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SOURCES AND MECHANISMS FOR THE ENRICHMENT OF HIGHLY REACTIVE IRON IN EUXINIC BLACK SEA SEDIMENTS

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ABSTRACT. The deep basinal euxinic sediments of the Black Sea are enriched in iron that is highly susceptible to sulfidization compared to oxic/suboxic continental margin sediments in the Black Sea and oxic/dysoxic continental margin and deep-sea sediments worldwide. A mass balance treatment of iron speciation data from three deep basin sediment cores shows that this enrichment is due to a combination of (1) highly reactive iron-bearing phases (sulfides and oxides) whose ultimate source was by diagenetic mobilization from the shelf (Wijsman and others, 2001) and (2) enhanced iron reactivity in the lithogenous component of deep basinal sediments. The cause of the enhanced reactivity of lithogenous iron is problematical. Possible mechanisms include microbial oxidation of non-reactive iron silicates and the preferential deposition of a fine-grained, reactive iron-enriched lithogenous component in the deep basin by the fractionation of the lithogenous flux during transport across the shelf. The application of paleoredox indicators based on iron reactivity (Degree of Pyritization, Indicator of Anoxicity) should take into account that the availability of highly reactive iron, and hence the concentration of reactive iron phases in the sediment, is controlled by a variety of chemical, physical and biological factors, some of which are not related directly to redox conditions in the water column.

INTRODUCTION

Recent studies of the Black Sea and the Cariaco Basin (Canfield and others, 1996; Raiswell and Canfield, 1998; Wijsman and others, 2001; Lyons and others, 2003) have shown that their deep-basin sediments, deposited under anoxic/euxinic bottom waters, are enriched in iron that is highly reactive towards sulfide compared to oxic continental margin and deep-sea sediments. The pool of highly reactive iron (Fe_{HR}) is defined as the sum of $FeP + FeD$ (Raiswell and Canfield, 1998), where FeP is the iron present as pyrite and FeD is the iron soluble in a dithionite extract (mainly iron oxides, see Raiswell and others, 1994). (The iron concentration terms and other parameters used in this study are listed and defined in table 1.) Enrichments in highly reactive iron comparable to the levels reported in the Black Sea have also been observed in analogous ancient sediments (Raiswell and others, 2001; Werne and others, 2002).

The mechanisms of highly reactive iron enrichment are uncertain, although several authors have suggested that lateral transport of iron from the basin margin to the interior is the dominant process (see for example, Canfield and others, 1996; Lyons, 1997; Raiswell and Canfield, 1998; Wijsman and others, 2001). The most cogent evidence for intra-basinal mobilization and transport is from Wijsman and others (2001), who demonstrated that the extent of highly reactive iron enrichment in Black Sea deep-basin sediments was within the range of iron release from oxic/dysoxic

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TABLE 1

Iron concentration terms and other parameters used in this paper (listed in the approximate order in which they appear in the text)

FeP	iron present as pyrite in the (total) sediment
FeD	iron that is soluble in a dithionite extract (mainly iron oxides)
FeHCl	iron in the sediment that is soluble during a one minute boil in 12N HCl
FeT	total iron in the sediment
DOP	Degree of Pyritization: $DOP = \frac{FeP}{FeP + FeHCl}$
IA	Indicator of Anoxicity: $IA = \frac{FeP + FeD}{FeT}$
Fe _{HR}	iron in the sediment that is highly reactive iron towards dissolved sulfide (= FeP + FeD)
Fe _{PR}	iron in the sediment that is poorly reactive towards dissolved sulfide (= FeHCl - FeD)
Fe _U	iron in the sediment that is unreactive towards dissolved sulfide (= FeT - FeP - FeHCl)
f	mass-fraction of the lithogenous component in the (total) sediment
g	mass-fraction of the biogenous component (CaCO ₃ , organic C) in the sediment
k	mass-fraction of the "imported" component (iron sulfides and reactive iron oxides) in the sediment
j	mass-fraction of iron in the imported component
Fe _L	total iron content of the lithogenous component
Fe _{ihr}	imported iron content in the sediment; all iron in the imported component is highly reactive by definition
Fe _{ip}	imported iron content in the sediment that is pyritized
K	fraction of lithogenous iron that is highly reactive to sulfidization
Q	fraction of lithogenous iron that is pyritized
m _{ihr}	slope of the Fe _{HR} -FeT regression line
b _{ihr}	intercept of the Fe _{HR} -FeT regression line
m _{ip}	slope of the FeP-FeT regression line
b _{ip}	intercept of the FeP-FeT regression line
ω	sedimentation rate
ρ	density of sediment grains
φ	bulk sediment porosity
A _{db}	fractional area of the deep euxinic basin
A _{cm}	fractional area of the continental margin

TABLE 1
(continued)

J (total sed.) _{deep basin}	flux of total sediment to the deep basin
J (Fe _{ih}) _{deep basin}	flux of imported iron to deep-basin sediments
J (total sed.) _{cont. margin}	flux of total sediments to the continental margin
J (lith. comp.) _{cont. margin}	flux of the lithogenous component to the continental margin
r	fraction of highly reactive lithogenous iron in continental-margin sediments that is dissolved and liberated
J (Fe _{diss.}) _{source area}	flux of dissolved iron released from continental-margin source regions by the reduction-dissolution mechanism of Raiswell and others (2001) (see text)
basin equiv. J (Fe _{diss.}) _{source area}	flux of dissolved iron over the entire deep-basin area that is generated by the flux from marginal source regions (see text)
J (Fe _{HR}) _{cont. margin}	flux of dissolved iron and particulate iron oxides from the margin that is generated by the diagenetic recycling mechanism of Wijsman and others (2001) (see text)
basin equiv. J (Fe _{HR}) _{cont. margin}	flux of dissolved iron and particulate iron oxides over the entire deep-basin area that is generated by the flux from the continental margin (see text)
J (lith.comp.) _{deep basin}	flux of lithogenous sediment to the deep basin
q	fraction of lithogenous sediment entering the Black Sea that is deposited in the deep basin

continental-shelf environments, as estimated from a model of diagenetic iron cycling and in situ measurements of iron fluxes. Wijsman and others (2001) proposed that highly reactive iron is transferred to the deep basin as dissolved Fe²⁺, a fraction of which was precipitated as iron sulfide and deposited. Based on results presented in a later section, we suggest that iron oxides formed by the reoxidation of Fe²⁺ mobilized from shelf sediments also contributed to the transfer of highly reactive iron, supported by effective lateral transport mechanisms, to the sediments of the deep basin. There is some independent evidence for that process operating in the Black Sea. For example, Murray and others (1995) showed that the oxidation of sulfide that occurs at the oxic/anoxic interface requires the transport of Mn and Fe oxides from the basin margins to the deep basin.

