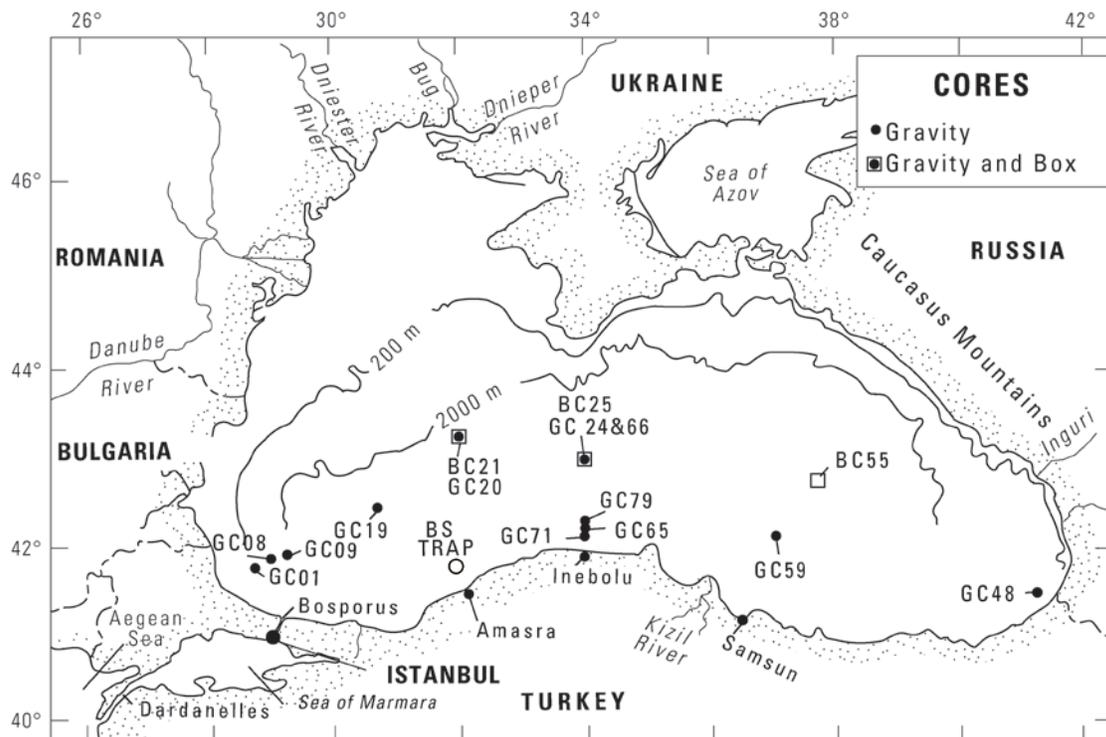

Figure 1. Map of the Black Sea and vicinity showing bathymetry and locations of key box cores (BC), gravity cores (GC), and a sediment trap (BS). Modified from Hanjo and others, 1988.

The water column of the Black Sea presently is salinity (density) stratified, with less saline surface waters (salinities of 18 to 20 parts per thousand) overlying more saline deep waters (about 22 parts per thousand), which are ultimately derived from the Mediterranean (35 to 39 parts per thousand) but have characteristics indicating mixing with Black Sea surface water (Grasshoff, 1975; Murray and others, 1991). The pronounced halocline and pycnocline occur at about 75 m in the center of the basin and at about 210 m at the margins (Murray and others, 1991). This salinity interface marks the transition between oxic surface water and anoxic deep water that persists to the maximum depth of about 2250 m (Brewer and Spencer, 1974; Grasshoff, 1975). The oxic/anoxic interface (23 μM H_2S) is at about 150 m in the center of the western basin and about 250 m on the margins. Near-zero concentrations of oxygen and sulfide co-exist in a suboxic zone (Codispodi and others, 1991; Lewis and Landing, 1991; Murray and others, 1991).

The late Holocene sediments in the Black Sea consist of two laminated organic-carbon-rich lithologic units (Ross and Degens, 1974): an upper laminated marl with distinctive white laminae of the $CaCO_3$-secreting coccolith *Emiliania huxleyi* (Unit 1), and a lower, finely laminated sapropel (Unit 2). We assume, as did Degens and Ross (1972) and Degens and others (1980), that the laminations in both units are annual (that is, varves) (see discussion by Arthur and others, 1994). Unit 2 is underlain by a sequence of bioturbated to coarsely banded lacustrine clays and marls that contain less than one percent total organic carbon (OC) (Unit 3 of Ross and Degens, 1974). Unit 3 is equivalent to the terrigenous lacustrine muds recovered in Deep Sea Drilling Project (DSDP) Leg 42B (Unit 3 in Hole 379; Unit Ic in Hole 380; Ross, 1978; Hsü, 1978). Stratigraphic studies of Black Sea sediments recovered by coring of the top few meters of sediment (Holocene to upper Pleistocene; Degens and Ross, 1972; this study) and DSDP drilling of the upper 1000 m (Holocene to upper Miocene; Neprochnov and Ross, 1978) have been hampered by inconsistencies between varve and ^{14}C chronologies in the upper part of the section (see discussion by Arthur and others, 1994) and shortage of definitive paleontological markers throughout the section (see discussion by Ross, 1978).

Unit 2 marks the onset of anoxia in the Black Sea that followed postglacial rise in sea level, influx of marine water from the Aegean Sea, and stratification of water masses of the Black Sea (Ross and Degens, 1974; Jones and Gagnon, 1994). This anoxia eliminated benthic organisms and allowed the preservation of laminated sediments in response to the strong seasonal pulses of sediment components in the Black Sea. Unit 2 records the evolution of anoxia, as marine waters from the Aegean poured into the Black Sea increasing the thickness and salinity of the anoxic bottom-water mass (discussed in greater detail herein). The salinity of the surface waters of the Black Sea also increased slowly until they reached the lower limit for production of *E. huxleyi*, reported to be about 11‰ (Bukry, 1974), about 2,000 calendar years (Arthur and others, 1994; Arthur and Dean, 1998).

Preliminary results of geochemical characteristics of Unit 1 have been reported elsewhere (Hay and others, 1991; Arthur and others, 1994; Arthur and Dean, 1998). The purpose of this report is to describe the geochemical characteristics of the upper part of lacustrine Unit 3 and the transition to marine conditions recorded in the laminated sapropels of Unit 2. In particular, we examine the physical and geochemical evidence that documents the evolution of anoxia in the bottom waters of the Black Sea and the sources of major and trace elements in the sediments of Units 2 and 3.

In any study of lithologic Units 2 and 3 in the Black Sea, one must keep in mind that they were deposited when the Black Sea was a freshwater lake (Unit 3) or transitioning into a saline lake (Unit 2). With an area of 423,000 square kilometers and a maximum depth of 2200 m, the Black Sea dwarfs all present freshwater lakes, including the Caspian Sea (table 1). The basins of both the Black and Caspian Seas probably date back to the Cretaceous as remnants of the Tethys Sea (Neprochnov and Ross, 1978).

Table 1. Morphometry of the Black Sea and other large Lakes.

[km^2, square kilometer; km^3, cubic kilometer; m, meter]

Name	Area (km^2)	Volume (km^3)	Mean depth (m)	Maximum depth (m)
Black Sea	423,000	520,000	na	2,200
Caspian	436,400	79,319	182	946
Baikal	31,500	23,000	730	1,620
Tanganyika	34,000	18,940	572	1,470
Superior	83,300	12,000	145	307

The thickness of the sedimentary section under the Black Sea is unknown but may be as much as 16 kilometers thick (Neprochnov and Ross, 1978). Influx from the Mediterranean Sea through the Bosporus Strait presently represents only 32% of the influx; the rest comes from rivers, especially the Danube (36% of total annual influx), Dnieper (10%), and Don (5%) (Shimkus and Trimonis, 1974). Turkish rivers contribute only about 4.5% of the total influx to the Black Sea. The Danube drains half of Europe, a fact emphasized by the recent completion of the Gabcikovo hydroelectric canal complex connecting the Danube with the Rhine and Main Rivers that drain the other half of Europe, flowing into the North Sea. Any climatic or other environmental change over most of eastern Europe and the southern part of the former Soviet Union will be felt by the Black Sea and recorded in its sediments.

Methods

Coring and Sediment Processing

Leg 1 of the 1988 *R/V Knorr* expeditions to the Black Sea (Honjo and others, 1988) recovered 28 box cores that provide undisturbed, laminated sequences of late Holocene sediment from the southern half of the Black Sea. A gravity core was attempted at most stations occupied during the cruise for sediment and water-column work. The gravity corer used a standard stainless-steel core cutter attached directly to a 5-m-long section of 4-in (10.2-cm) diameter, thick-walled PVC water-well casing. The core barrel was attached to a 167-kg weight stand, and the entire rig lowered at a winch speed of about 125 m/min at penetration. Average recovery of 62 gravity cores was about 2.5 m. Cores were recovered in a vertical position, the overlying water was drained off, and the PVC core barrel was cut and capped before lowering to a horizontal position so that core tops were preserved. Cores were cut into 1.0- to 1.5-m sections, capped, sealed, labeled, and stored vertically at 9°C in a refrigerated van. Due to time limitations and lack of

facilities, only two gravity cores were opened on board. These cores were sectioned into 50-cm lengths and extruded with a fixed piston into presplit sections of 4-in (10.2-cm) PVC pipe. After the presplit halves were separated, one half was used for pore-water squeezing and the other half was photographed, described, and saved as an archive. Additional box and gravity-core sections were split longitudinally at Woods Hole into working and archive halves. The archive halves of two gravity cores were shipped to the University of Rhode Island for magnetic secular variation studies (Arthur and others, 1994). Working halves of box and gravity cores were sampled for geochemical analyses at Woods Hole Oceanogaphic Institution. This paper discusses results from two key box cores and 11 gravity cores.

Age Model

Dating of Unit I was by 32 accelerometer mass spectrometry (AMS) radiocarbon dates and varve counts on sediments from subcores of box cores (Arthur and others, 1994; Jones and Gagnon, 1994; Arthur and Dean, 1998). The unit I/II and II/III boundaries in six gravity cores were dated by AMS (Jones and Gagnon, 1994). A Santorini volcanic ash layer, dated at 3350±75 calendar years, was identified in two gravity cores (Guichard and others, 1993). Finally, geomagnetic secular variation events reflected in inclination and declination data from two cores provide datums that allow us to assign ages to points in Unit II (Arthur and others, 1994; Arthur and Dean, 1998). All calibrated ages are expressed in thousands of calendar years before present (cal. ka BP), where "present" is AD 1950, and ranges of ages are expressed in thousands of years (ky).

