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A MODEL FOR IRON DEPOSITION TO EUXINIC BLACK SEA SEDIMENTS

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ABSTRACT. High degrees of Fe mineral sulfidation are found in the euxinic sediments of the Black Sea. With the short time scale of diagenesis (2000-3000 yr or less) and the slow reaction kinetics between sulfide and Fe-containing silicates, extensive sulfidation of silicate Fe cannot account for these results. Also, the extent of Fe sulfidation in Black Sea sediments is much higher than sulfidic normal marine sediments encountering similar exposure times to sulfide. Sediment trap results indicate that sulfidized Fe is delivered to the sediment with depositing organic matter and independently of lithogenic particles containing unreactive Fe silicate phases. We combine these observations and propose that Fe mineral sulfidation in the euxinic Black Sea is driven by the decomposition, by sulfate reduction, of particulate organic matter settling through the anoxic water-column as marine snow aggregates. Locally rapid rates of sulfate reduction at the site of organic decomposition produce elevated sulfide concentrations, encouraging dissolved Fe^{2+} precipitation as Fe sulfide minerals in the upper Fe-rich portion of the anoxic zone. The high deposition rate of this sulfidized Fe, compared to lithogenic particulates, generates the high extents of Fe sulfidation.

Sediments from some regions in the euxinic Black Sea have low extents of Fe sulfidation, similar to those from sulfidic normal marine environments. In some instances these low extents of sulfidation are associated with turbidites originating from the basin margins. In other instances sedimentology is poorly constrained so that an association between turbidite deposition and extents of Fe mineral sulfidation cannot be certain. We note a seasonality in the extent of Fe mineral sulfidation from sediment trap results such that in the summer months highly sulfidized Fe deposits, whereas in the winter, the depositing Fe is less sulfidized. Thus, variability in the proportion of winter-like and summer-like particle deposition can provide a mechanism, in addition to turbidites, by which variable extents of Fe mineral sulfidation can be generated in euxinic basin sediments.

INTRODUCTION

The sulfide produced from bacterial sulfate reduction reacts with Fe minerals forming a variety of metastable intermediate Fe-sulfide species and eventually pyrite (Berner, 1970, 1984). The extent to which sulfide reacts with sedimentary Fe minerals depends on the particular types of Fe minerals present, their respective reaction kinetics, and the exposure

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time of the sediment to sulfide (Canfield, Raiswell, and Bottrell, 1992). Observations from ancient sediments have shown that the highest degrees of Fe mineral sulfidation are found in euxinic environments, devoid of benthic fauna, and with sulfide-rich bottom-water (Raiswell and others, 1988). The lowest extents of sulfidation are found in normal marine environments—those with oxic bottom waters and supporting an active benthic fauna. Hence, Fe mineral sulfidation has been correlated with sedimentary depositional redox conditions (Raiswell and others, 1988).

In the standard method for assessing the degree to which sedimentary iron minerals are sulfidized, sediment samples are digested for 1 min in boiling 12 N HCl (Berner, 1970; Raiswell and Berner, 1985). This procedure extracts all iron oxide phases, as well as appreciable levels of Fe from silicate minerals, particularly chlorite and Fe-containing smectites (Raiswell, Canfield, and Berner, 1994). The iron contents thus determined (Fe-HCl) are combined with the amounts of Fe bound as sulfide (Fe-S) to yield the degree of sediment pyritization (DOP) (see Berner, 1970; Raiswell and Berner, 1985; Raiswell and others, 1988):

$$\text{DOP} = \text{Fe-S}/[\text{Fe-S} + \text{Fe-HCl}] \tag{1}$$

DOP is the parameter that has been correlated with sedimentary environment (see Raiswell and others, 1988), with values of between 0 to 0.45 indicative of deposition in normal, well oxygenated, marine waters with a well developed benthic fauna. Values of between 0.45 to 0.75 indicate a restricted environment with low or no oxygen and a limited epifauna, whereas DOP values of 0.75 to 1.0 indicate euxinic depositional conditions. Implicit is that lower bottom water oxygen leads to more sulfidic conditions, more exposure of iron minerals to sulfide, and, correspondingly, more complete pyritization.

In an effort to calibrate the extent of Fe mineral sulfidation with sedimentary environment and exposure time to sulfide, Canfield, Raiswell, and Bottrell (1992) have summarized the kinetics of the sulfidation of sedimentary iron minerals during reaction with a nominal 1 mM solution of dissolved sulfide. Results indicate that sedimentary iron minerals may be broadly separated into two groups. The first, "reactive" Fe, consists of iron oxides, all of which are consumed by reaction with sulfide on time scales of less than 1 yr (except magnetite). In fact, during sediment burial and diagenesis, sulfide generally builds into pore solution only after the Fe oxides have become completely sulfidized (Canfield, 1989; Canfield and Raiswell, 1991). The second group consists of Fe silicates whose reaction kinetics are much slower, requiring at least 10^5 yrs for significant sulfidation and more than 10^6 yrs for complete sulfidation (Canfield, Raiswell, and Bottrell, 1992; Raiswell and Canfield, 1996). On early diagenetic time scales of 10^4 yrs or less, most of the pyrite in marine sediments is thus formed from reaction between sulfide and Fe oxide minerals.