Wijsman and others (2001) suggested that intra-basinal mobilization of iron from the continental shelf probably occurs in other basins. Their contention is supported by Landing and Bruland (1987) and Saager and others (1989), who reported the shelf mobilization and lateral transport of iron in the Pacific and Indian Oceans. Intra-basinal mobilization and transport of highly reactive iron has potential significance in a variety of contexts – for example, the role of iron as a limiting nutrient on primary productivity (see for example Johnson and others, 1999), the source of iron for the origin of Banded Iron Formations (see for example Holland, 1984), and indicators of paleoredox conditions based on iron reactivity.

Paleoredox indicators based on iron reactivity are potentially able to distinguish sediments deposited under euxinic (H₂S-bearing) bottom waters from those deposited

under anoxic (Fe-bearing) or oxic bottom waters. Two paleoredox indicators have been proposed. First, Degree of Pyritization (DOP) is defined as:

$$\text{DOP} = \frac{\text{FeP}}{\text{FeP} + \text{FeHCl}} \quad (1)$$

where FeHCl is the iron soluble during a one minute boil in 12N HCl (Berner, 1970; Raiswell and others, 1994). Raiswell and others (1988) suggest that values of DOP > 0.75 represent deposition from bottom waters that are euxinic or have dissolved oxygen contents too low to support benthic fauna (0.1–0.3 ml/l O₂; Wignall, 1994). Second, Raiswell and others (2001) have proposed an Indicator of Anoxicity (IA) defined as:

$$\text{IA} = \frac{\text{FeP} + \text{FeD}}{\text{FeT}} = \frac{\text{Fe}_{\text{HR}}}{\text{FeT}} \quad (2)$$

where FeD represents the iron soluble in a dithionite extract (mainly iron oxides and small concentrations of iron-bearing silicates; see below and Raiswell and others, 1994) and FeT is the total iron in the sediment. Raiswell and others (2001) suggested that values of IA > 0.4 are apparently diagnostic for euxinic bottom waters.

Both indicators are based on the locus of sulfate reduction and pyrite formation in marine sediments. In oxic bottom waters, pyrite is formed only during diagenesis when anoxic conditions develop in the sediments (Goldhaber and Kaplan, 1974; Berner, 1984). By contrast, in euxinic environments, pyrite can form both in the water column and in the sediments (Berner, 1984; Raiswell and Berner, 1985). The extent of pyrite formation in both redox settings is commonly limited by the availability of iron phases (iron oxides and dissolved iron) that are reactive towards the dissolved sulfide generated during sulfate reduction (Canfield and others, 1992). As noted above, sediments deposited in euxinic environments tend to have relatively high concentrations of iron that was originally reactive towards dissolved sulfide and is now almost entirely converted to pyrite (Canfield and others, 1996; Raiswell and Canfield, 1998).

Both DOP and IA are sensitive to sedimentological parameters such as the availability of reactive iron (in turn dependent on grain-size and mineralogy) and siliclastic accumulation rates (Canfield and others, 1996; Lyons, 1997; Werne and others, 2002; Lyons and others, 2003). Thus, although values of DOP > 0.75 and IA > 0.4 may be diagnostic of euxinic environments, lower values do not necessarily exclude euxinic environments (Shen and others, 2002; Lyons and others, 2003). A better understanding of the sources of highly reactive iron would clearly improve the diagnostic potential of these iron paleoredox indicators.

Although there is an emerging consensus that intra-basinal mobilization of iron from continental shelves accounts for the enrichment of highly reactive iron in anoxic, sulfidic sediments, there are alternative explanations. For example, the transport of lithogenous sediment across continental shelves and deposition through anoxic water columns may enhance the reactivity of lithogenous iron towards dissolved sulfide, resulting in a relatively high iron sulfide content. Such an enhancement of iron reactivity may operate in addition to intra-basinal iron mobilization and transport. In this paper, we quantify the extent of reactive iron enrichment in the deep-basin euxinic sediments of the Black Sea that arise from (1) intra-basinal mobilization and transport and (2) enhanced reactivity, and attempt to identify the mechanisms involved in those enrichments.

EVIDENCE FOR IRON ENRICHMENT

Quantifying the extent of reactive iron enrichment requires a measure of reactive contents in anoxic sediments and a set of base-line data against which the degree of

enrichment is assessed. Two criteria of reactive iron enrichment have been used. The first is high values of the ratio of Fe_{HR} to FeT (Raiswell and Canfield, 1998; Raiswell and others, 2001). The second is high values of the FeT/Al ratio (Werne and others, 2002; Lyons and others, 2003).

The first criterion is based on the mechanism of pyrite formation in anoxic marine environments, where a fraction of the dissolved sulfide produced by microbial sulfate reduction reacts with dissolved Fe^{2+} in the water-column or with certain iron-bearing minerals (Bernier, 1970, 1984). The initial reaction products are often iron sulfide minerals, which are transformed to pyrite by reaction with dissolved sulfide (Rickard, 1997; Rickard and Luther, 1997) and/or polysulfides (Goldhaber and Kaplan, 1974; Rickard, 1975; Luther, 1991; Schoonen and Barnes, 1991). Modern sediment studies (Canfield, 1989; Canfield and Raiswell, 1991; Canfield and others, 1992) have shown that iron oxides (ferrihydrite, goethite, hematite and lepidocrocite) react rapidly with dissolved sulfide. However, only relatively small fractions of silicate iron react even over time-scales of millions of years (Canfield and others, 1992; Raiswell and Canfield, 1996). In general (except in deep-sea sediments) the amount of H_2S generated exceeds the amount of iron oxide available. Thus, in many basin-margin sediments, the concentration of pyrite is limited by the concentration of reactive oxide iron.

As noted above, the concentration of iron that is highly reactive towards dissolved sulfide (Fe_{HR}) is the sum of the iron that has already reacted with sulfide (FeP , iron present as pyrite or other sulfides) plus iron extracted by dithionite (FeD , iron present as oxides plus small amounts from silicates; Raiswell and others, 1994). The small concentrations of silicate-bound iron extracted by dithionite may not be reactive towards dissolved sulfide. Thus, our measure of Fe_{HR} is operational and may overestimate slightly the concentration of highly reactive iron. However, we believe that the error introduced by including dithionite-extractable silicate iron as a component of highly reactive iron is small enough to be ignored. Normalizing Fe_{HR} to FeT has several advantages: (1) it corrects for the dilution effects of biogenous sediment, and (2) it provides some correction for grain-size effects where higher Fe_{HR} is associated with higher FeT in more fine-grained material (Forstner, 1989; Secieru and Secieru, 2002). Values of Fe_{HR}/FeT that are higher than the upper range for base-line data (that is, lithogenous sediments deposited in oxic environments) suggest an addition to the Fe_{HR} pool by highly reactive iron from an external source (intra-basinal mobilization) or by enhanced reactivity of lithogenous iron.

The second criterion for recognizing highly reactive iron enrichment in anoxic sediments is the occurrence of relatively high values of the FeT/Al ratio (Werne and others, 2002; Lyons and others, 2003). This criterion assumes that values of FeT/Al higher than those for base-line data are due solely to additions to Fe_{HR} . Thus, the FeT/Al criterion is not sensitive to highly reactive iron enrichment that arises from enhancement in the reactivity of lithogenous iron (and hence may limit its utility as a paleoredox indicator). Use of the FeT/Al ratio also eliminates the effects of dilution by biogenous sediment and provides some correction for grain-size effects (see Forstner, 1989); nonetheless, small changes in the Fe_{HR} fraction may be difficult to identify within a large FeT content.