Carbon Analyses

Concentrations of total carbon (TC) and inorganic carbon (IC) in samples from two box cores and 11 gravity cores were determined by coulometric titration of CO_2 following extraction from the sediment by combustion at 950°C and acid volatilization, respectively (Engleman and others, 1985), in USGS laboratories, Denver, CO. Weight percent IC was converted to weight percent calcium carbonate ($CaCO_3$) by dividing by 0.12, the fraction of carbon in $CaCO_3$. Organic carbon (OC) was determined by difference between TC and IC. The accuracy and precision for both TC and IC, determined from hundreds of replicate standards (reagent-grade $CaCO_3$ and a sample of Cretaceous black shale), usually are better than 0.10 weight percent. Results of analyses of box-core samples are discussed in Arthur and others (1994).

Inorganic Geochemical Analyses

Splits of samples from the 11 gravity cores used for carbon analyses were analyzed for 30 major and trace elements by induction-coupled, argon plasma atomic emission spectrometry (ICP-AES; Baedecker, 1987). The samples were oven dried at 90° C and ground in a ceramic mill to pass a 100-mesh sieve. The precision, determined by analyzing rock standards and duplicate sediment samples, is usually better than 10%. Only selected major and trace elements from six gravity cores will be discussed in this paper, but other elements will be mentioned in context of those selected (for example, many elements are associated only with the terrigenous clastic fraction). Complete datasets are available through the National Oceanic and Atmospheric Administration's National Climatic Data Center:

Carbonate and Organic Carbon Stratigraphies—Definition of Lithologic Units

The $CaCO_3$ and OC contents of box and gravity cores can be used to clearly define the lithologic units in Holocene Black Sea sediments (Arthur and Dean, 1998). We place the contact between the upper laminated coccolith marl (Unit 1 of Ross and Degens, 1974) and a lower, finely laminated sapropel (Unit 2 of Ross and Degens, 1974) at the first occurrence of white laminae containing abundant $CaCO_3$ remains of *E. huxleyi* (fig. 2). The first invasion of *E. huxleyi* produced a pulse of carbonate sedimentation (fig. 2) that only lasted long enough (about 50 varves) to accumulate about 1 cm of $CaCO_3$-rich sediment before salinity apparently decreased to levels below which *E. huxleyi* could calcify (11‰), and sedimentation reverted back to deposition of another 5 cm of $CaCO_3$-poor sapropel typical of Unit 2 (transition sapropel; fig. 2), after which *E. huxleyi* became permanently established in the Black Sea (fig. 2). This position of the Unit 1/2 contact differs from that of Ross and Degens (1974), who placed the Unit 1/2 boundary at the top of the transition sapropel (see discussions in Hay and others, 1991 and Arthur and others, 1994). We will therefore use Units I and II to distinguish our units from those of Ross and Degens (1974).
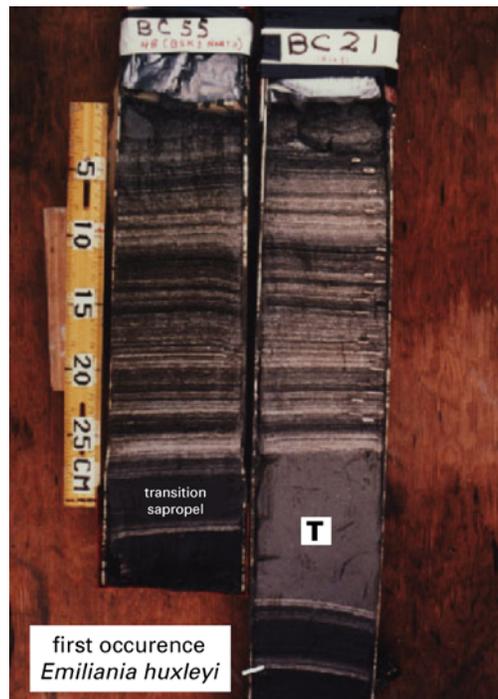

Figure 2. Photographs of subcores of box cores 21 and 55 showing all of Unit I and the top of Unit II. In BC21 a turbidite (T) interrupted deposition of the coccolith varves. The Unit I/II boundary is defined as the first occurrence of the calcareous remains of the coccolith *Emiliania huxleyi*.

Unit I, as defined herein, has an average thickness of about 30 cm below about 2,000 m in the Black Sea (fig. 1), and contains 1-5% OC and 10-75% $CaCO_3$ that consists almost entirely of remains of the coccolith *E. huxleyi,* and a remainder that consists mostly of detrital clay (Arthur and others, 1994). Both Unit I and Unit II are sapropels by definition, that is, high concentrations of algal organic matter (>2% OC) accumulating under an anoxic water column (Tyson, 1987). The dark-light laminations in Unit I (fig. 2) average about 0.2 mm thick and consist of white, coccolith-rich material and dark organic- and clay-rich material. As illustrated in figure 2, individual laminations can be correlated over 1000 km across the floor of the Black Sea. Such long distance covariance was unexpected because of interregional differences in the influx of terrigenous material and coccolith productivity. However, the fact that lamina thicknesses are so uniform indicates that depositional processes are extremely uniform throughout the Black Sea.

Unit II consists of about 50 cm of finely laminated olive-gray to black sapropel in the deep basins (for example, cores GC20, GC19, and GC66, fig. 3), but thickens to 100 cm or more in shallower water (for example, cores GC01, G59, and GC71, fig. 3). Unit II becomes lighter in color in shallow water due to a much higher accumulation rate of terrigenous clastic material that makes up the bulk of Unit II. In addition to terrigenous clastic material, Unit II contains 1-20% OC and 5-15% $CaCO_3$ (fig. 4; Arthur and Dean, 1998). The contents of the latter two components are highest in the deep basins and become less in shallower water due to dilution with terrigenous clastic material. The organic-clastic laminae couplets in Unit II average about 0.12 mm thick. Arthur and Dean (1998) subdivided Unit II into an upper subunit IIa and a lower subunit IIb on the basis of the higher organic content and darker color of subunit IIb (fig. 4).
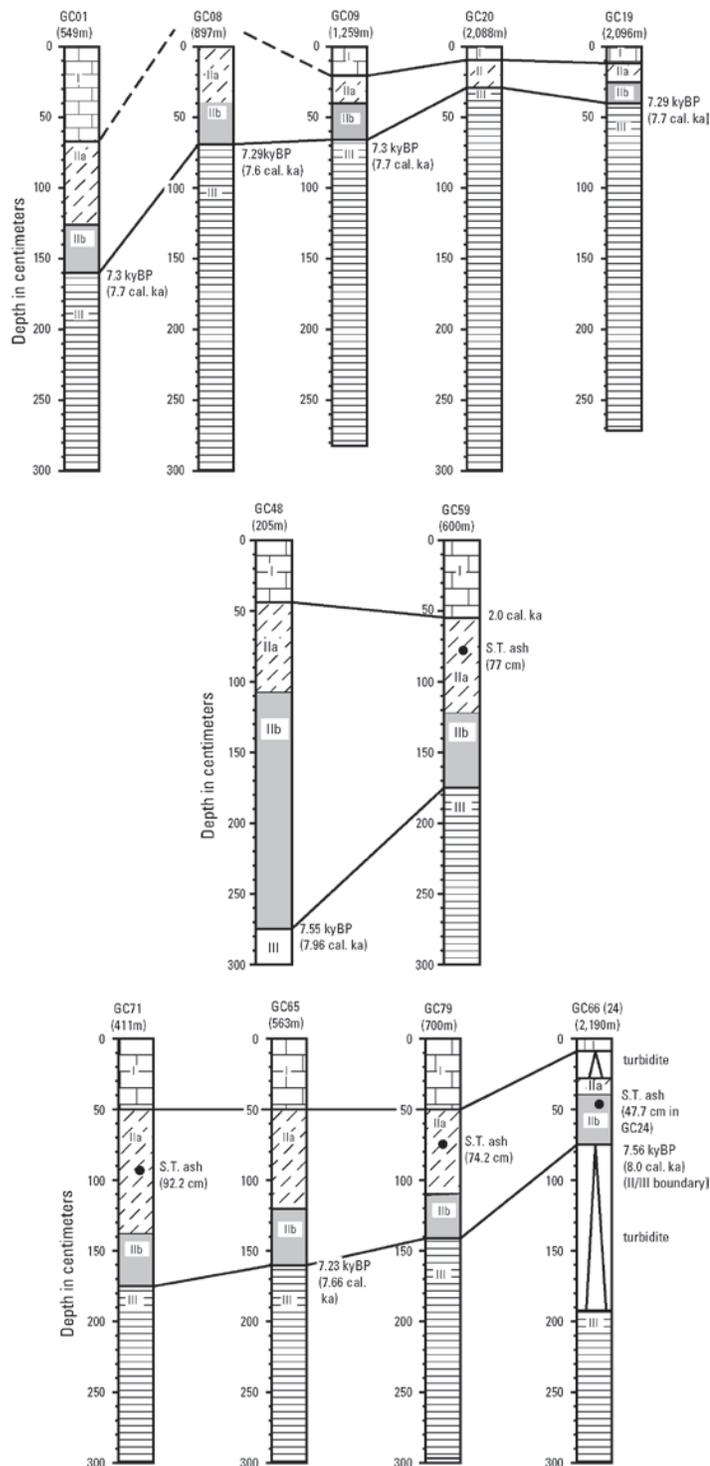
Figure 3. Diagrammatic correlation of lithologies in Units I, II, and III in 11 gravity cores. See text for definition of lithologic units and subunits. Radiocarbon dates for the Unit II–III boundary are shown for six of the cores. S.T., Santorini volcanic ash.