In aerobic environments, the rapidly reacting iron oxide phases deposit onto sediments as surface coatings on terrigenous detrital minerals such as clays and on the more slowly reacting Fe-containing silicates (Gibbs, 1973; Trefry and Presley, 1982). In euxinic water-bodies, such an intimate association between "reactive" Fe and detritus may not be realized due to the potential reduction and dissolution of the Fe oxide surface coatings in the anoxic water-column. In this report we discuss how circumstances unique to the Black Sea (and euxinic water-bodies in general) cause a decoupled deposition of reactive and recalcitrant Fe phases. This decoupling produces high degrees of Fe mineral sulfidation, in excess of what might be expected given the short time scale for diagenesis within Black Sea sediments.

SITE DESCRIPTION

The Black Sea is the largest modern permanently euxinic water body in the world. A strong pycnocline develops at the sea surface and extends to about 250 m depth. This pycnocline inhibits vertical mixing and enhances the stability of the anoxic interface which varies spatially and temporally between about 60 and 200 m (Brewer and Spencer, 1974; Murray and Izdar, 1989; Murray and others, 1989). A fine particulate layer (FPL) is found within the pycnocline, just above the oxic/anoxic interface and is composed primarily of fine-grained lithogenic material and Mn oxides (Neuymin, 1973, reported in Honjo and others, 1987; Kempe and others, 1991). Surface currents act to disperse this fine material widely throughout the basin (Honjo and others, 1987; Hay and others, 1990; Kempe and others, 1991). Dissolved sulfide concentrations reach maximum values of 400 to 500 μM by 1500 to 2000 m depth (Brewer and Spencer, 1974), whereas dissolved Fe^{2+} varies in concentration from maximum values of between 300 to 1000 nM just below the oxic/anoxic interface to about 40 nM by 2000 m depth (Lewis and Landing, 1991; Brewer and Spencer, 1974).

Modern sediments of the euxinic basin consist of alternating white (coccolith-dominated) and dark (siliciclastic-dominated) laminae (Hay, 1988; Lyons, ms). Millimeter-scale laminated couplets result from seasonal patterns of sediment deposition, with the white laminae associated with coccolithophorid blooms (Hay and others, 1990). The dark laminae result from diatom blooms where lithogenic material is codeposited with the sinking diatoms. Subsequent dissolution of the diatoms leaves a layer enriched in lithogenic particles (Hay and others, 1990). Laminated sediment sequences may be correlated for up to 1000 km (Hay and Honjo, 1989; Hay and others, 1991; Lyons, 1991 and ms) documenting relatively uniform depositional conditions over broad regions of the basin. However, strong regional patterns in $CaCO_3$ content (Shimkus and Trimonis, 1974) may suggest that the relative contributions of white and dark laminae vary within the basin. Alternatively, turbidites derived from the basin margins, containing low amounts of $CaCO_3$, have been found throughout the central and southern portions of the euxinic basin

(Lyons, 1991; Arthur and others, 1994). The emplacement of turbidites should contribute low $CaCO_3$ sediment and hence could influence the regional patterns in $CaCO_3$ as mentioned above. The distribution of turbidites has not, however, been systematically mapped, and the overall contribution of turbidites to broad regional surveys of sediment chemistry (Shimkus and Trimonis, 1974; Rozanov, Volkov, and Yagodinskaya, 1974) is unknown.

There is a well described sequence of sediment horizons (Ross and Degens, 1974) that have deposited since the time the Black Sea was first inundated with Mediterranean water about 9000 yr BP (Ross and Degens, 1974; Jones and Gagnon, 1994). The deposition of a pronounced sapropel layer at about 7500 yr BP is thought to indicate the initiation of euxinic conditions in the basin (Ross and Degens, 1974; Jones and Gagnon, 1994). Sometime between about 3500 to 1700 yr BP the coccolithophorid *Emiliania huxleyi* invaded the basin (Ross and Degens, 1974; Hay and others, 1991; Jones and Gangon, 1994) initiating the deposition of laminated coccolith-containing sediment couplets, defined as Unit I sediments by Hay and others. (1991). Unit I is composed of an upper layer of *E. huxleyi*-containing sediment couplets (Ross, Degens, and MacIlvaine, 1970; Ross and Degens, 1974), separated from an earlier invasion by a transition sapropel (Hay and others, 1991), comprising between 400 to 1000 years of time (Ross and Degens, 1974; Hay and others, 1991; Jones and Gagnon, 1994; Arthur and others, 1994). Unit I sediments still deposit in the euxinic basin.

METHODS

Many of the interpretations of the present study rely on previously published data (Rozanov, Volkov, and Yagodinskaya, 1974; Lyons, 1991 and ms; Lyons and Berner, 1992), and where appropriate, comments on methodology will be provided as the data are presented. New results are provided on total-Fe (Fe-T) content of sediments collected by one of us (Lyons, ms) during the 1988 Black Sea expedition (Murray, 1991). Analysis of Fe-T was performed using the wet chemical method described by Aller, Mackin, and Cox (1986), where samples were first treated for 12 hrs in a muffle furnace at 450°C and then leached for 24 hrs in near-boiling 12N HCl. This method was calibrated by Raiswell and Canfield (1996) by independent X-ray fluorescence (XRF) analysis of 30 modern sediment samples, yielding the following regression for Fe-T values ranging from 1 to 6 wt percent:

$$Fe_{XRF} = 0.997(Fe_{wet}) + 0.016 \qquad (R = 0.985)$$

We also report on Fe speciation for a number of sulfide-rich coastal sediments from Long Island Sound, Connecticut, Gulf of California, Santa Barbara Basin, and coastal Chile. Fe-T was measured as described above, and S was partitioned into acid-volatile sulfide (FeS) and pyrite following the distillation methods in Canfield and others (1986) and Canfield (1989).