In this paper, we use the criterion of elevated Fe_{HR}/FeT ratios to identify enrichment in highly reactive iron. The choice of base-line data is somewhat problematical. Raiswell and Canfield (1998) used a threshold Fe_{HR}/FeT value of 0.4, which represents the upper limit for a geographically widespread compilation of oxic continental margin and deep-sea sediments. This approach may, however, fail to detect enrichments in highly reactive iron imposed on local detrital sediment fluxes that have Fe_{HR}/FeT ratios well below the typical 0.4 threshold. In principle, it is preferable to identify reactive iron enrichments by comparison with oxic sediments within the same basin. Werne and others (2002) and Lyons and others (2003) used this

approach for the detection of reactive iron enrichment via FeT/Al ratios. The application of this approach for either the FeT/Al or Fe_{HR}/FeT criterion assumes that there is relatively little or no intra-basinal fractionation of iron and thus that the composition of lithogenous components deposited in marginal and deep-basin sites are identical. As discussed in a subsequent section, this assumption may not be valid.

SOURCES OF IRON FOR EUXINIC ENRICHMENT

Anoxic environments, such as the Black Sea and the Cariaco Basin, have stratified water columns that are well oxygenated at the surface but depleted in dissolved oxygen (O₂) with depth. Early results on the Black Sea water column indicated that O₂ declines to zero at about 125m, but H₂S first appears at 95m. Thus, O₂ and H₂S coexist over a thin zone, which varies laterally and seasonally (Sorokin, 1964, 1983). Once O₂ is removed, dissolved iron can be liberated through the microbial reduction and dissolution of iron oxide-bearing grains. Concentrations of dissolved iron increase sharply to a maximum of 1 μM at about 120 to 180m depth (Brewer and Spencer, 1974). Dissolved sulfide progressively increases through this zone and continues to accumulate down to the sediment surface. More recent data suggests that the O₂/H₂S interface has shoaled (Murray and others, 1989; Jørgensen and others, 1991; but compare Anderson and others, 1994), with O₂ declining to 5 μM at 55m and H₂S appearing at 95m depth. No coexistence of O₂ and H₂S was reported, but a suboxic interval with O₂ < 5 μM existed between 55 to 95m (Murray and others, 1989). These data also show dissolved iron increasing to a maximum at about 200m depth (Lewis and Landing, 1991) or more (Haraldsson and Westerlund, 1988). Deeper waters are saturated with FeS at all depths below the dissolved iron maximum (Landing and Lewis, 1991).

Collectively, these data suggest a generalized state of the water column in which there is an upper layer where dissolved iron is relatively high and through which dissolved sulfide rapidly increases to approach saturation with FeS (fig. 1). Below this zone, dissolved iron decreases rapidly but dissolved sulfide continues to increase, maintaining saturation with FeS. Iron sulfides can precipitate in two ways in such water columns. The first process occurs through sulfate reduction in the upper, iron-rich layer. Organic matter in settling biogenous-rich debris is degraded by sulfate reduction in the dissolved iron-rich regions of the water column, with the resulting H₂S producing local supersaturation and precipitation of iron sulfides (Canfield and others, 1996). The second process occurs through the transport of dissolved iron into the lower, sulfide-bearing layer, and vice versa. For example, eddy diffusion in the Black Sea transports iron downwards into the sulfide zone and sulfide up into the iron zone (Brewer and Spencer, 1974; Lewis and Landing, 1991); in both cases precipitation as iron sulfides may occur.

Now, consider a flux of lithogenous sediment depositing through a stratified water column with a dissolved iron-rich layer overlying a sulfidic layer. A portion of the pyrite that precipitates in the water column results from the sulfidization of iron from external sources that are decoupled from the local lithogenous flux: dissolved Fe²⁺ released from marginal sediments by microbial diagenesis, and particulate highly reactive iron oxides formed by oxidation of a fraction of that mobilized Fe²⁺. Pyrite precipitation by this process may occur so long as dissolved Fe²⁺ and highly reactive iron oxides are transported from their marginal sources to the deep-basin water column. In addition, highly reactive iron oxides in the lithogenous sediment can be pyritized either in the water column or after deposition. In either case, the concentration of highly reactive iron oxides in the lithogenous sediment limits the amount of pyrite that can be formed from that source. Thus, the maximum FeP/FeT ratio in the sediment is limited by the amount of external, decoupled iron supplied to the water column and the maximum Fe_{HR}/FeT ratio of the lithogenous component. The latter ratio should be determined largely by provenance but may be modified (increased or

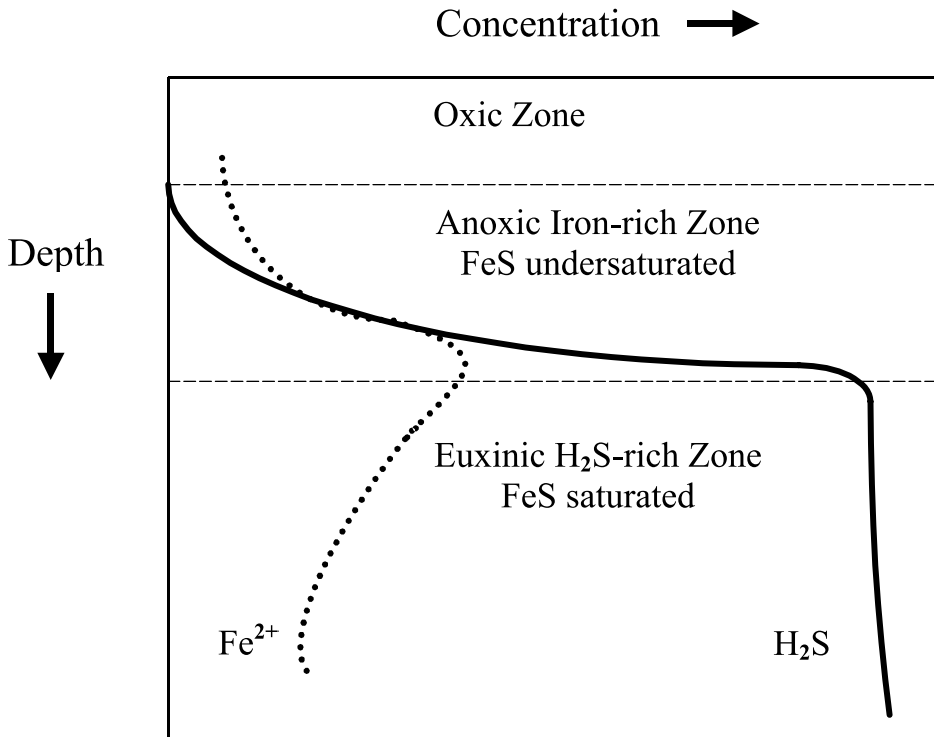


Fig. 1. Generalized geochemistry of the Black Sea water column.

decreased) by processes that occur during lateral transport and deposition through the stratified water column, such as margin-to-basin fractionation of reactive iron oxides and chemical and microbial alteration of iron-bearing phases.