Another distinctive feature of subunit IIb is the presence at the base of the subunit of about 100 white laminations (fig. 5), which consist of rounded needles of aragonite ("rice grains" of Ross and Degens, 1974). In addition to the distinctive white aragonite-

8

rich laminations observed in all cores, the base of Unit II is marked by an increase in $CaCO_3$ content that can be correlated in cores from all depths (Fig. 4; Arthur and Dean, 1998). The transition between Units II and III is marked by a sharp decrease in OC content to values that are generally <1.0% in Unit III (fig. 4), and a change downward from laminated sapropel typical of Unit II, to microbioturbated clay typical of Unit III. This transition in OC content and bioturbation occurs over a stratigraphic interval of 2-5 cm.
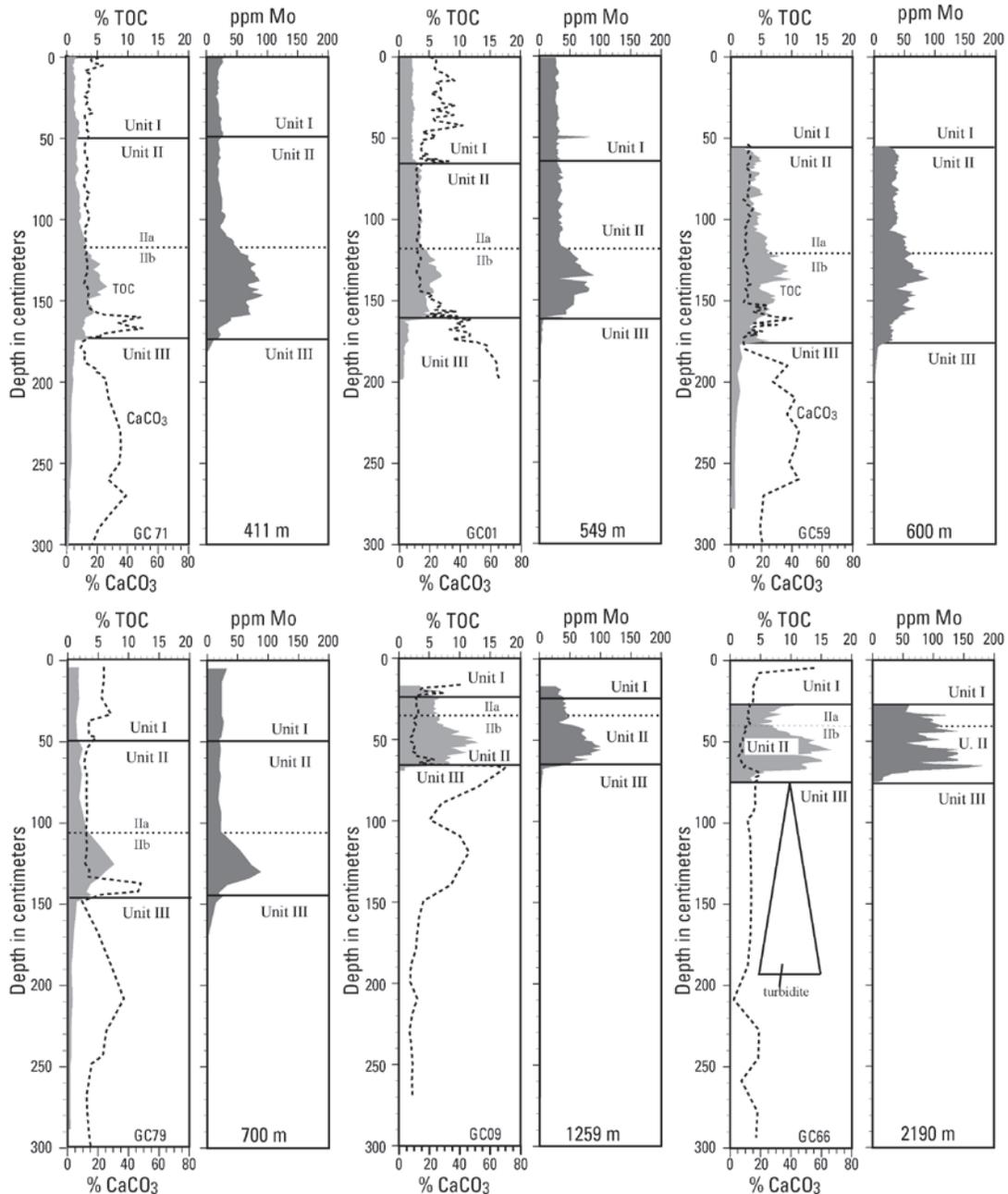
Figure 4. Profiles of percent organic carbon (% OC), percent calcium carbonate (% CaCO3), and parts per million molybdenum (ppm Mo) in six gravity cores from progressively deeper water.

The upper part of Unit III that was recovered in gravity cores consists predominantly of greenish gray to olive-gray clay that is either massive, coarsely banded, or with black streaks, pods, or laminae of iron monosulfide(?) (fig. 5). In gravity cores from shallower depths along the margin of the Black Sea, near the Bosporus (GC01, GC08, GC09, GC19, and GGC20; fig. 1), the clay of Unit III generally is pale reddish brown to pink below the top few meters. The $CaCO_3$ content of Unit III sediments typically has one or two maxima of as much as 60% near the top of the Unit (fig. 4; Arthur and Dean, 1998).

Figure 5.   Photograph of the bottom of Unit II and top of Unit III in GGC71. The bottom of Unit II is marked by white aragonite laminae. The black blotches in Unit III are due to iron monosulfide.

Ages of Lithologic Units

It has been suggested that the dark-light laminae couplets of Unit I represent annual accumulations of sediment (varves) (Ross and Degens, 1974; Degens and others, 1980). The present seasonal pattern of sedimentation in the Black Sea, outlined by eight years of sediment-trap investigations (Honjo and others, 1988; Hay, 1988; Hay and others, 1990), consists of a large pulse of terrigenous clastic material and diatom debris in the winter and spring, a summer OC and $CaCO_3$ pulse from coccolith blooms, and a fall-early winter pulse of $CaCO_3$ and terrigenous clastic material from river runoff and resuspension of coccolith debris on the shelves during storms. Sediment-trap studies have shown the coccolith debris is mostly delivered to the sediment/water interface as zooplankton fecal pellets in marine snow (Hay, 1988; Pilskaln, 1991; Pilskaln and Pike, 2001). The diatom debris (biogenic silica; ~50% in sediment traps) does not survive into the sediments but is dissolved in the water column and at the sediment/water interface in the benthic "fluff" layer (~2 cm thick) recovered in box cores (Pilskaln, 1991; Pilskaln and Pike, 2001). Therefore, the varves in Unit I sediments consist of white $CaCO_3$ laminae produced by a summer-fall pulse of coccolith-rich sediment and a winter-spring dark clastic laminae (Hay, 1988; Hay and others, 1990; Hay and others, 1991; Pilskaln and Pike, 2001).

The original radiocarbon age for the Unit II/III boundary was 7.09 thousand years (Ross and others, 1970; Ross and Degens, 1974). AMS radiocarbon ages for this boundary measured on organic carbon from nine cores collected on Leg 1 of the 1988 *R/V Knorr* cruise are given by Jones and Gagnon (1994). There is remarkably good agreement among these measurements with a range of 7.05 thousand years to 7.64 thousand years and an average of about 7.35 thousand years , which gives an average calendar age of about 7.9 cal. ka, and a duration of Unit II of about 5.9 ky. Magnetic secular variation curves, also gave an age of 7.9 cal. ka for the age of the Unit II/III boundary (Arthur at el., 1994; Arthur and Dean, 1998). Additional ages within Unit II are available from a volcanic ash layer in the upper part of Unit II (fig. 3). This ash comes from the Santorini (Thera) eruption in the Aegean Sea dated at 3350±75 calendar years based on radiocarbon analyses from numerous sites (Guichard and others, 1993). Finally, geomagnetic secular variation events reflected in inclination and declination data, tied to calibrated radiocarbon ages in European archeomagnetic sites, also provide datums that allow us to assign ages to points in several cores (Arthur and Dean, 1998).

Distribution of Inorganic Elements

In marine sediments most major elements and certain trace elements, such as cobalt (Co), gallium (Ga), cerium (Ce), lanthanum (La), lithium (Li), thorium (Th), and yttrium (Y), are derived mainly from terrigenous aluminosilicate sources (Brumsack, 1986; Piper and Dean, 2002). The application of trace elements to track variations in productivity and redox conditions in the ocean is relatively new. Several trace elements, such as rhenium (Re), uranium (U), vanadium (V), nickel (Ni), zinc (Zn), copper (Cu), cadmium (Cd), and molybdenum (Mo), are concentrated in OC-rich sediments where sulfate reduction has occurred (Jacobs and others, 1985; Emerson and Huested, 1991; Crusius and others, 1996). These elements may have two sources: (1) a biogenic source represented by trace elements taken up mostly in the photic zone by phytoplankton

and(or) adsorbed onto organic particulates, and (2) a hydrogenous fraction derived from bottom water and(or) sediment pore water by adsorption and precipitation reactions under low-dissolved-oxygen (DO), sulfate-reducing conditions (Piper, 1994; Piper and Dean, 2002). Low-DO, sulfate-reducing conditions in the Black Sea are due to anoxic bottom waters and a high biological oxygen demand imposed by decomposition of produced organic matter.

As a measure of variations in sulfate-reducing conditions and, therefore, sequestration of elements in a hydrogenous fraction, we focus on Mo in this study because, of the elements for which we have data, Mo is the most diagnostic element in sediments that accumulate under seawater sulfate-reducing conditions (Bruland, 1983; Jacobs and others, 1985; Emerson and Huested, 1991; Piper, 1994; Crusius and others; 1996, Piper and Dean, 2002; Algeo and Lyons, 2006). In seawater, Mo occurs predominantly as MoO_4^{2-}, but in the presence of H_2S in concentrations as low as $11x10^{-6}$ M MoS_4^{2-} dominates over MoO_4^{2-} (Erickson and Helz, 2003). In continental margin oxygen-minimum zones (OMZs), elevated concentrations of Mo (above 1ppm) usually, but not always, are associated with laminated sediments, another indicator of anoxic or near anoxic bottom-water conditions (Dean and others, 2006). Elevated concentrations of Ni (above about 40 ppm) might also be used as a geochemical indicator of low-DO bottom-water conditions and incorporation in a sulfidic hydrogenous fraction. However, because Ni, along with Cu, V, and Zn, are found in high concentrations in particulate organic matter (table 2; Martin and Knauer, 1973; Collier and Edmond, 1984; Brumsack, 1986) or adsorbed onto organic material, excess concentrations, above terrigenous clastic material, are likely contributed from biogenic sources. The most important transport of organic particles to the deep ocean is in zooplankton fecal pellets (Fowler, 1977; Honjo and others, 1987).

Table 2. Concentrations of selected elements in Upper Continental Crust, Pacific pelagic clay, and seawater particulate organic matter.