RESULTS AND DISCUSSION

Fe speciation in euxinic sediments.—The speciation of Fe in euxinic basin sediments is evaluated from the data of Rozanov, Volkov, and Yagodinskaya (1974) and by combining the results of Lyons and Berner (1992) and Lyons (ms) with those derived from the new Fe-T analysis (table 1). Surface grab samples of the upper several centimeters were collected by Rozanov, Volkov, and Yagodinskaya (1974), and presumably these samples represent both the deposition of laminated Unit I sediments and turbidites, though no detailed sediment description was provided. A complete description of sediments from the 1988 expedition is given in Lyons (1991 and ms) and Lyons and Berner (1992). We note that during the 1988 expedition, both turbidites and laminated sediments were sampled, and these two sediment types are designated separately in table 1. Overall, sediments have experienced less than 2000 to 3000 yr of diagenesis. Also, an extensive region of the euxinic Black Sea basin has been explored.

Sedimentary Fe is divided into two fractions: (1) Fe that has reacted with sulfide (Fe-S), and (2) iron that has remained unreacted (Fe-U). Consistent with the kinetics of Fe mineral reactivity as mentioned above and discussed in detail in Canfield, Raiswell, and Bottrell (1992), Fe-S represents the "reactive" Fe fraction, consisting of Fe originally present as oxides, or otherwise derived from the water-column as discussed below. Fe-U represents, to a first approximation, the Fe bound in the silicate fraction of the depositing sediment. Stable S isotope data provide supporting evidence for the rapid water-column formation of Fe-S, since sedimentary sulfides within Unit I are isotopically very similar to the sulfides intercepted by sediment traps positioned at intermediate depths in the water-column (Lyons, submitted). Further, the "refractory" nature of Fe-U is demonstrated by the very limited formation of Fe-S during the burial of Unit I sediment (Lyons and Berner, 1992; Lyons, submitted).

Within the euxinic basin, the concentration of Fe-U varies inversely with $CaCO_3$ ($R = 0.92$) over the range <0.5 wt percent to around 4 wt percent Fe-U, while Fe-S shows low variability and no correlation ($R = 0.04$) with $CaCO_3$ content (fig. 1A). Hence, while Fe-U shows systematic and apparently variable dilution by $CaCO_3$ within the euxinic basin, the deposition of Fe-S displays no such trend, and in this way, the deposition of Fe-S and Fe-U are decoupled.

In addition, the fraction of total Fe sulfidized, represented by the ratio Fe-S/Fe-T, positively correlates with $CaCO_3$ (fig. 1B) and reaches values of up to 0.75 at high carbonate content. We find an apparent sedimentological control on Fe-S/Fe-T, with, using the results from the 1988 expedition, high values ranging from 0.54 to 0.75 for laminated Unit I sediments (table 1; fig. 2). For turbidite intervals, believed to originate from the basin margins (Lyons, 1991; Arthur and others, 1994), much lower values of between 0.22 to 0.33 are found.

The high amounts of Fe sulfidation observed for laminated Unit I sediments are anomalous compared to normal marine sediments (sites of