Thus, the sources of iron for enrichment in anoxic/euxinic basins fall into two broad categories based on the relationship between the flux of highly reactive iron from external sources and the flux of lithogenous sediment. First, dissolved Fe^{2+} and suspended iron oxides from the oxidation of Fe^{2+} in the water column can be derived from the basin margin. Highly reactive iron from this source is separated (and decoupled) from the flux of lithogenous sediment to the deep basin. Second, iron oxides are supplied by lithogenous sediment transported to the deep basin. Highly reactive iron from this source is always associated (coupled) with a lithogenous sediment component. The distinction between iron sources that are decoupled from or coupled to lithogenous sediment is important and forms the basis for the quantitative treatment of sources developed in a subsequent section.

RESULTS

The results utilized in this paper are summarized in tables 2 - 5. Table 2 presents the results for euxinic, deep-basin sediments for three cores from the Black Sea (Stations 9 and 14: Calvert and Karlin, 1991; Lyons, 1992; Lyons and Berner, 1992; Lyons, 1997; Raiswell and Canfield, 1998; and Station 22: Wijsman and others, 2001). Results from modern sediments deposited in oxic and dysoxic continental-shelf and deep-sea environments are given in table 3 (Raiswell and Canfield, 1998). Table 4 gives the results for basin-margin sediments from the northwestern Black Sea (Wijsman and others, 2001). The content of biogenous sediments was not reported for those cores.

TABLE 2

Iron contents (wt. %) and weight-fraction biogeneous sediment (CaCO₃ + organic C) for euxinic sediments from the deep basin of the Black Sea. Average value (\pm std. dev.). Stations 9 and 14 from Lyons (ms, 1992), Lyons and Berner (1992), Calvert and Karlin (1991) and Raiswell and Canfield (1998). Station 22 from Wijsman and others (2001). (Three samples from Station 9 for which FeP \geq FeT where excluded.)

	Station 9 <i>R.V. Knorr</i> (1988) (n=16)	Station 14 <i>R.V. Knorr</i> (1988) (n=19)	Station 22 <i>R.V. Prof.</i> <i>Vodyanitsky</i> (1997) (n=10)	Combined Results of the Three Stations
FeT	1.76 (\pm 0.62)	1.97 (\pm 0.58)	1.92 (\pm 0.43)	1.88 (\pm 0.57)
FeP	1.35 (\pm 0.42)	1.11 (\pm 0.34)	0.87 (\pm 0.17)	1.15 (\pm 0.39)
FeD	0.14 (\pm 0.06)	0.25 (\pm 0.09)	0.01 (\pm 0.01)	0.16 (\pm 0.11)
FeHCl	0.38 (\pm 0.17)	0.64 (\pm 0.20)	0.38 (\pm 0.14)	0.48 (\pm 0.21)
FeHR	1.49 (\pm 0.46)	1.36 (\pm 0.39)	0.88 (\pm 0.17)	1.31 (\pm 0.45)
FePR	0.24 (\pm 0.11)	0.39 (\pm 0.12)	0.37 (\pm 0.13)	0.32 (\pm 0.14)
FeU	0.03 (\pm 0.22)	0.23 (\pm 0.26)	0.67 (\pm 0.26)	0.24 (\pm 0.34)
FeP/FeT	0.77 (\pm 0.08)	0.56 (\pm 0.12)	0.45 (\pm 0.06)	0.61 (\pm 0.08)
FeHR/FeT	0.85 (\pm 0.12)	0.69 (\pm 0.12)	0.46 (\pm 0.06)	0.70 (\pm 0.19)
FePR/FeT	0.13 (\pm 0.03)	0.20 (\pm 0.03)	0.19 (\pm 0.06)	0.17 (\pm 0.05)
FeU/FeT	0.02 (\pm 0.11)	0.11 (\pm 0.12)	0.35 (\pm 0.08)	0.13 (\pm 0.17)
wt. fract. biog. sedts.	0.68 (\pm 0.08)	0.60 (\pm 0.08)	n.r. ¹	0.64 (\pm 0.09) ²

¹Not reported.

²Assuming that the weight fraction of biogenous sediments at Station 22 is the average of Stations 9 and 14.

We have listed in table 4 the biogenous content for the nearest stations (Wijsman, 2001). The results in table 5 are for turbiditic sediments from the Black Sea basin (Rozanov and others, 1974; see also Raiswell and Canfield, 1998). More recent results on turbidites in Wilkin and Arthur (2001) and Lyons and Berner (1992) are comparable with the data of Rozanov and others (1974).

The tabulated results give the concentration of the analytically determined iron pools FeD (dithionite-extractable iron from reactive iron oxides), FeHCl (iron extracted by HCl from iron oxides and some iron-silicates such as chlorite and nontronite), and FeP (sulfidized iron) as well as total iron (FeT). Those determinations allow us to define three operational iron fractions of different reactivity toward dissolved sulfide (Raiswell and Canfield, 1998). The sum FeP + FeD represents iron oxides that were highly reactive towards dissolved sulfide at deposition ($Fe_{HR} = FeP + FeD$). The difference between the iron soluble in HCl and that soluble in dithionite represents iron that is poorly reactive towards dissolved sulfide ($Fe_{PR} = FeHCl - FeD$). The difference between the total iron and sulfidic iron plus HCl-soluble iron represents iron that is essentially unreactive towards dissolved sulfide ($Fe_U = FeT - FeP - FeHCl$). The concentration of these operationally defined iron fractions and their ratios with respect to total iron are given in the tables.

TABLE 3

Iron contents (wt. %) and weight-fraction biogenous sediment (CaCO₃ + organic C) for continental-margin and deep-sea sediments deposited in aerobic and dysaerobic environments (Raiswell and Canfield, 1998). Average value (\pm std. dev.)