[ppm, parts per million]

Element	Concentration in upper continental crust[a] (ppm)	Concentration in Pacific Pelagic Clay[b] (ppm)	Concentration in Particulate Organic Matter[c] (ppm)
Copper	30	230	11
Cadmum	0.1	0.4	12
Cobalt	12	113	1
Chrome	70	64	2
Molybdenum	1	10	2
Nickel	44	210	7.5
Vanadium	95	120	3
Zinc	60	165	110

[a] Wedepohl, 1971.

[b] Bischoff and others, 1979.

[c] Brumsack, 1986; Piper, 1994.
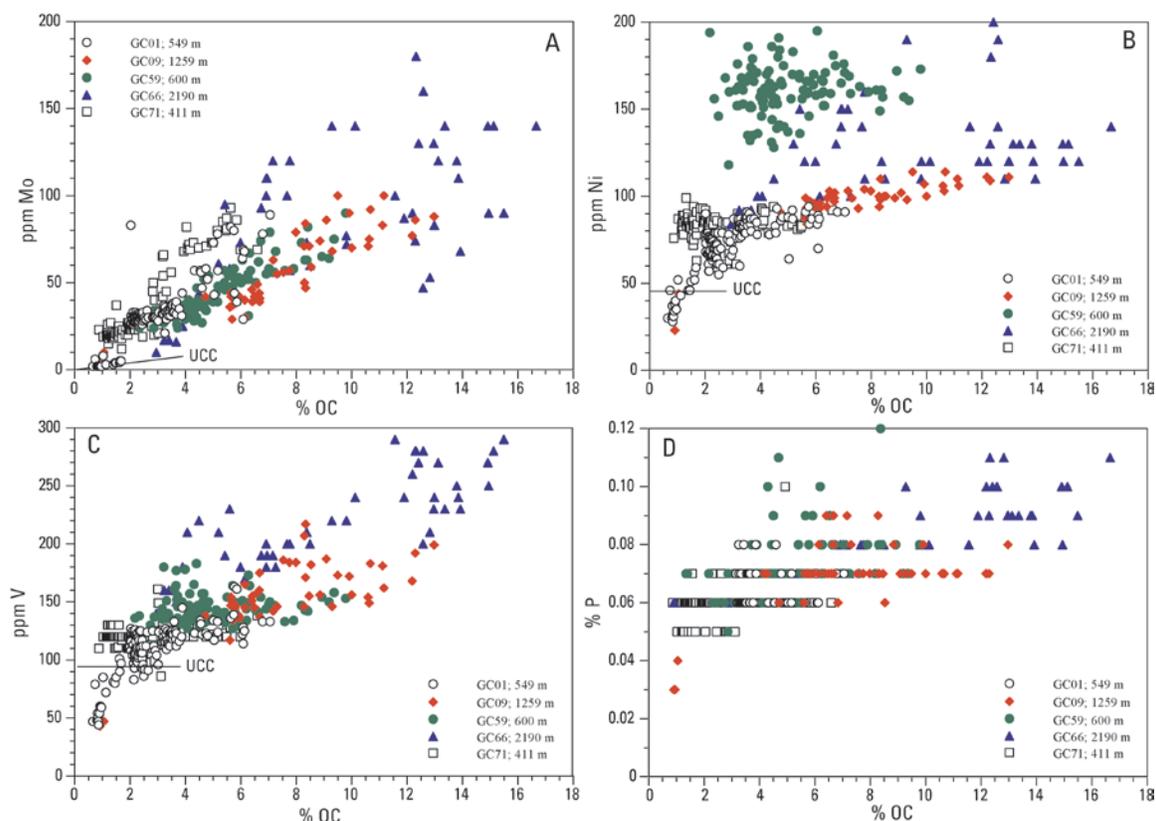
Figure 6. Cross plots of parts per million molybdenum (ppm Mo) (A), parts per million nickel (ppm Ni) (B), parts per million vanadium (ppm V) (C), and percent phosphorus (% P) (D) compared to percent organic carbon (% OC) in Unit II sediments in five gravity cores from different depths. UCC = concentration of an element in average upper continental crust (Wedepohl, 1971).

The positive covariance between OC and three redox-sensitive trace elements (Mo, Ni, and V) and a nutrient (phosphorus, P) are shown for Unit II sediments in five cores in figure 6. Strong covariance between OC and metals such as Mo implies that most of that metal resides in organic matter as do nutrients such as P (that is, the metal is scavenged by organic matter [Algeo and Lyons, 2006]). Sediments in the highly restricted Black Sea have much lower Mo/OC ratios than other silled anoxic basins (for example, Framvaren Fjord, Cariaco Basin, and Saanich Inlet) because Black Sea deep water contains only 3-5 % as much Mo as sea water because there is not adequate resupply of Mo to replace Mo removed to the sediments. In silled basins with sulfidic bottom waters, most Mo accumulation occurs at or below the sediment/water interface (Algeo and Lyons, 2006).

Concentrations of OC and metals are highest in deeper-water, offshore settings (for example, cores GC66 and GC59) where there is less dilution by terrigenous clastic material. Core GC66 appears to have two different sources of Ni, each with a different regression with OC (fig. 6B). The concentration of Ni in GC59 is unusually high and does not covary with OC suggesting that this site has a high terrigenous source of Ni. As mentioned earlier, Arthur and Dean (1998) subdivided Unit II into IIa and IIb on the basis of the higher OC content of subunit IIb (fig. 4). Because of the positive covariances

between OC and some metal concentrations, the subdivisions of Unit II based on OC content can also be made on the basis of redox metal content (for example, Mo, fig. 4). These trace elements (as well as Cu in Black Sea sediments) clearly have a marine source, but it is not clear if that source is biogenic or hydrogenous. It is also not clear how much of each of these metals is contributed from the marine source and how much is contributed from terrigenous sources. Previous studies have shown that all but Mo have a major or dominant terrigenous source. Concentrations of metals are near crustal abundances at low OC concentrations (for example, UCC in figs. 6B and 6C) indicating terrigenous sources, at least at low OC concentrations. In Cariaco Basin sediments, Piper and Dean (2002) calculated that 97 percent of Mo was hydrogenous, and 86 percent of Cd was biogenic. Dean and others (2006) concluded that almost all of the Cd in anoxic sediments from the Pacific Baja California margin was contributed from phytoplankton production. Unfortunately, we do not have analyses of Cd on our Black Sea sediment samples, but we would anticipate high concentrations indicating high plankton productivity during deposition of Unit II and, particularly, during deposition of subunit IIb.