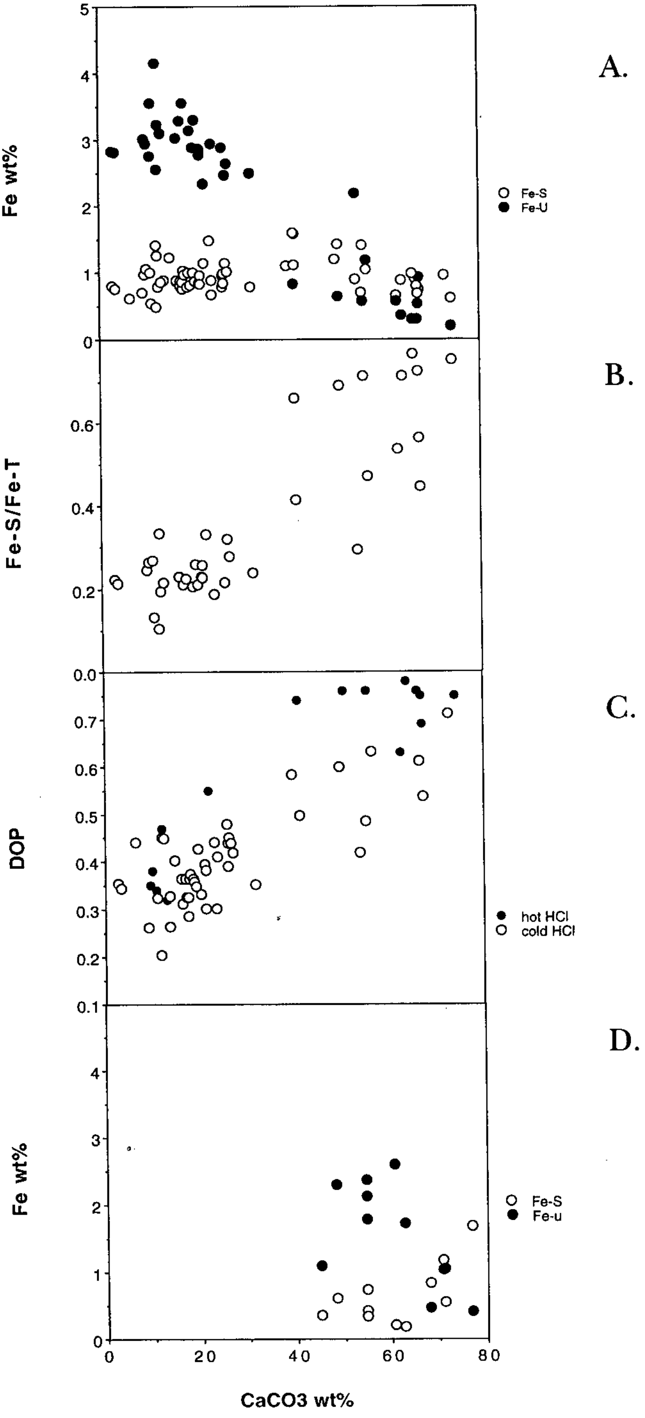

Fig. 1(A) The Fe in euxinic Black Sea sediments (laminated and turbidite) is separated into Fe bound as sulfide phases (Fe-S) and unreacted Fe that is most likely present as Fe-containing silicates (Fe-U). The concentrations of these phases are plotted as a function of sedimentary $CaCO_3$ content. (B) The proportion of total Fe present as sulfide (Fe-S/Fe-T) is plotted versus $CaCO_3$. (C) The degree of pyritization (DOP; eq 1) is plotted versus $CaCO_3$. Data utilizing both hot and a cold HCl digestions are included and give similar results. Data from Calvert and Karlin (1991) are not included as $CaCO_3$ contents were not reported. See text for details. (D) Fe-S and Fe-U are plotted against $CaCO_3$ concentration for sediment trap material from site BS.

TABLE 1

Fe speciation and $CaCO_3$ contents for euxinic Black Sea sediments with sedimentological control

Station	(depth)*	T/L**	Fe-T***	Fe-S***	Fe-U***	Fe-S/Fe-T	$CaCO_3$***
5	(0-2)	T	3.95	0.85	3.10	0.22	12.98
5	(16-18)	T	4.00	1.06	2.94	0.26	9.94
5	(30-32)	T	3.81	1.27	2.54	0.33	12.01
7	(2-4)	T	3.48	1.15	2.33	0.33	21.88
7	(8-10)	T	3.99	0.98	3.01	0.25	9.53
7	(32-34)	T	3.75	1.01	2.74	0.27	10.68
9	(6-8)	L	2.44	1.61	0.83	0.66	40.79
9	(8-10)	L	2.07	1.43	0.64	0.69	50.34
9	(12-14)	L	1.25	0.89	0.36	0.71	63.66
9	(14-16)	L	0.81	0.61	0.20	0.75	74.11
9	(20-22)	L	1.99	1.42	0.57	0.71	55.39
9	(22-24)	L	1.11	0.81	0.30	0.73	66.88
9	(24-26)	L	1.29	0.99	0.30	0.77	65.94
14	(10-12)	L	1.23	0.70	0.53	0.57	67.12
14	(20-22)	L	1.24	0.67	0.57	0.54	62.59

* depth in cm.
** T = turbidite, L = laminated.
*** wt percent.

oxic deposition) containing comparable amounts of dissolved sulfide (fig. 2). By contrast, values of Fe-S/Fe-T in normal marine sediments are similar to those from the turbidite intervals (fig. 2).

As described above, the short time scales for diagenesis in euxinic Black Sea sediments do not allow for the differences observed in Fe-S/Fe-T to result from variable extents of reaction between sulfide and the Fe silicate pool; only small amounts of such Fe should have reacted. We further note that turbidites are emplaced with no erosion of the underlying sediment (Lyons, 1991; Arthur and others, 1994). Turbidite intervals, then, have been exposed to sulfide for the same time as the immediately underlying laminated sediment; yet strong differences in the extent of Fe sulfidation occur across the turbidite/laminated sediment boundary (Lyons and Berner, 1992).

The issues raised above are two-fold. First, we must explain the mechanism(s) by which the deposition of Fe-S and Fe-U to euxinic Black Sea sediments are decoupled. Second, and possibly related, we need to explain the high extents of Fe sulfidation (high Fe-S/Fe-T) in laminated sediments. An examination of particle deposition as intercepted by sediment traps will help to clarify these issues.

Sediment traps.—From the end of October 1982 to early April 1985, an automated time series sediment trap array was maintained by Honjo and others (1987) at site BS, approx 40 km north of Amasra on the Turkish coast. In addition, between June 1986 and April 1988, particles were collected with a similar trap array at site BSC, located southwest of BS and 80 km from shore (Hay and others, 1990; Muramoto and others, 1991). Water depth at both sites was approx 2200 m, and traps were