	Continental Margin (n=46)	Deep-Sea (n=56)	Dysoxic (n=26)	Total (n=128)
FeT	2.92 (\pm 0.78)	3.07 (\pm 1.20)	3.42 (\pm 1.06)	3.09 (\pm 1.06)
FeP	0.09 (\pm 0.14)	0.06 (\pm 0.10)	0.57 (\pm 0.32)	0.17 (\pm 0.27)
FeD	0.73 (\pm 0.34)	0.66 (\pm 0.32)	0.36 (\pm 0.34)	0.63 (\pm 0.36)
FeHCl	1.32 (\pm 0.36)	1.45 (\pm 0.72)	1.43 (\pm 0.71)	1.40 (\pm 0.62)
FeHR	0.82 (\pm 0.31)	0.71 (\pm 0.33)	0.93 (\pm 0.46)	0.80 (\pm 0.36)
FePR	0.64 (\pm 0.27)	0.78 (\pm 0.59)	1.06 (\pm 0.51)	0.80 (\pm 0.51)
FeU	1.46 (\pm 0.39)	1.58 (\pm 0.74)	1.43 (\pm 0.64)	1.49 (\pm 0.62)
FeP/FeT	0.03 (\pm 0.05)	0.02 (\pm 0.03)	0.19 (\pm 0.11)	0.06 (\pm 0.09)
FeHR/FeT	0.28 (\pm 0.06)	0.23 (\pm 0.10)	0.27 (\pm 0.10)	0.26 (\pm 0.09)
FePR/FeT	0.22 (\pm 0.07)	0.25 (\pm 0.15)	0.31 (\pm 0.09)	0.26 (\pm 0.12)
FeU/FeT	0.50 (\pm 0.06)	0.52 (\pm 0.16)	0.42 (\pm 0.12)	0.48 (\pm 0.13)
wt. fract. biog. sed.	0.22 (\pm 0.16) ¹	0.31 (\pm 0.24) ¹	— ¹	0.26 (\pm 0.21) ¹

¹Biogenous content reported for 26 of 46 continental-margin sediments, 39 of 56 deep-sea sediments, no dysaerobic sediments.

Different techniques were used to determine the FeD and FeHCl in Black Sea sediments. Wijnsman and others (2001) measured FeHCl by a cold 1N HCl extraction, which extracts less iron from silicates (as well as from goethite and hematite; see Raiswell and others, 1994) than the boiling 12N HCl technique used by Raiswell and Canfield (1998). For example, the results of Leventhal and Taylor (1990) and of experiments conducted by us suggest that about 10 percent less iron is extracted from modern anoxic sediments by the “cold” HCl method than the “hot” HCl method. Accordingly, sediments analyzed by the “cold” HCl method (for example, table 2, Station 22; table 4) would have comparatively lower Fe_{PR} and Fe_{PR}/FeT values and higher Fe_U and Fe_U/FeT values than the same sediments analyzed by the “hot” HCl method (see for example, table 2, Stations 9 and 14; table 3; table 5). We tested the effect of normalizing the “cold” FeHCl results of Wijnsman and others (2001) to “hot” FeHCl using our and Leventhal and Taylor’s (1990) results. The changes in iron contents and ratios are small enough to ignore. In addition, some of the Black Sea literature data used by Raiswell and Canfield (1998) only have values for FeHCl and/or the iron extractable by hydroxylamine hydrochloride. Raiswell and Canfield (1998) estimated FeD for these data by cross-calibrating from the FeHCl and hydroxylamine hydrochloride iron values. Wijnsman and others (2001) suggested that cross-calibration resulted in values of FeD and hence Fe_{HR} that are too high (see table 2). We have reassessed the cross-calibration method of Raiswell and Canfield (1998) by determining

TABLE 4
Iron contents (wt. %) for sediments from the northwest margin of the Black Sea (Wijsman and others, 2001). Average value (\pm std. dev.)

	Delta Areas			Central Shelf					Shelf Edge			Total
	Sta. 2 (n =12)	Sta. 13 (n=12)	Total (n=24)	Sta. 6 (n=12)	Sta. 9 (n=12)	Sta. 10 (n=11)	Sta. 16 (n=11)	Total (n=46)	Sta. 19 (n=11)	Sta. 24 (n=11)	Total (n=22)	(n=92)
FeT	4.33 (± 0.41)	1.48 (± 1.03)	2.91 (± 1.64)	1.27 (± 0.42)	2.72 (± 0.74)	1.32 (± 0.47)	0.71 (± 0.13)	1.49 (± 0.87)	2.60 (± 1.06)	1.97 (± 0.63)	2.27 (± 0.90)	2.05 (± 1.27)
FeP	0.15 (± 0.16)	0.08 (± 0.05)	0.12 (± 0.12)	0.17 (± 0.13)	0.28 (± 0.23)	0.13 (± 0.17)	0.05 (± 0.06)	0.16 (± 0.18)	0.24 (± 0.33)	0.22 (± 0.23)	0.23 (± 0.28)	0.17 (± 0.20)
FeD	0.33 (± 0.14)	0.27 (± 0.19)	0.30 (± 0.16)	0.18 (± 0.16)	0.07 (± 0.05)	0.06 (± 0.10)	0.08 (± 0.10)	0.10 (± 0.12)	0.46 (± 0.69)	0.01 (± 0.01)	0.23 (± 0.52)	0.18 (± 0.29)
FeHCl	1.43 (± 0.19)	0.52 (± 0.23)	1.01 (± 0.51)	0.75 (± 0.20)	0.95 (± 0.21)	0.50 (± 0.41)	0.58 (± 0.19)	0.70 (± 0.31)	1.02 (± 0.58)	0.45 (± 0.12)	0.73 (± 0.50)	0.79 (± 0.44)
Fe _{HR}	0.48 (± 0.19)	0.36 (± 0.20)	0.42 (± 0.20)	0.35 (± 0.10)	0.35 (± 0.18)	0.20 (± 0.15)	0.14 (± 0.08)	0.26 (± 0.16)	0.70 (± 0.60)	0.23 (± 0.23)	0.45 (± 0.50)	0.35 (± 0.30)
Fe _{PR}	1.09 (± 0.17)	0.28 (± 0.20)	0.72 (± 0.45)	0.57 (± 0.09)	0.87 (± 0.19)	0.43 (± 0.34)	0.49 (± 0.13)	0.59 (± 0.26)	0.56 (± 0.21)	0.44 (± 0.12)	0.50 (± 0.18)	0.60 (± 0.32)
Fe _U	2.76 (± 0.45)	0.84 (± 0.69)	1.77 (± 1.20)	0.35 (± 0.40)	1.50 (± 0.66)	0.69 (± 0.43)	0.08 (± 0.22)	0.64 (± 0.68)	1.34 (± 0.61)	1.30 (± 0.50)	1.32 (± 0.55)	1.10 (± 0.95)
FeP/FeT	0.03 (± 0.04)	0.05 (± 0.06)	0.04 (± 0.05)	0.13 (± 0.09)	0.10 (± 0.07)	0.10 (± 0.13)	0.07 (± 0.09)	0.11 (± 0.10)	0.09 (± 0.12)	0.11 (± 0.10)	0.10 (± 0.10)	0.08 (± 0.09)
Fe _{HR} /FeT	0.11 (± 0.04)	0.24 (± 0.12)	0.14 (± 0.12)	0.28 (± 0.08)	0.13 (± 0.05)	0.15 (± 0.12)	0.20 (± 0.14)	0.17 (± 0.12)	0.27 (± 0.13)	0.12 (± 0.09)	0.20 (± 0.13)	0.17 (± 0.12)
Fe _{PR} /FeT	0.25 (± 0.04)	0.19 (± 0.27)	0.25 (± 0.18)	0.45 (± 0.18)	0.32 (± 0.10)	0.33 (± 0.23)	0.69 (± 0.24)	0.40 (± 0.25)	0.22 (± 0.12)	0.22 (± 0.14)	0.22 (± 0.13)	0.29 (± 0.23)
Fe _U /FeT	0.64 (± 0.05)	0.57 (± 0.24)	0.61 (± 0.19)	0.27 (± 0.23)	0.55 (± 0.11)	0.52 (± 0.28)	0.11 (± 0.32)	0.43 (± 0.32)	0.51 (± 0.09)	0.66 (± 0.11)	0.58 (± 0.12)	0.54 (± 0.28)
wt. fract. biog.seds ¹	0.11	0.11	0.11 (± 0.00)	0.32	0.11	0.44	0.53	0.33 (± 0.18)	0.30	0.36	0.33 (± 0.04)	0.28 (± 0.16)

¹Biogenous content not reported for these cores. Results are from nearby stations (Wijsman, ms, 2001).