In order to determine how much of the concentration of an element is contributed from sources other than terrigenous clastic material, we assumed that the terrigenous material had a composition close to some standard reference material such as average upper continental crust or average shale. For this exercise, we chose average upper continental crust (UCC) (Wedepohl, 1971), realizing that the terrigenous debris reaching the Black Sea from numerous complex geologic sources could not simply be represented by UCC, but this provides a baseline for comparison. We normalized the elemental composition relative to the crustal abundance of an element compared to Al at 7.8%, the average Al content for UCC. The concentration of an element greater than its crustal abundance we called "excess". This is represented graphically for six elements in Unit II and Unit III sediments from cores from the western Black Sea (fig. 7; GC09), the eastern Black Sea (fig. 8; GC59), one of a transect of cores offshore from Inebolu, Turkey in the south-central Black Sea (fig. 9; GC71; see Honjo and others, 1988, and Arthur and Dean, 1998, for details of this transect), and the deep central Black Sea (fig. 10; GC66). An "excess" concentration is indicated by how far the element-Al regression line passes above point representing the UCC element concentration at 7.8% Al in figures 7, 8, 9, and 10.
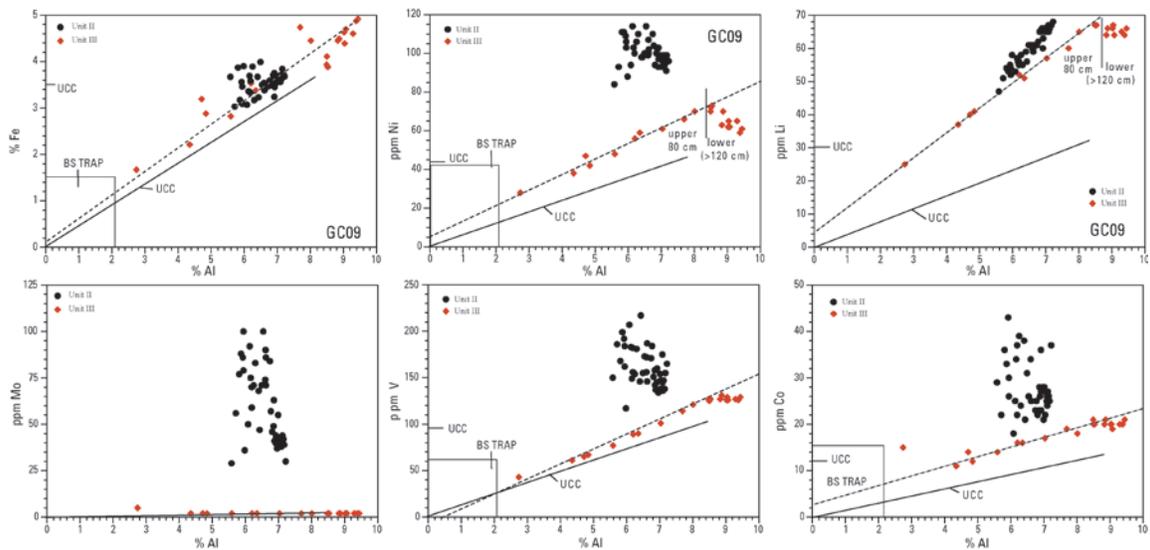
Figure 7. Cross plots of percent iron (% Fe), parts per million molybdenum (ppm Mo), parts per million nickel (ppm Ni), parts per million vanadium (ppm V), parts per million lithium (ppm Li), and parts per million cobalt (ppm Co) compared to percent aluminum (% Al) in Unit II and Unit III sediments from gravity core GC09. UCC = concentration of an element in average upper continental crust (Wedepohl, 1971). Dashed line is the regression for the upper 80 centimeters of Unit III sediments. Ranges of values in samples from a sediment trap in 1,200 meters of water in the southern Black Sea (see figure 1 for location) are shown by the boxes in the lower left corner for plots of Fe, Ni, V, and Co.
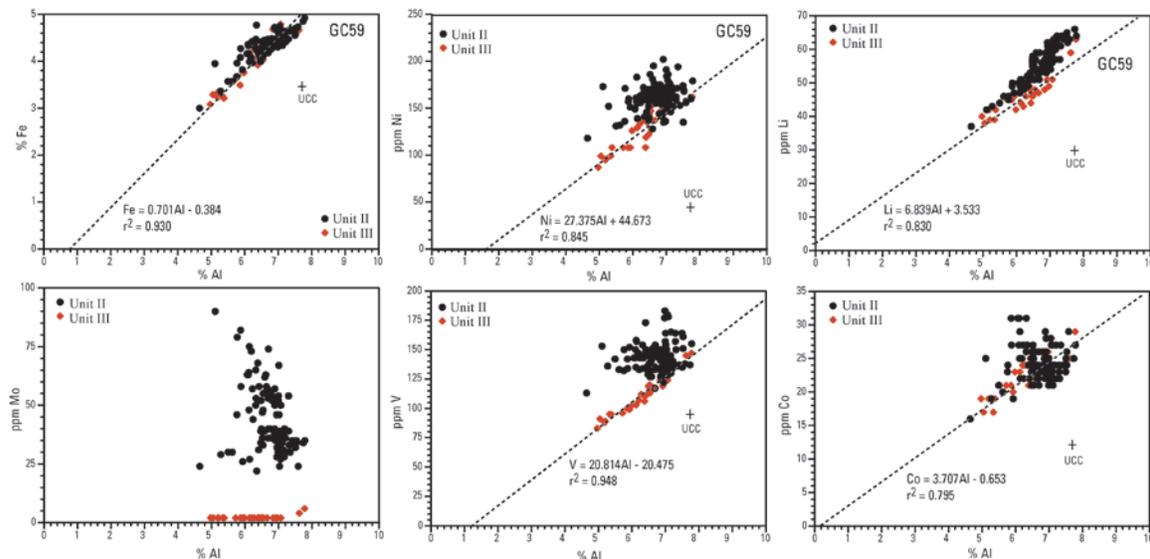
Figure 8. Cross plots of percent iron (% Fe), parts per million molybdenum (ppm Mo), parts per million nickel (ppm Ni), parts per million vanadium (ppm V), parts per million lithium (ppm Li), and parts per million cobalt (ppm Co) compared to percent aluminum (% Al) in Unit II and Unit III sediments from gravity core GC59. UCC = concentration of an element in average upper continental crust (Wedepohl, 1971). Dashed line is the regression for all samples of Unit III sediments.
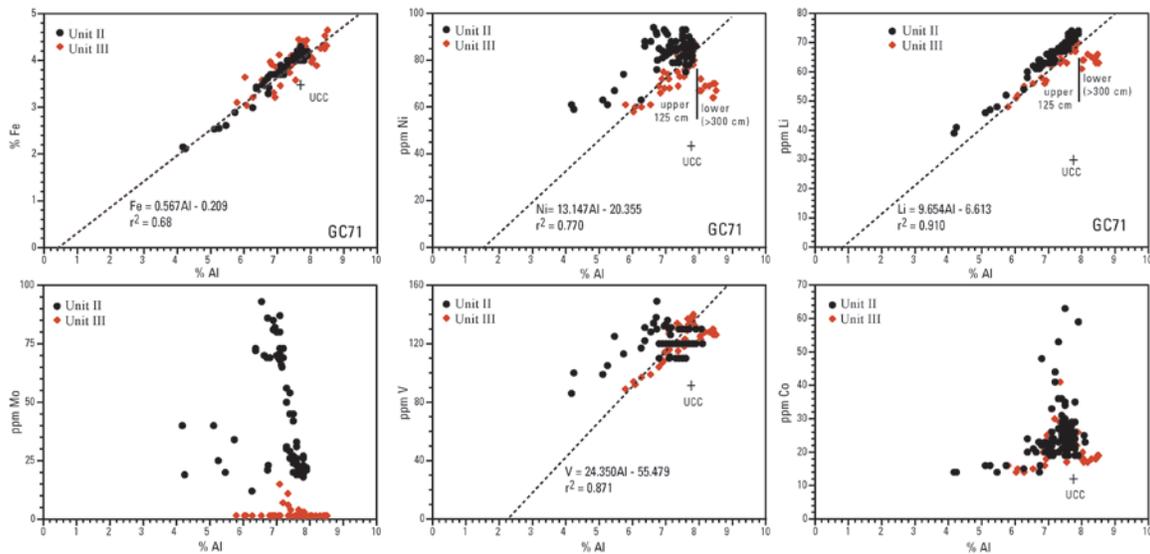
Figure 9. Figure 9. Cross plots of percent iron (% Fe), parts per million molybdenum (ppm Mo), parts per million nickel (ppm Ni), parts per million vanadium (ppm V), parts per million lithium (ppm Li), and parts per million cobalt (ppm Co) compared to percent aluminum (% Al) in Unit II and Unit III sediments from gravity core GC71. UCC = concentration of an element in average upper continental crust (Wedepohl, 1971). Dashed lines in plots for Fe, Ni, Li, and V are the regressions for the upper 125 cm of Unit III sediments.
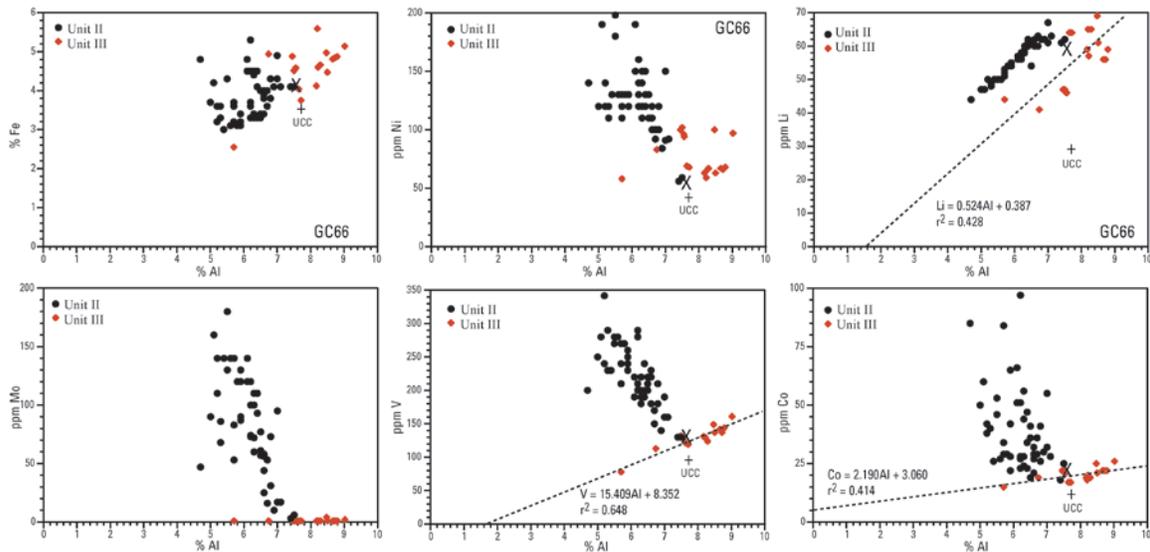

Figure 10. Figure 10. Cross plots of percent iron (% Fe), parts per million molybdenum (ppm Mo), parts per million nickel (ppm Ni), parts per million vanadium (ppm V), parts per million lithium (ppm Li), and parts per million cobalt (ppm Co) compared to percent aluminum (% Al) in Unit II and Unit III sediments from gravity core GC66. UCC = concentration of an element in average upper continental crust (Wedepohl, 1971). Dashed lines in plots for Li, V and Co are the regressions for all samples of Unit III sediments below the turbidite (greater than 192 centimeters). The average composition of the turbidite is indicated by the X-symbol.

Elements derived predominantly from terrigenous clastic material will have an element-Al regression that extrapolates to, or close to, the origin and passes close to the element concentration in UCC at 7.8% Al (iron [Fe] in Unit III sediments in GC09 is an example; fig. 7). The departure of the regression line from the point representing the element-Al concentration in UCC is a measure of how different an element's concentration in the Black Sea terrigenous source material is from that in UCC. Elements with a clear dominant excess concentration relative to UCC will plot well above the UCC element-Al concentrations for that element and will not have a discernible slope (Mo in Unit II sediments in all cores is a good example).

Sediments were collected in a sediment trap between 1983 and 1984 from a depth of 1,200 m (water depth of 2,200 m) in the southern Black Sea at site BS off Amasra, Turkey (fig. 1). Concentrations of selected metals in this trap are given in table 3. Unfortunately concentrations of Mo were below the detection limit of the method used (2 ppm) in all trap samples. The regressions of Fe, Ni, V, and Co compared to Al for sediments in the trap, although not significant, have slopes that are similar to plots of those elements compared to Al in Unit III sediments (fig. 11), but have absolute concentrations that are much lower due to dilution in the traps by $CaCO_3$ and biogenic silica (diatom debris, which is dissolved in the water column and at the sediment/water interface). Ranges of these four elements are shown in the lower left corners of the plots of these elements for core GC09 (fig. 7). A factor analysis (StatView software) of the elements in the trap sediments reveals a dominant lithogenic factor with Al, Fe, Cr, V, P, Ti, Co, Cu, Ni, and Pb, a carbonate factor with Ca, Sr, and Ba, and a redox factor with Mn, Cu, Ni, Co, and Pb. In the BS trap, lithogenic material composes only 28% of the total trap material; the rest is biogenic (Hay and others, 1990; see also Honjo and others, 1987). Flux data for the BS trap (and other Black Sea sediment traps) are available at: *http://usjgofs.whoi.edu/mzweb/data/honjo/sed_traps.html.*

Table 3. Composition of sediments collected between 1983 and 1984 in a sediment trap at a depth of 1,200 meters below the surface (water depth = 2,200 meters) in the southern Black Sea. [ppm = parts per million]