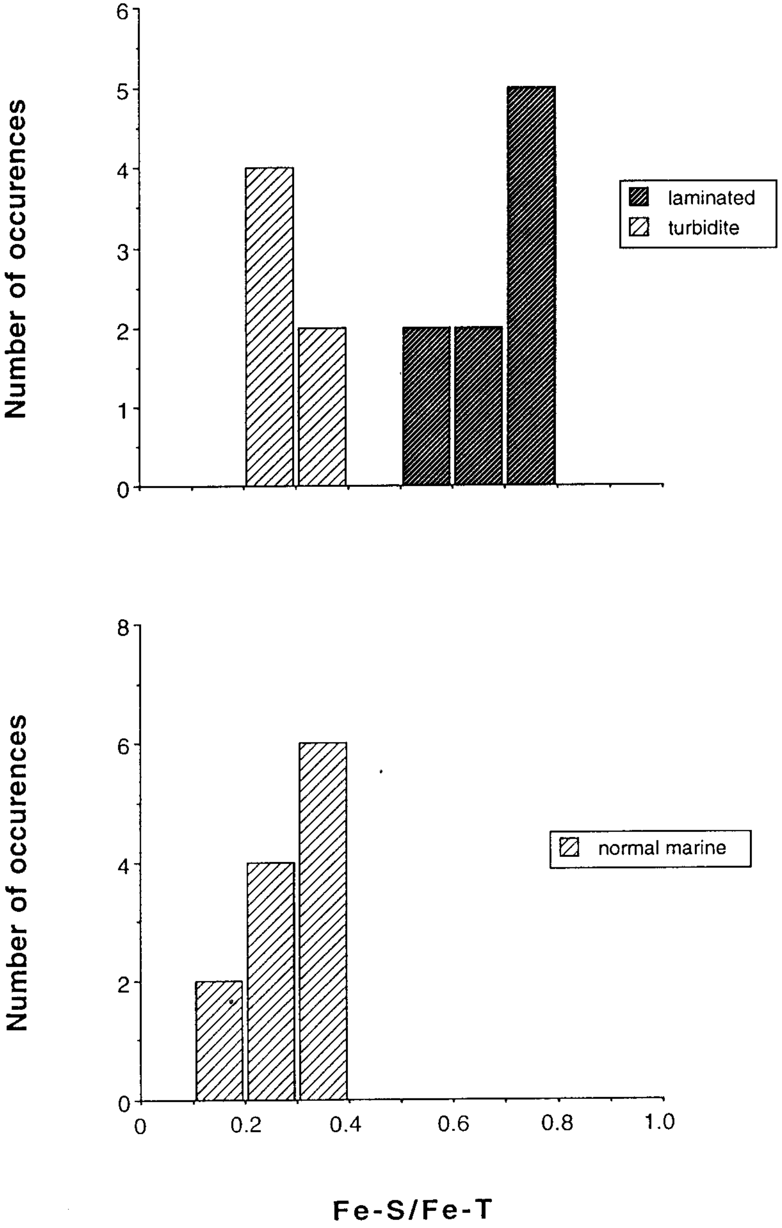

Fig. 2. The extent of total Fe sulfidation (Fe-S/Fe-T) is compared for laminated and turbidite sediments from the Black Sea and sulfide-containing normal marine sediments. Normal marine sediments are from Long Island Sound, Connecticut, Gulf of California, Santa Barbara Basin, and coastal Chile.

moored at 250 and 1200 m. A complete accounting of exact station locations, particle fluxes, and elemental compositions can be found in Honjo and others (1987), Hay and others (1990), and Muramoto and others (1991), and the reader is referred to these sources for primary information. At site BS, seasonal cycles of deposition were recorded, with summer to early winter blooms of *E. huxleyi* contributing a high flux of organic matter and $CaCO_3$ to the sediments (Honjo and others, 1987; Hay and others, 1990). High fluxes of biogenic silica were associated with winter and spring diatom blooms, while large contributions of lithogenic material were associated with riverine flooding events. The composition of sediment trap particulates from the data in Honjo and others (1987) averaged over two month intervals is presented in figure 3A. At site BSC (Hay and others, 1990), seasonal cycles of deposition were also reported, though the deposition of lithogenic material was less associated with riverine input and more with scavenging by sinking biogenic material. It is possible that the fine particulate layer (FPL) is the source of the scavenged lithogenics (Honjo and others, 1987).

From Muramoto and others (1991), concentrations of organic carbon, reduced inorganic S, and total Fe, averaged over two month periods, have been compiled and are presented in figure 3, B to D. Strong seasonal variations in the concentrations of organic carbon and S are observed, with the highest concentrations associated with high proportions of biogenic material, particularly $CaCO_3$. Also clear, and as noted by Muramoto and others (1991), a striking positive correlation is observed between the concentrations of organic carbon and reduced particulate S. Seasonality in Fe concentrations is not observed (fig. 3D, Muramoto and others, 1991), and no correlation was found by Muramoto and others (1991) between the concentrations of particulate Fe and reduced S or organic carbon. This observation led Muramoto and others (1991) to suggest that Fe and S are "associated with different major components of the bulk flux."

We develop this idea further by computing the proportion of total Fe bound as sulfide phases (Fe-S/Fe-T) assuming that S deposits with Fe with an average molar ratio Fe:S of 1:2, as in pyrite. No S speciation results are available for site BS, but for site BSC, the average mix of S found as elemental S, AVS (FeS), and pyrite (FeS_2) yields an Fe:S ratio of nearly 1:2. Uncertainties in our calculated Fe-S/Fe-T ratio are proportional to the errors imposed by our assumed S speciation, which, unfortunately, are impossible to evaluate. Results indicate, however, a strong seasonality in Fe-S/Fe-T (fig. 3E), with the highest ratios (0.6-0.8) found in summer and fall in association with high concentrations of organic carbon. These high ratios are comparable to the highest ratios observed in the sediments (figs. 1A, 2) and outside the range observed for a wide variety of sulfide-rich continental margin sediments, as well as Black Sea turbidites (fig. 2). Also, when Fe-S and Fe-U are plotted against $CaCO_3$ content the trends (fig. 1D) are reminiscent of those for the sediments in the euxinic basin (fig. 1A). However, the very low $CaCO_3$-containing,