TABLE 5
Iron contents (wt. %) and weight-fraction biogeous sediment (CaCO₃ + organic C) for turbiditic sediments from the deep Black Sea basin (Rozanov and others, 1974; Raiswell and Canfield, 1998). Average value (± std. dev.)

FeT	3.52 (±0.71)
FeP	0.91 (±0.19)
FeD	0.14 (±0.14)
FeHCl	1.36 (±0.45)
FeHR	1.05 (±0.22)
FePR	1.24 (±0.43)
FeU	1.26 (±0.66)
FeP/FeT	0.26 (±0.09)
FeHR/FeT	0.30 (±0.09)
FePR/FeT	0.35 (±0.10)
FeU/FeT	0.35 (±0.14)
wt. fract. biog. seds.	0.28 (±0.18)

the iron extractable in dithionite, hydroxylamine hydrochloride, and boiling HCl from a suite of 27 marine sediments representing a range of depositional environments. Our results confirm that the cross-calibration method of Raiswell and Canfield (1998) for determining FeD was appropriate. Finally, Raiswell and Canfield (1998) estimated FeD and FeHCl for Black Sea turbiditic sediments (table 4) from the analytical data of Rozanov and others (1974); see Raiswell and Canfield (1998) for details.

A MASS-BALANCE MODEL OF IRON SOURCES

Consider a sediment made-up of lithogenous particles (silicates, oxides, etc.) and biogenous debris (CaCO₃, organic C, biogenic SiO₂) settling through a stratified (oxic/anoxic/euxinic) water column of a sedimentary basin. During deposition, a component comprised predominantly of iron sulfides and reactive iron oxides is added to the sediment. The source of the “imported” iron in those sulfides and oxides was the mobilization and transport of iron from the basin margin.

Mass-balance requires that the sum of mass-fractions of the lithogenous, biogenous, and imported component equal unity, that is:

$$f + g + k = 1 \quad (3)$$

where f , g , and k are the mass-fractions of the lithogenous, biogenous, and imported component, respectively. Assuming that biogenous component contains negligible iron, the total iron content can be expressed as:

$$\text{FeT} = f * \text{Fe}_L + \text{Fe}_{\text{thr}} \quad (4)$$

where Fe_L is the total iron content of the (undiluted) lithogenous component, and Fe_{ihr} is the imported iron content of the total sediment. (All of the iron in the imported component is highly reactive by definition.) Thus, total iron content is the sum of contributions from a lithogenous-coupled source ($f * Fe_L$) and a lithogenous-decoupled source (Fe_{ihr}).

The mass fraction of the lithogenous component, f , can be determined from equation (3) given the measured value of g (mass-fraction of biogenous components) and an estimated value of k (mass-fraction of the imported component) defined as:

$$k = \frac{Fe_{ihr} \text{ (wt. \%)} * 10^{-2}}{j} \quad (5)$$

where j is the mass-fraction of Fe in the imported component. The value of j depends on the proportions of iron sulfides and iron oxides in the imported component. For an imported component made up of pyrite (FeS_2) and hematite (Fe_2O_3), j may vary from 0.47 for 100 percent FeS_2 to 0.70 for 100 percent Fe_2O_3 . As shown in a subsequent section (see table 8), about 90 percent of the iron in the imported component in Black Sea euxinic sediments occurs as pyrite and 10 percent as oxide, equivalent to an imported component consisting of 95 percent FeS_2 and 5 percent Fe_2O_3 . The corresponding j value for this composition is 0.48, which we use to estimate k , the mass-fraction of the imported component.

The expression for pyritic iron content is analogous to that for total iron:

$$FeP = f * Q * Fe_L + Fe_{ip} \quad (6)$$

where Q is the fraction of lithogenous iron that is pyritized (that is, the ratio of pyritic iron to total iron in the lithogenous component) and Fe_{ip} is the imported iron content of the sediment that is pyritized. As with FeT , pyritic iron is expressed as the sum of contributions from a lithogenous-coupled source ($f * Q * Fe_L$) and a lithogenous-decoupled source (Fe_{ip}).

Dithionite-extractable iron (FeD) remaining in the sediment is derived from lithogenous iron as well as from (non-pyritized) reactive iron oxides in the imported component:

$$FeD = f * (K - Q) * Fe_L + (Fe_{ihr} - Fe_{ip}) \quad (7)$$

where K is the fraction of lithogenous iron that is highly reactive to sulfidization (the ratio of highly reactive iron to total iron in the lithogenous component). The content of highly reactive iron is thus:

$$Fe_{HR} = FeP + FeD = f * K * Fe_L + Fe_{ihr} \quad (8)$$

The model has five unknown parameters: the total and pyritized imported iron content of the total sediment (Fe_{ihr} and Fe_{ip} , respectively), the concentration of iron in the lithogenous component (Fe_L), and two reactivity coefficients of lithogenous iron (Q and K). The model parameters are related to one another and to analytical iron-pool contents through the three independent equations (4), (6), and (8). Rearranging terms in those equations leads to the following useful expressions:

$$Fe_L = \frac{FeT - Fe_{ihr}}{f} \quad (9)$$

$$Q = \frac{FeP - Fe_{ip}}{f * Fe_L} = \frac{FeP - Fe_{ip}}{FeT - Fe_{ihr}} \quad (10)$$