[m, meter; %, percent]

| Trap depth (m)	Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	Na (%)	P (%)	Ti (%)	Mn (ppm)	Sr (ppm)	Ba (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
1,200	0.19	21.00	0.18	0.18	0.88	4.70	0.07	0.008	86	1,400	150	4	6	21	13	9	11	240
1,200	0.13	9.20	0.12	0.62	2.20	11.00	0.05	0.005	47	640	100	3	3	13	8	7	6	41
1,200	0.57	19.00	0.54	0.19	0.55	1.60	0.10	0.020	160	1,200	2,200	12	12	61	28	32	16	180
1,200	0.61	22.00	0.62	0.17	0.32	0.66	0.09	0.020	200	1,300	960	15	13	66	30	30	14	200
1,200	1.30	17.00	0.82	0.31	0.43	0.43	0.14	0.040	180	940	240	12	35	96	30	45	25	160
1,200	2.10	14.00	1.10	0.47	0.59	0.55	0.16	0.060	170	720	190	11	45	71	33	40	41	150
1,200	2.00	5.70	1.20	0.46	0.76	1.60	0.12	0.060	160	330	200	14	38	170	39	42	56	270
1,200	0.28	1.30	0.08	0.84	2.50	16.00	0.01	0.008	93	180	10	2	6	26	6	10	3	170
1,200	1.30	1.30	0.18	0.75	2.50	25.00	0.05	0.050	360	190	30	10	17	120	20	50	20	760
1,200	0.31	0.98	0.01	0.82	2.50	15.00	0.01	0.007	41	170	8	1	3	14	3	9	3	100
1,200	0.50	0.90	0.06	0.60	2.30	29.00	0.05	0.060	100	160	30	10	10	50	20	40	20	220
1,200	0.14	0.94	0.01	0.88	2.40	13.00	0.01	0.006	17	170	1	1	2	8	2	4	2	68
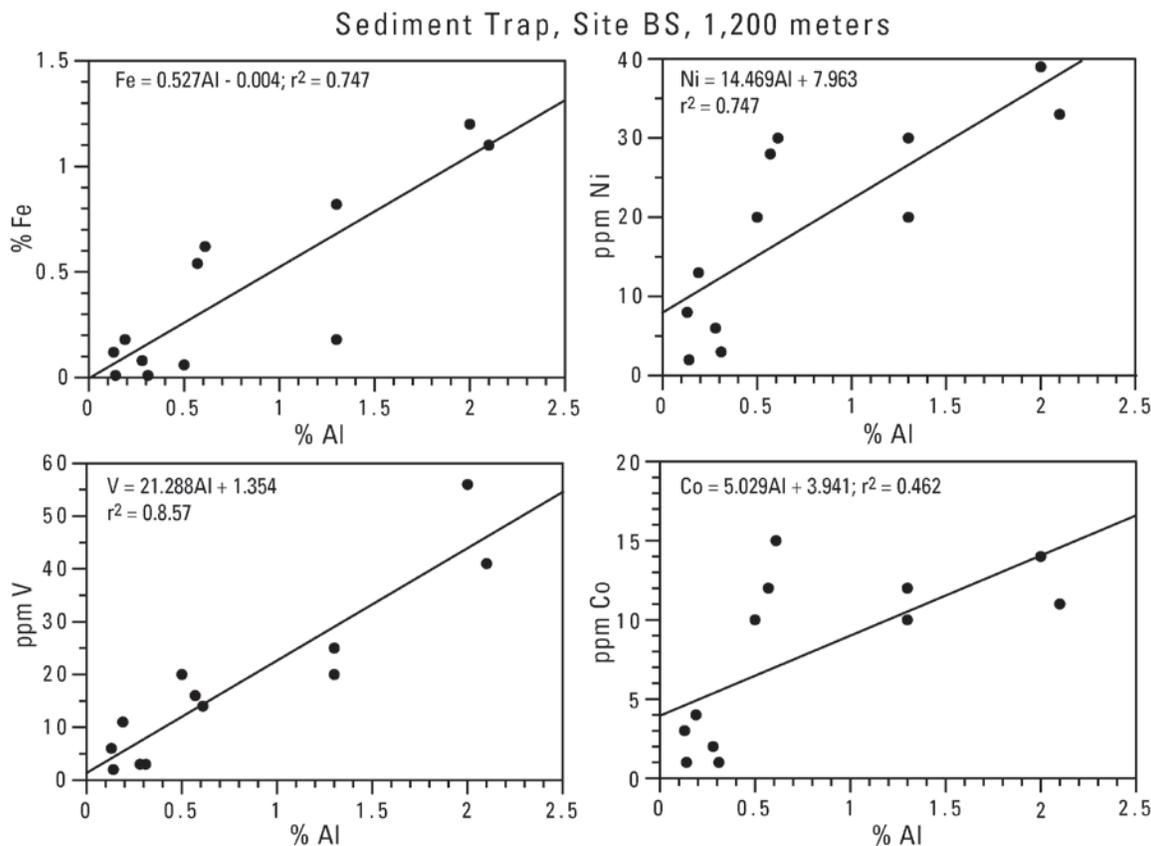
Figure 11.   Cross plots of percent iron (% Fe), parts per million nickel (ppm Ni), parts per million vanadium (ppm V), and parts per million cobalt (ppm Co) compared to percent aluminum (% Al) in Unit II and Unit III sediments from gravity core in a sediment trap at a depth of 1,200 meters (water depth 2,200 meters) in the southern Black Sea (see fig. 1 for trap location).

The plot for Co-Al appears to have two populations of samples. The high-Co, high-Al population consists of sediments deposited in the traps during the fall, winter, and early spring, whereas the low-Co, low-Al population consists of sediments deposited in the trap in late spring and summer. This pattern is also true for Fe, Ni, and V although the dichotomy is not as obvious. This seasonal relation is undoubtedly the result of higher terrigenous components in the fall-winter-spring trap sediments and higher biogenic components (CaCO$_3$ and biogenic silica) in the spring-summer trap sediments, diluting the terrigenous components. This seasonal relation is also present in samples of sediment from traps at 250 m and 2000 m at the same site.

In GC09 from the western end of the Black Sea (fig. 1), Unit II sediments have clear excesses of Mo, Ni, V, and Co (fig. 7), most likely as significant hydrogenous components, although Ni and V probably have some biogenic components because, as mentioned earlier, they have high concentrations in particulate organic matter (table 2) and, except for Co, have positive covariances with OC (figs. 6B and C). Model calculations based on analyses of sediments in the Cariaco Basin by Piper and Dean

(2002) indicated that 25% of Ni had a biogenic source, but only 1% of V had a biogenic source.

The correlations between Al and Fe, Ni, V, Co, and lithium (Li) in the upper 80 cm of Unit III sediments in GC09 are highly significant, and the regression lines extrapolate close to the origin, indicating a dominant terrigenous source (fig. 7). The concentrations of Ni, V, Li, and Co in the lower part of Unit III in GC09 (below about 150 cm) are clearly different from those in the upper part as is the Al concentration (all are higher), indicating a change in source material. The average Al concentration in carbonate- and organic-free Unit III sediments in all cores is about 9.0. The Fe and V regression lines for upper Unit III sediments passes close to the element-Al concentrations in UCC indicating that the Fe and V concentrations, relative Al, in the terrigenous source material in GC09 are close to those of UCC. However, the regression lines for Ni, Li, and Co in upper Unit III sediments are above element-Al concentrations in UCC indicating that the Ni, Li, and Co concentrations, relative Al, in terrigenous material in GC09 are higher those in UCC.

Unit II sediments in GC59 from the eastern basin of the Black Sea (fig. 1), like those in GC09 from the western end, have clear excesses of Mo, Ni, V, and Co in Unit II sediments (fig. 8), most likely as significant hydrogenous components but, again, we cannot rule out significant biogenic components of Ni and V. In GC59, the Al-Fe regressions are about the same for Unit II and Unit III sediments and both can be projected to near the origin indicating a dominant terrigenous Fe source. This is somewhat unexpected because abundant Fe-sulfides (pyrite, mackinawite, and greigite) form in the water column and in the sediments (Lewis and Landing 1991; Wilkin and others, 1997; Lyons, 1997) and, therefore, we would expect at least some contributions of excess hydrogenous Fe. Alternatively, Fe-sulfides may have been formed by reduction of ferric iron coatings on terrigenous material. The Ni, V, and Co concentrations are very high in both Unit II and Unit III sediments relative to UCC. Unlike in GGC09 there is not a clear separation between the Ni, V, and Co concentrations in Unit II and Unit III sediments. The Li-Al regressions in GC59 are similar to those in GC09 in that Li concentrations are high in both units, and the regressions project to near the origin indicating terrigenous sources.

The element-Al relations in GC71 (fig. 9) are similar to those in GC59 (fig. 8) in that there are clear excesses of Mo, Ni, V, and Co in Unit II sediments, and there are no clear separations of element concentrations between Unit II and Unit III sediments as there are in GC09. As in GC09, the Fe-Al regressions are about the same in Units II and III sediments, and both can be projected to near the origin indicating a dominant terrigenous source of Fe. This terrigenous Fe concentration, relative to Al, is close to than in UCC. The Ni-Al, V-Al, and Li-Al regressions for Unit II sediments in GC71 have slight slopes, indicating significant terrigenous sources for these three elements. As in GC09, the Ni and Li concentrations in the lower part of Unit III in GC71 (below about 300 cm) are clearly different from those in the upper part (upper 125 cm), indicating a change in source material. The element-Al regression lines for Ni, Li, and V Unit III sediments are well above the concentrations of these elements in UCC indicating that the concentrations of these elements in Black Sea terrigenous material are higher than in

UCC. Unlike the Unit III sediments in GC09, GC59, and GC66, Co in Unit III sediments in GC 71 does not correlate with Al.

The element-Al relations in GC66 (fig. 10) are more similar to those in GC09 (fig. 7) than those in GC59 (fig. 8) and GC71 (fig. 9) in that there are the expected excesses of Mo, Ni, V, and Co, and there are clear separations between concentrations in Unit II and Unit III sediments as there are in GC09 (fig. 7). However, in GC66 there are much greater variations in these four elements in Unit II sediments within a fairly narrow range of Al concentrations. In fact, these four elements have negative covariations with Al suggesting that there is a dilution of Al in the terrigenous material with a metal-rich (hydrogenous?) material. The higher concentrations of hydrogenous elements and lower terrigenous influx is in GC66 sediments is consistent with its much deeper location (2200 m; fig. 1). The Unit III samples plotted in figure 10 are those from below the turbidite (>192 cm; figs. 3 and 4). The average composition of this turbidite is indicated by an X-symbol in each of the plots in figure 10, which seems to be about the same as average concentration for each element in Unit III sediments. Only Li, V, and Co in Unit III sediments in GC66 have weak correlations with Al. Unlike the other three cores, Fe shows little covariation with Al.