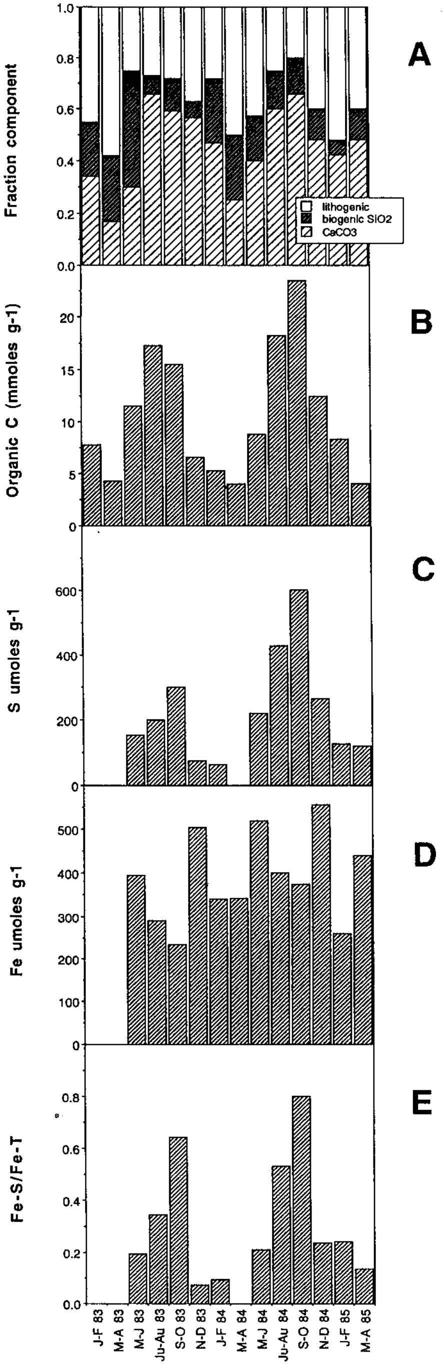

Fig. 3(A) Two month averages for the proportion of major components, including lithogenic material, biogenic SiO_2, and $CaCO_3$, are shown for particulates collected by sediment traps at 1200 m depth for site BS in the southwestern Black Sea. (B) Two month average organic matter concentrations for sediment trap material from site BS. (C) Two month average concentrations of reduced inorganic sulfur from site BS. (D) The concentration of total Fe (Fe-T) from site BS in two month averages. (E) Extent of Fe mineral sulfidation (Fe-S/Fe-T) computed over 2 month averages for site BS. See text for details.

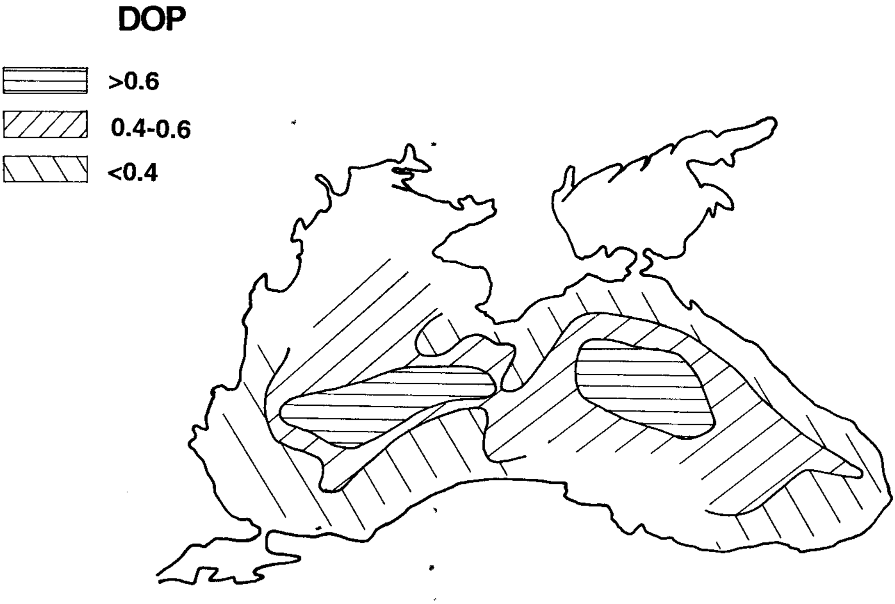

Fig. 4. Distribution of degree of pyritization (DOP) throughout the euxinic Black Sea basin. Contours generated from all available DOP data (see text).

high Fe-U sediments found in the euxinic basin are not represented in the trap material.

An accounting of seasonal variations in particulate concentrations in trap material at site BSC, as done for site BS, is complicated by a paucity of results for reduced inorganic S. However, S results were obtained from approximately August, 1986 to February, 1987, (Muramoto and others, 1991) during which a correlation was observed between the concentrations of reduced inorganic S and organic carbon, as at site BS. Also, the average molar ratio of Fe-T to S was 0.96 (Muramoto and others, 1991), yielding an average Fe-S/Fe-T of 0.52, assuming that S associates with Fe with an Fe/S ratio of ½ as discussed above. An Fe-S/Fe-T value of 0.52 is within the range of laminated Unit I sediments and outside the range for sulfidic normal marine sediments and deep-basin turbidites (fig. 2).