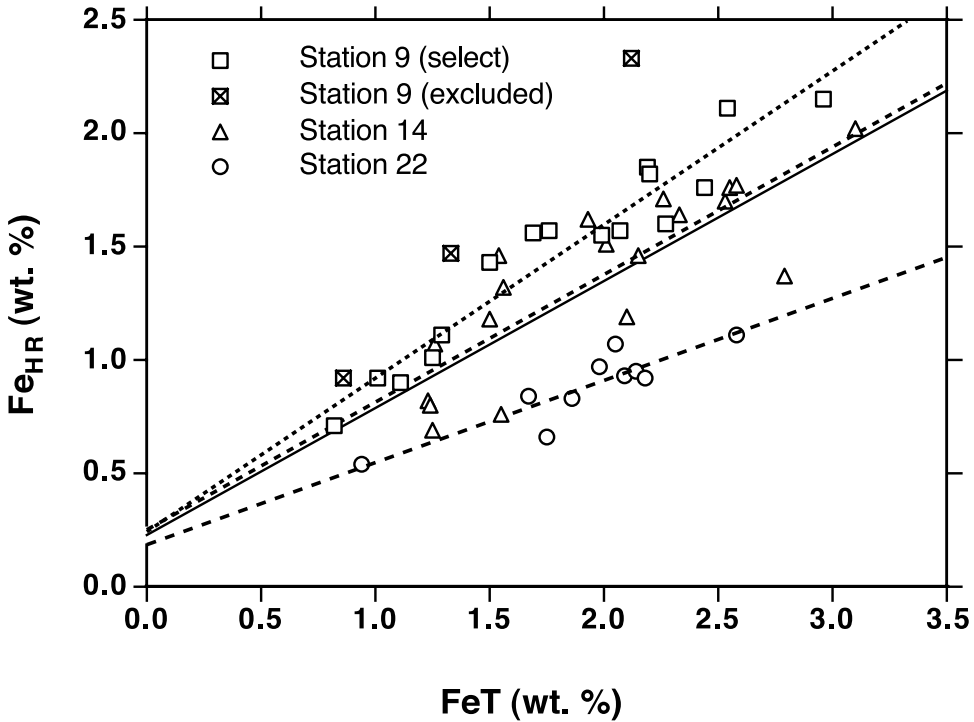


Fig. 2. Fe_{HR} versus FeT for euxinic Black Sea sediments. A least-squares best-fit regression line was calculated for each station and for the combined data from the three stations. The parameters of the lines are shown in table 8. Station 9: open squares, dotted line; Station 14: open triangles, short-dashed line; Station 22: open circles, long-dashed line; Combined: solid line. Three samples from Station 9 for which $Fe_{HR} \geq FeT$ were excluded from the best-fit calculations; those samples are plotted in the figure (crossed squares).

$$K = \frac{Fe_{HR} - Fe_{ihr}}{f * Fe_L} = \frac{Fe_{HR} - Fe_{ihr}}{FeT - Fe_{ihr}} \quad (11)$$

Imported iron should be negligible to absent in most of the oxic-dysoxic sediments considered in this study. In particular, mobilization of iron from the margin sediments of the Black Sea and transport to the deep basin would deplete the former in highly reactive iron (Wijsman and others, 2001). As discussed in a later section, iron may be mobilized and transported from continental-shelf sediments to deep-sea sediments in general. Thus, continental margins (including the Black Sea) should be sources, not sinks, for imported iron. The correlation of Fe_{HR} with FeT for deep-sea sediments shown by Raiswell and Canfield (1998, fig. 2, p. 227) suggest that the contribution of imported iron to highly reactive iron is negligible in those sediments. The contribution of imported iron in Black Sea turbiditic sediments is also likely to be small. Thus, for sediments in which Fe_{ihr} and Fe_{ip} approach zero, equations (9), (10), and (11) become:

$$Fe_L = \frac{FeT}{f} \quad (12)$$

$$Q = \frac{FeP}{FeT} \quad (13)$$

TABLE 6
Mass-balance model parameters for environments where contribution from an imported iron component is negligible

	Q (= FeP/FeT)	K (= Fe _{HR} /FeT)	Fe _L (= FeT/f)
Continental Margin (table 3)	0.03 (±0.05)	0.28 (±0.06)	3.84 (±0.91)
Deep-Sea (table 3)	0.02 (±0.03)	0.23 (±0.10)	4.15 (±1.14)
Dysoxic (table 3)	0.19 (±0.03)	0.27 (±0.10)	---
Total (table 3)	0.06 (±0.05)	0.26 (±0.09)	4.01 (±1.03)
Black Sea Delta Area (table 4)	0.04 (±0.09)	0.14 (±0.12)	3.27 (±2.29)
Black Sea Central Shelf (table 4)	0.11 (±0.10)	0.17 (±0.12)	2.20 (±0.66)
Black Sea Shelf Edge (table 4)	0.08 (±0.10)	0.20 (±0.13)	3.39 (±0.44)
Total (table 4)	0.08 (±0.09)	0.17 (±0.12)	2.77 (±1.16)
Black Sea Turbidites (table 5)	0.26 (±0.09)	0.30 (±0.09)	5.00 (±0.53)

$$K = \frac{Fe_{HR}}{FeT} \quad (14)$$

The values of those model parameters for oxic-dysoxic sediments (tables 3 - 5) are given in table 6. For continental-margin and deep-sea sediments, the average K value is 0.26 with relatively little variation (± 0.09), as noted previously by Raiswell and Canfield (1998). Average Q values are higher in dysoxic sediments (0.19) than in oxic sediments (0.02 - 0.03), suggesting a greater extent of lithogenous iron pyritization in the former. The lithogenous iron content (Fe_L) of oxic continental-margin and deep-sea sediments are in the range 4.0 ± 1.0 weight percent, compatible with but somewhat lower than the mean of other literature estimates (for example, 4.9 ± 0.4 weight percent from Poulton and Raiswell, 2002).

K values for Black Sea marginal sediments (0.17 ± 0.12) are lower than other marginal environments. This comparison prompted Wijsman and others (2001) to suggest that highly reactive iron is transported from oxic marginal settings in the Black Sea to the deep basin. Q values for Black Sea marginal sediments (0.08 ± 0.09) are intermediate between those of oxic and dysoxic sediments in the world ocean. The lithogenous iron content of Black Sea marginal sediments (2.8 ± 1.2 wt. %) is low relative to other marine sediments. Black Sea turbiditic sediments have an average K value (0.30 ± 0.09) comparable to continental-margin and deep-sea sediments but higher than Black Sea marginal sediments. In addition, the average Q value for turbiditic sediments (0.26 ± 0.09) is high, implying that most of the highly reactive lithogenous iron in Black Sea turbidites has been pyritized. The observation that the K value of turbidites is higher than that of marginal sediments may imply that the turbidites are sourced from anoxic upper slope sediments rather than the oxic/dysoxic shelf sediments (see Lyons, 1997). The lithogenous iron content of turbidites (5.0 ± 0.5 wt. %) is consistent with the values noted previously for marine sediments.