Summary—Development of Anoxia in the Black Sea

Results of Deep Sea Drilling Project (DSDP) coring in the Black Sea indicate that the Black Sea was a lake of unknown but varying salinity that existed during most of the Neogene (Hsü, 1978). The fresh/saltwater interface is presently above the level of the Bosporus sill, but the level of this interface undoubtedly fluctuated considerably in response to river influx to the Black Sea, precipitation, evaporation, and winds (Scholten, 1974). During times of intense net evaporation and(or) minimum freshwater influx, the level of the Black Sea may have been below that of the Mediterranean Sea, resulting in net influx of marine water. At least three major marine incursions into the Black Sea are recorded in Neogene sediments of the Black Sea (Hsü, 1978). The transition from a freshwater to brackish lacustrine environment with net freshwater outflow (Unit III) to a near-normal marine environment with balanced inflow of marine water and outflow of freshwater (Unit I) is recorded in the laminated sapropel of Unit II.

Unit III

Sediments recovered from Unit III contain the lowest concentrations of OC (1.0% or less) observed in all three lithologic units (fig. 4) and the lowest concentrations of redox-sensitive trace elements (figs. 7-10). As discussed herein, the upper part of Unit III was deposited in brackish to fresh waters based on studies of dinoflagellate cysts (Marret and others, 2009). The low OC content of Unit III sediments is consistent with high bottom-water oxygen levels during deposition of Unit III. Such bottom-water conditions are also indicated by the high degree of bioturbation of the sediments and the reddish or pinkish color of some sediments observed in several cores from water depths ranging from 900 to 2,090 m. Occasional faint laminations, however, suggest that bottom-water concentrations of dissolved oxygen sometimes reached very low levels. Based on these observations, we suggest that the Black Sea probably was freely circulating as a normal,

temperate dimictic lake, or perhaps a cold monomictic lake, during deposition of at least the upper part of Unit III that was recovered by gravity cores during the 1988 *R/V Knorr* cruise.

Unit III-Unit II Transition

The base of Unit II is marked by two synchronous geochemical events that can be correlated across the entire Black Sea in cores from the deep abyssal plains (about 2,200 m) to cores from as shallow as 400 m. These events are marked by an increase in OC in the lowest part of the laminated sapropel of Unit II (fig. 4) and an increase in $CaCO_3$, as aragonite laminae (fig. 5). The increase in OC at the base of Unit II (Fig. 4) is not so abrupt as the increase in $CaCO_3$, and tends to be more of a step-wise increase (fig. 4; Arthur and Dean, 1998). The zone of maximum OC concentration is manifested in cores as the darkest part of the Unit II sapropel that Arthur and Dean (1998) designated as subunit IIb (fig. 4). Absolute OC concentrations ranged from about 5% in cores from shallower sites to about 15% in cores from abyssal-plain sites (fig. 4), but the high OC subunit IIb can be correlated in cores from all depths (fig. 4). The presence of aragonite probably is related to the buildup of magnesium in surface and bottom waters of the Black Sea due to the influx of Mediterranean Sea water. Freshwater environments tend to have a low Mg:Ca ratio so that the dominant carbonate mineral in most lacustrine sediments is low-magnesium calcite (Müller and others, 1972). With increasing Mg:Ca ratio, high-magnesium calcite and aragonite may be precipitated (Müller and others, 1972). In the Black Sea, the Mg concentration of the water, and hence the Mg:Ca ratio, may have varied in response to either the precipitation:evaporation ratio or seawater influx. In older Black Sea lacustrine sediments, both high-magnesium calcite and aragonite are common components in sediments containing brackish-water marine organisms (Hsü, 1978).

Unit II

It has been suggested (for example, Calvert and others, 1987; Calvert, 1990; Calvert and others, 1991) that the finely laminated Unit II sapropel was deposited in well-oxygenated bottom water, and that anoxia did not develop in the Black Sea until after deposition of the sapropel. We contend that it is impossible to preserve finely laminated, OC-rich sediments under well-oxygenated bottom waters, and that these laminated sediments, like the laminated sediments of Unit I, were deposited in anoxic bottom waters beginning about 7.9 cal. ka. During deposition of most of Unit II the Black Sea was probably a meromictic lake with a stagnant, anoxic, more saline, bottom-water mass (monimolimnion) and an oxygenated, less saline surface-water mass (mixolimnion) that gradually increased the salinity of the surface waters of the Black Sea until it reached about 24‰ at the top of Unit II and base of Unit I based on the hydrogen isotopic composition of long-chain alkenones (van der Meer and others, 2008). The alkenone-based salinity then decreased upward in Unit I to 20‰, the present surface-water salinity. The main difference between Unit I and Unit II is the addition of coccolith carbonate to the varves of Unit I and hence a dilution of the concentration of OC (fig. 4). The mass accumulation rate (MAR) of OC, however, is essentially the same in both Unit I (0.20 to

0.38 grams per square centimeter per thousand years) and Unit II (0.26 to 0.50 grams per square centimeter per thousand years) (Arthur and Dean, 1998). If *E. huxleyi* is supposed to calcify at 11‰ (Bukry, 1974), it is not known why its remains are not present at the top of Unit II. Its absence may be due to severe dissolution or *E. huxleyi* was not the only source of long-chain alkenones (van der Meer and others, 2008). Alternatively, *E. huxleyi* in the Black Sea may require a higher salinity than 11‰.

Conclusions

1. The sedimentary sections recovered in box and gravity cores throughout the Black Sea consist of three lithologic units: an upper laminated coccolith marl (Unit I); a finely laminated OC-rich sapropel (Unit II); and massive to coarsely banded OC-poor lacustrine clays and marls (Unit III). The base of Unit II marks the first postglacial incursion of Mediterranean Sea water into the Black Sea at about 7.9 cal. ka and the onset of bottom-water anoxia. Units II and III were deposited when the Black Sea was essentially a fresh- to brackish-water lake.

2. Several trace elements, such as Re, U, V, Ni, Zn, Cu, Co, Cd, and molybdenum (Mo) are often concentrated in OC-rich sediments where sulfate reduction has occurred. We focus on Mo in this study because of the elements for which we have data, it is the diagnostic element that accumulates under hydrogenous sulfate-reducing conditions. We also examined the behavior of Ni, Zn, V, and Co but these elements can also have significant biogenic and terrigenous sources.

3. Positive covariances between OC and three redox-sensitive trace elements (Mo, Ni, and V, and a nutrient (P) in five gravity cores suggest a biogenic (Ni and V) or hydrogenous (Mo) source for these elements. Concentrations of OC and metals are highest in deeper water where there is less dilution by terrigenous clastic material.

4. Five elements (Fe, Ni, Li, V, and Co) in Unit III sediments, and Fe and Li in Unit II sediments, have significant regressions with Al in four gravity cores, indicating that these elements are derived predominantly from terrigenous clastic material. The concentration of Mo is below the limit of detection (2 ppm) in most Unit II sediments. Concentrations of Ni, Mo, V, and Co in Unit II sediments usually do not have a positive covariance with Al and plot well above the regression of Unit III sediments, and most likely have dominant marine components, either hydrogenous or biogenic. The marine source for Mo is hydrogenous likely as MoS_4^{2-}. The marine source for Ni, V, and Co is most likely seawater suspended organic matter (plankton debris).

5. Sediments were collected in a sediment trap between 1983 and 1984 from a depth of 1,200 m in the southern Black Sea. The regressions of Fe, Ni, V, and Co compared to Al for sediments in the trap, although not significant, have slopes that are similar to plots of those elements compared to Al in Unit III sediments but have absolute concentrations that are much lower due to overall dilution in the traps by $CaCO_3$ and biogenic silica. Also, there is a seasonal relation to the metal-Al covariation. The higher metal and Al samples were deposited in the trap during

the fall-winter-spring period when there was less dilution of the terrigenous fraction by $CaCO_3$ and biogenic silica.

Acknowledgments

References

Algeo, T.J., and Lyons, T.W., 2006, Mo-total organic carbon covariation in modern anoxic marine environments—Implications for analysis of paleoredox and paleohydrographic conditions: Paleoceanography, v. 21, PA1016, doi:1029/2004PA001112.

Arthur, M.A., and Dean, W.E., 1998, Organic-matter production and preservation, and evolution of anoxia in the Holocene Black Sea: Paleoceanography, v. 13, p. 395–411.

Arthur, M.A., Dean, W.E., Neff, E.D., Hay, B.J., King, J., and Jones, G.A., 1994, Late Holocene (0-2,000yBP) organic carbon accumulation in the Black Sea: Global Biogeochemical Cycles, v. 8, p. 195–217.

Baedecker, P.A., editor, 1987, Geochemical methods of analysis: U.S. Geological Survey Bulletin 1770, 129 p.

Bischoff, J.L., Heath, G.R., and Leinen, M., 1979, Geochemistry of deep-sea sediments from the Pacific manganese nodule province—Domes Sites A, B, and C., *in* Bischoff, J.L., and Piper, D.Z., eds., Marine geology and oceanography of the Pacific manganese nodule province: New York, Plenum Press, p. 397–436.

Brewer, P.G., and Spencer, D.W., 1974, Distribution of some trace elements in the Black Sea and their flux between dissolved and particulate phases, *in* Ross, D.A., and Degens, E.T., eds., The Black Sea—Geology, chemistry and biology: American Association of Petroleum Geologists Memoir 20, American Association of Petroleum Geologists, Tulsa, Oklahoma, p. 137–143.

Bruland, K.W., 1983, Trace elements in sea-water, *in* Riley, J.P., and Chester, R., eds., Chemical Oceanography: v. 8: New York, Academic Press, p. 158–220.

Brumsack, H.J., 1986, The inorganic geochemistry of Cretaceous black shales (DSDP Leg 41) in comparison to modern upwelling sediments from the Gulf of California, *in* Summerhayes, C.P., and Shackleton, N.J., eds., North Atlantic paleoceanography: Geological Society of London, Special Publication 21, p. 447–462

Bukry, D., 1974, Coccoliths as paleosalinity indicators—Evidence from the Black Sea, *in* Ross, D.A., and Degens, E.T., eds., The Black Sea, Geology, chemistry, biology: American Association of Petroleum Geologists Memoir 20, American Association of Petroleum Geologists, Tulsa, Oklahoma, p. 353–363.

Calvert, S.E., 1990, Geochemistry and origin of the Holocene sapropel in the Black Sea, *in* Ittekot, V., Kempe, S., Michaelis W., and Spitzy, A., eds., Modern biogeochemistry: New York, Springer-Verlag, p. 326–352.