Model(s) for Fe and S deposition.—Integrating the above discussion, there are two mechanisms by which the deposition of sulfidized Fe (Fe-S) and unreacted Fe (Fe-U) may be decoupled, yielding the trends in Fe speciation as presented in figure 1, A and B. The first mechanism involves the independent deposition of two endmember sediment sources, each with distinct Fe speciation. Hence, turbidites, originating from the basin margins and depositing as event horizons, represent a sediment source with high amounts of unreacted silicate Fe (Fe-U), yielding low amounts of Fe sulfidation (Fe-S/Fe-T), and containing relatively low concentrations of $CaCO_3$ (table 1). Laminated Unit I sediments, by contrast, depositing from particulates dispersed in the water-column, are relatively $CaCO_3$-rich, with similar concentrations of sulfidized Fe (Fe-S) as turbidites. However, Unit I sediments have much lower amounts of unreacted Fe (Fe-U), yielding high amounts of Fe sulfidation (Fe-S/Fe-T). In this way, sediments with low $CaCO_3$ contents would consist mainly of turbidites, with their characteristic Fe speciation, whereas laminated sediments are represented at high $CaCO_3$ contents. Sampling of sediment containing both endmember types would produce chemical compositions intermediate between the two. This model is supported by the sedimentological observations and geochemical results from the 1988 Black Sea expedition (table 1; fig. 2). One difficulty with this model is that very regular patterns in the distribution of $CaCO_3$ contents are found within the deep basin of the Black Sea (Shimkus and Trimonis, 1974). This would imply a regular distribution of turbidites, yet, based on available limited information, the distribution of turbidites is very inhomogenous with impressive variability over small distances (Lyons, 1991; Arthur and others, 1994).

An alternative model is suggested by the sediment trap results from site BS, where Fe speciation varied seasonally (fig. 3). Specifically, particles with high extents of Fe sulfidation (Fe-S/Fe-T) and high $CaCO_3$ content deposit in the summer and fall when biogenic debris dominate the particle flux. In the winter and spring when lithogenic particles are more important, $CaCO_3$ content is lower, as well as the extent of Fe sulfidation (Fe-S/Fe-T). Consequently, spatial and interannual variations in Fe-S/Fe-T with $CaCO_3$ content (fig. 1B) could reflect varying relative contributions of summer/fall particle deposition and winter/spring deposition. A difficulty with this model is that particles with high concentrations of unreacted Fe (Fe-U) and low extents of Fe sulfidation (Fe-S/Fe-T), as found in some sediments in the euxinic basin (fig. 1A), have not yet been intercepted by sediment traps. Also, it is not clear the extent to which the same seasonal cycles of particle deposition, as found at site BS, represent particle deposition at other sites in the Black Sea (Hay, 1988).

Either of the above two models could be supported or rejected by further detailed work coupling sediment geochemistry with sedimentological observations, as well as further information on sediment particle fluxes and their chemical composition. Each model, however, shares a common characteristic; that is, the independent deposition, either seasonally or spatially, of "lithogenic" particulates sharing chemical characteristics of sulfidic normal marine sediments, in combination with "biogenic"-associated particles with a chemical composition all their own. This latter class of particles yields, in the Black Sea, the high degree of Fe sulfidation (high Fe-S/Fe-T), is apparently unique among modern marine sediments (though the further exploration of other euxinic basins may show similarities), and requires further explanation.

To explain the formation of this unique class of particles, we focus on two important observations (fig. 3). First, the concentration of reduced inorganic S (as well as the flux) correlates positively with organic carbon in sediment trap material (fig. 3; see above and Muramoto and others, 1991). Next, large variations in the extent of Fe sulfidation (Fe-S/Fe-T), as seen for trap material, require that reactive Fe (comprising all Fe pools contributing to Fe-S) deposits independently of unreacted Fe (Fe-U) which derives from lithogenic mineral grains. We need, then, to find a source of S related to the deposition of organic carbon, as well as a source of reactive Fe unrelated to the deposition of lithogenic mineral grains. The main clue is the association between the deposition of organic matter and S (fig. 3). We emphasize the idea, originally proposed by Muramoto and others (1991), that settling organic matter, such as marine snow aggregates, would be a likely site of elevated rates of sulfate reduction. Indeed, sulfate reduction has been observed in marine snow, even in particles submerged in well oxygenated marine water (Shanks and Reeder, 1993).

Muramoto and others (1991) proposed that "reactive" Fe oxides were scavenged by organic aggregates at the oxic/anoxic interface, to be sulfidized by sulfide produced within the aggregates in the anoxic zone. We modify this suggestion and propose that in the upper reaches of the anoxic water column, where dissolved Fe^{2+} is relatively high (Brewer and Spencer, 1974; Lewis and Landing, 1991), organic matter in settling marine snow is a site of elevated rates of sulfate reduction in the same way as described for sedimentary organic aggregates (Berner, 1980; Canfield and Raiswell, 1991; Raiswell and others, 1993). In this way, rapid rates of sulfate reduction and sulfide generation promote Fe sulfide precipitation at the site of the decomposing organic matter, depleting dissolved Fe^{2+} and establishing a diffusional flux of Fe^{2+} to the site of decomposition. Sulfidized Fe, then, is largely derived from the water-column, and the relationship between particulate S and organic matter is promoted by the decomposition of sinking, organic-rich, marine snow behaving as sites of enhanced sulfate reduction. The positive correlation between $CaCO_3$ and the extent of Fe sulfidation (Fe-S/Fe-T; fig. 1, 3) is indirect, through the association between the sinking tests of coccolithophorids and their decomposing biomass. While the $CaCO_3$ comes from the sedimenting test, the high extent of Fe sulfidation results from the addition of sulfidized Fe to the sinking, decomposing, biomass.

With this scenario for the deposition of sulfidized Fe (Fe-S), no necessary relationship between sulfidized Fe (Fe-S) and unsulfidized Fe (Fe-U) is expected, consistent with the sedimentary record and sediment trap results. This is because a large portion of the sulfidized Fe originates from dissolved Fe^{2+} in the water-column and not from the sulfidation of Fe oxide-coated, silicate Fe-containing, terrigenous clastics. Finally, the dissolved Fe^{2+} in the Black Sea water-column could originate from the chemical or biological reduction of iron oxides sinking into the anoxic waters or from the reduction and dissolution of Fe oxides at the basin margins in response to a fluctuating oxycline as proposed by Shaffer (1986) and Kempe and others (1991).

Degree of pyritization (DOP).—The decoupled deposition of Fe-S and Fe-U, as reported above, and the subsequent generation of highly sulfidized Fe, has consequences for the recognition and interpretation of paleodepositional environments using the degree of pyritization (DOP) as outlined by Berner (1970) and Raiswell and others (1988) (eq 1). In fact, DOP and the extent of total Fe sulfidation are related measures of Fe sulfidation. The difference between the two is the amount of total Fe not liberated by hot HCl in the DOP determination. Hence, values of DOP should be somewhat higher than and correlate with the extent of total Fe sulfidation (Fe-S/Fe-T).

Direct determinations of DOP utilizing the hot HCl digestion (eq 1) have been made on euxinic Black Sea sediments by Lyons (ms), Lyons and Berner (1992) and for some of these same sites by Calvert and Karlin (1991). In addition DOP may be calculated from the data in Rozanov, Volkov, and Yagodinskaya (1974). In the study of Rozanov, Volkov, and Yagodinskaya (1974) a dilute HCl digestion was employed, with exact acid concentrations and reaction conditions (time, temperature) not specified. In principle, however, such an HCl digestion may be similar to the hot 12N HCl digestion described above (eq 1) (Levanthal and Taylor, 1990). Indeed, from the trend in DOP versus $CaCO_3$ concentration (fig. 1C), it is clear that results from the hot and cold acid treatment are broadly similar. When contoured on a basin-wide scale (fig. 4), the highest values of DOP are found in the central regions of the eastern and western lobes of the basin, the same locations where $CaCO_3$ concentrations are also highest (Shimkus and Trimonis, 1974).

Overall, DOP values range from 0.2 to 0.78 (fig. 1C). The highest values are consistent with deposition in a euxinic basin as outlined above. These values are, however, inconsistent with the short amount of time available for the significant sulfidation of Fe-containing silicate phases (Canfield, Raiswell, and Bottrell, 1992; see above). Also, a large number of DOP values fall below the range indicating deposition in an euxinic environment (fig. 1C; see Raiswell and others, 1988). It is clear that factors other than simple sulfide availability and reaction kinetics are controlling DOP in Black Sea sediments. Since DOP and Fe-S/Fe-T are closely related, the same mechanism producing high extents of total Fe sulfidation (Fe-S/Fe-T) must also produce high DOP values in euxinic Black Sea sediments. High values of DOP, then, arise from the scavenging of sulfidized dissolved Fe^{2+} (contributing to Fe-S; see eq 1) from the water-column into decomposing marine snow particles where rapid sulfidation occurs. As described previously, these particles contain low amounts of lithogenic material and hence low amounts of silicate Fe to be liberated during the hot acid DOP Fe digestion. High DOP values, then, do not arise from the prolonged exposure of sedimentary Fe phases to sulfide.

These results might imply that high DOP values in other modern and ancient euxinic basins could arise from a similar mechanism, if the decoupling of Fe deposition as reported here is generally operable. We thus provide an explanation for the generation of high DOP values in euxinic basins where extensive time for Fe mineral sulfidation is not available.

CONCLUSIONS

The deposition of sulfidized Fe (Fe-S) and unreacted Fe, mostly as Fe-containing silicates (Fe-U), to euxinic Black Sea sediments is uncoupled. Hence, while Fe-U deposits with lithogenic material, Fe-S deposits with biogenic debris, particularly in association with organic carbon and $CaCO_3$ from coccolithophorid tests. Lithogenic debris is supplied from the water-column, possibly from the fine particulate layer (FPL) located along the pycnocline, as well as by turbiditic transport along the basin floor, with particles originating at the basin margin. We postulate that Fe is sulfidized in the upper dissolved Fe^{2+}-rich region of the anoxic water-column. Sulfide originates from the decomposition of organic matter in sinking marine snow particles by sulfate reduction, and Fe^{2+} diffuses from the ambient water to form Fe sulfide minerals. This mechanism explains the association between organic carbon and Fe-S in sediment trap particulates. The association between Fe-S and $CaCO_3$ is indirect through the connection between the tests of depositing organisms and their decaying biomass. Overall, basin-wide variations in the proportion of sulfidized Fe (Fe-S/Fe-T) results from variability in either the seasonal or spatial deposition of biogenic material and lithogenic debris.

In $CaCO_3$-rich Black Sea sediments up to 80 percent of the total Fe may be sulfidized, leading to very high degrees of pyritization (DOP). Whereas these DOP values are consistent with deposition in an euxinic environment, they arise from the decoupled deposition of Fe-S and Fe-U to the sediments and not from prolonged exposure of sedimentary particles to sulfide. DOP values as low as 0.2 are also found in the euxinic basin. Decoupled Fe deposition in euxinic basins, as reported here for the first time, may provide a mechanism explaining the poorly understood, but frequently observed, empirical relationship between DOP and depositional redox conditions.

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