Calvert, S.E., Vogel, J.S., and Southon, J.R., 1987, Carbon accumulation rates and the origin of the recent sapropel in the Black Sea: Geology, v. 15, p. 918–921.

Calvert, S.E., Karlin, R.E., Toolin, L.J., Donahue, D.J., Southon J.R., and Vogel, J.S., 1991, Low organic carbon accumulation rates in Black Sea sediments: Nature, v. 350, p. 692–695.

Codispodi, L.A., Friederich, G.E., Murray, J.W., and Sakamoto, C.M., 1991, Chemical variability in the Black Sea—Implications of continuous vertical profiles that penetrated the oxic/anoxic interface: Deep-Sea Research, v. 38, Supplement 2, p. S691–S710.

Collier, R., and Edmond, J., 1984, The trace element chemistry of marine biogenic particulate matter: Progresses in Oceanography, v. 13, p. 113–119.

Crusius, J., Calvert, S., Pedersen, T., and Sage, D., 1996, Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic, and sulfidic conditions of deposition: Earth and Planetary Science Letters, v. 145, p. 65–78.

Dean, W.E., Zheng, Y., Ortiz, J.D., and van Geen, A., 2006, Sediment Cd and Mo accumulation in the oxygen-minimum zone off western Baja California linked to global climate over the past 52 kyr: Paleoceanography, v. 21, PA4209, doi:10.1029/2005PA001239.

Degens, E.T. and Ross, D.A., 1972, Chronology of the Black Sea over the last 25,000 years: Chemical Geology, v. 10, p. 1–16.

Degens, E.T., Michaelis, W., Garrasi, C., Mopper, K., Kempe, S., and Ittekkot, A., 1980, Warven-Chronologie and Fruhdiagenetische Umsetzungen organischer Substanzen holozaner Sediments des Schwarzen Meeres: Neues Jahrbuch Geologisch-Palaontologischer Monatshefte, v. 83, p. 65–86.

Demaison, G.J., and Moore, G.T., 1980, Anoxic environments and oil source bed genesis: American Association of Petroleum Geologists Bulletin: v. 64, p. 1179–1209.

Emerson, S.R., and Huested, S.S., 1991, Ocean anoxia and concentrations of molybdenum and vanadium in seawater: Marine Chemistry, v. 34, p. 177–196.

Engleman, E.E., Jackson, L.L., and Norton, D.R., 1985, Determination of carbonate carbon in geological materials by coulometric titration: Chemical Geology, v. 53, p. 125–128.

Erickson, B.E. and Helz, G.R., 2003, Molybdenum (VI) speciation in sulfidic water—Stability and lability of thiomolybdates: Geochimica et Cosmochimica Acta, v. 64, p. 1149–1158.

Fowler, S.W., 1977, Trace elements in zooplankton particulate products: Nature, v. 260, p. 51–53.

Grasshoff, K., 1975, The hydrochemistry of landlocked basins and fjords, *in* Riley, J.P., and Skirrow, G., eds., Chemical Oceanography, 2d ed.: New York, Academic Press, p. 56–93.

Guichard, F., Carey, S., Arthur, M.A., Sigurdsson H., and Arnold, M., 1993, Tephra from the Minoan eruption of Santorini in sediments of the Black Sea: Nature, v. 363, p. 610–612.

Hay, B.J., 1988, Sediment accumulation in the central western Black Sea over the past 5100 years: Paleoceanography, v. 3, p. 491–508.

Hay, B.J., Honjo, S., Kempe, S., Ittekkot, V.A., Degens, E.T., Konuk, T., and E. Izdar, 1990. Interannual variability in particle flux in the southwestern Black Sea: Deep-Sea Research, v. 37, p. 911–928.

Hay, B.J., Arthur, M.A., Dean, W.E., Neff, E.D., and Honjo, S., 1991, Sediment deposition in the Late Holocene abyssal Black Sea with climatic and chronological implications: Deep-Sea Research, v. 38, Supplement 2, p. S1237–S1254.

Honjo, S., Hay, B.J., Manganini, S.J., Asper, V.L., Degens, E.T., Ittekkot, V., Izdar, E., Konuk, T., and Benlio, H.A., 1987, Seasonal cyclicity of lithogenic partical fluxes at southern Black Sea sediment trap station, *in* Degens, E.T., Izdar, E., and Honjo, S. eds., Particle flux in the ocean: Mitteilungen des Geologisch-Paläontologischen Institutes, Universität Hamburg. v. 62, p. 19–40.

Honjo, S., Hay, B.J., and Members of the Shipboard Party, 1988, Temporal and spatial variability in sedimentation in the Black Sea: Cruise Report R/V Knorr 138-4, Leg 1, April 16-May 7, 1988: Black Sea Sedimentation Data File, v. 2, Woods Hole Oceanographic Institution Technical Report WHOI 88-35, 156 p.

Hsü, K. J., 1978, Stratigraphy of the lacustrine sedimentation in the Black Sea, *in* Ross, D. A., Neprochnov, Y.P., and others: Initial Reports of the Deep Sea Drilling Project, v. 42, part 2, Washington (U.S. Government Printing Office), p. 509–524.

Jacobs, L., Emerson, S., and Skei, J., 1985, Partitioning and transport of metals across the O_2/H_2S interface in a permanently anoxic basin, Framvaren Fjord, Norway: Geochimica et Cosmochimica Acta, v. 49, p. 1433–1444.

Jones, G., and Gagnon, A., 1994, AMS radiocarbon dating of sediments in the Black Sea: Deep-Sea Research, v. 41, p. 531–557.

Lewis, B.L., and Landing, W.M., 1991, The biogeochemistry of manganese and iron in the Black Sea: Deep-Sea Research, v. 38, Supplement 2, p. S773–S804.

Lyons, T.W., 1997, Sulfur isotopic trends and pathways of iron sulfide formation in upper Holocene sediments of the anoxic Black Sea: Geochimica et Cosmochimica Acta, v. 61, p. 3367–3382.

Marret, F., Musie, P., Aksu, A., and Hiscott, R.N., 2009, A Holocene dinocyst record of a two-step transformation of the Neoeuxinian brackish water lake into the Black Sea: Quaternary International, v. 197, p. 72–86.

Martin, J.K., and Knauer, G.A., 1973, The elemental composition of plankton: Geochimica et Cosmochimica Acta, v. 37, p. 1639–1653.

Müller, G., Irion, G., and Forstner, U., 1972, Formation and diagenesis of inorganic Ca-Mg carbonates in the lacustrine environment: Naturwissenschaften, v. 59, p. 158–164.

Murray, J. W., Top, Z., and Özsov, E., 1991, Temperature and salinity distributions in the Black Sea: Deep-Sea Research, 38, Supplement 2, p. S663–S689.

Neprochnov, Y. P., and Ross, D. A., 1978, Black Sea geophysical framework, *in* Ross, D. A., Neprochnov, Y. P., and others: Initial Reports of the Deep Sea Drilling Project, v. 42, part 2. Washington (U.S. Government Printing Office), p. 1043–1056.

Pilskaln, C.H., 1991, Biogenic aggregate sedimentation in the Black Sea Basin, *in* Izdar, E., and Murray, J.W., eds., Black Sea oceanography: Nowell, Mass., Kluwer, p. 293–306.

Pilskaln, C.H., and Pike, J., 2001, Formation of Holocene sedimentary laminae in the Black Sea and the role of the benthic flocculent layer: Paleoceanography, v. 16, p. 1–19.

Piper, D.Z., 1994, Seawater as the source of minor elements in black shales, phosphorites, and other sedimentary deposits: Chemical Geology, v. 114, p. 95–114.

Piper, D.Z., and Dean, W.E., 2002, Trace-element deposition in the Cariaco Basin under sulfate reducing conditions—A history of the local hydrography and global climate, 20 ka to the Present: U.S. Geological Survey Professional Paper 1670, 41 p.

Ross, D.A., 1978, Black sea stratigraphy, *in* Ross, D.A., Neprochnov, Y.P., and others: Initial Reports of the Deep Sea Drilling Project, v. 42, part 2, Washington (U.S. Government Printing Office), p. 17–26.

Ross, D.A., and Degens, E.T., 1974, Modern sedimentation in the Black Sea, *in* Ross, D.A., and Degens, E.T., eds., The Black Sea—Geology, chemistry and biology: American Association of Petroleum Geologists Memoir 20, American Association of Petroleum Geologists, Tulsa, Oklahoma, p. 183–199.

Ross, D.A., Neprochnov, Y.P., and others, 1978, Initial reports of the Deep Sea Drilling Project, v. 42, (U.S. Government Printing Office), Washington, D.C.

Ross, D.A., Degens, E.T., and MacIlvaine, J., 1970, Black Sea: Recent sedimentary history: Science, v. 170, p. 163–165.

Scholten, R., 1974. Role of the Bosporus in Black Sea chemistry and sedimentation*, in* Ross, D.A., and Degens, E.T., eds., The Black Sea—Geology, chemistry and biology: American Association of Petroleum Geologists Memoir 20, American Association of Petroleum Geologists, Tulsa, Oklahoma, p. 115–126.

Shimkus, K. M., and Trimonis, E. S., 1974, Modern sedimentation in the Black Sea, *in* Ross, D.A., and Degens, E.T., eds., The Black Sea—Geology, chemistry and biology: American Association of Petroleum Geologists Memoir 20, American Association of Petroleum Geologists, Tulsa, Oklahoma, p. 249–278.

Tyson, R.V., 1987, The genesis and palynofacies characteristics of marine petroleum source rocks, *in* Brooks, J., and Fleet, A. eds., Marine petroleum source rocks: Geological Society of London, p. 47–67.

Van der Meer, M.T.J., Sannngiorgi, F., Baas, M., Brinkhuis, H., Sinninghe Damste, J.S., and Schouten, S., 2008, Molecular isotopic and dinoflagellate evidence for Late Holocene freshening of the Black Sea: Earth and Planetary Science Letters, v. 267, p. 426–434.

Wedepohl, K.H., 1971, Geochemistry: New York, Holt, Rinehart, and Winston, 231 p.

Wilkin, R.T., Arthur, M.A., and Dean, W.E., 1997, History of water-column anoxia in the Black Sea indicated by pyrite framboid size distribution: Earth and Planetary Science Letters, v. 148, p. 517–525.