Application of the mass-balance model to deep basinal euxinic sediments of the Black Sea is problematic because there are more unknown parameters (5) than independent relationships involving those parameters (3). However, systematic varia-

TABLE 7
Parameters of Fe_{HR} -FeT and FeP-FeT regression lines for euxinic Black Sea sediments

	Station 9	Station 14	Station 22	Combined	
Fe_{HR} vs. FeT	slope, m_{ihr}	0.68	0.56	0.36	0.56
	intercept, b_{ihr}	0.24	0.25	0.19	0.23
	std.dev. on b_{ihr} , $\sigma(b_{ihr})$	± 0.12	± 0.21	± 0.08	± 0.16
	corr. coeff., r_{ihr}^2	0.93	0.70	0.79	0.83
FeP vs. FeT	slope, m_{ip}	0.61	0.47	0.36	0.48
	intercept, b_{ip}	0.23	0.18	0.19	0.22
	std.dev. on b_{ip} , $\sigma(b_{ip})$	± 0.19	± 0.33	± 0.08	± 0.14
	corr. coeff., r_{ip}^2	0.89	0.66	0.77	0.80

tions among analytical iron pools provide a method for estimating the mean and range of uncertainty (standard deviation) for each of the model parameters. A feature of the deep basinal sediments that has not previously been identified or discussed is the strong correlation between Fe_{HR} and FeT. Figure 2 shows Fe_{HR} versus FeT plots for the data from Stations 9, 14, and 22. A least-squares linear regression was calculated for the data set of each station as well as for the combined data, using conventional statistical methods (and neglecting the analytical uncertainty in each iron pool). The parameters of those linear regressions are given in table 7.

The importance of Fe_{HR} versus FeT linear correlations for evaluating model parameters is demonstrated by solving equation (11) for Fe_{HR} :

$$Fe_{HR} = K * FeT + (1 - K) * Fe_{ihr} \quad (15)$$

Equation (15) is a linear expression of Fe_{HR} as a function of FeT with

$$\text{slope, } m_{ihr} = K \quad (16)$$

$$\text{intercept, } b_{ihr} = (1 - K) * Fe_{ihr} \quad (17)$$

Combining equations (16) and (17) yields an expression for Fe_{ihr} :

$$Fe_{ihr} = \frac{b_{ihr}}{1 - m_{ihr}} \quad (18)$$

Thus, the slope and intercept of the Fe_{HR} versus FeT line allow us to calculate the mean value of the parameters K and Fe_{ihr} for the deep basinal stations. The value of Fe_L for each sample from a station is calculated from equation (9) by substituting the mean Fe_{ihr} value for that station. The model parameters derived from the Fe_{HR} versus FeT correlations are shown in table 8.

Pyritic iron (FeP) also correlates well with total iron (FeT) in deep basinal sediments of the Black Sea (fig. 3). Given that FeP is the dominant contributor to Fe_{HR} , this correlation is expected. The parameters of the FeP versus FeT least-squares linear regressions for each station and the combined data are also shown in table 7.

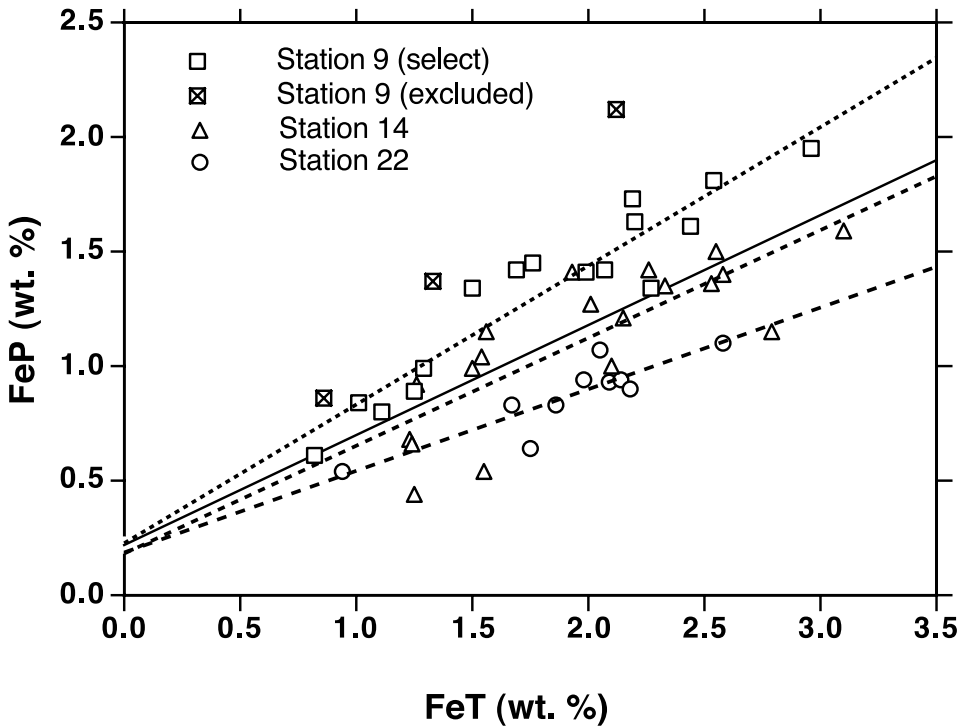


Fig. 3. FeP versus FeT for euxinic Black Sea sediments. See figure 2.

Evaluation of model parameters Q and Fe_{ip} follows the procedure described above. Thus, rearranging terms in equation (10) yields a linear relation between FeP and FeT:

$$FeP = Q * FeT + (Fe_{ip} - Q * Fe_{ihr}) \quad (19)$$

$$\text{slope, } m_{ip} = Q \quad (20)$$

$$\text{intercept, } b_{ip} = Fe_{ip} - Q * Fe_{ihr} \quad (21)$$

Rearranging equation (21) yields an expression for Fe_{ip} :

$$Fe_{ip} = b_{ip} + Q * Fe_{ihr} = b_{ip} + b_{ihr} * \frac{m_{ip}}{1 - m_{ihr}} \quad (22)$$

The model parameters derived from the FeP versus FeT correlations are also shown in table 8.

One important result from the mass-balance model is a quantitative estimate of the imported iron deposited in deep-basinal, euxinic Black Sea sediments. Average imported highly reactive iron contents (Fe_{ihr}) are 0.76, 0.57, and 0.29 weight percent in Stations 9, 14, and 22, respectively (table 8); average Fe_{ihr} for the combined euxinic data is 0.52 ± 0.16 weight percent. Average contents of imported highly reactive iron that is pyritized (Fe_{ip}) are 0.69, 0.45, and 0.29 weight percent for those stations; average Fe_{ip} for the combined data is 0.47 ± 0.14 weight percent. The difference between Fe_{ihr} and Fe_{ip} (0.05 wt. %) represents imported reactive iron oxides (or relatively nonreactive iron-bearing silicates) that escaped pyritization. The combined average imported iron contents are equivalent to about 40 (± 20) percent of both the average total and

TABLE 8
Mass-balance model parameters for euxinic Black Sea sediments
See text for derivations

	Station 9	Station 14	Station 22	Combined
$K = (\text{Fe}_{\text{HR}}/\text{FeT})_{\text{lith.comp.}}$	0.68 (± 0.05)	0.56 (± 0.09)	0.36 (± 0.07)	0.56 (± 0.08)
$Q = (\text{FeP}/\text{FeT})_{\text{lith.comp.}}$	0.61 (± 0.06)	0.47 (± 0.08)	0.36 (± 0.07)	0.48 (± 0.07)
Fe_{hr} (wt. %)	0.76 (± 0.12)	0.57 (± 0.22)	0.29 (± 0.08)	0.52 (± 0.16)
Fe_{ip} (wt. %)	0.69 (± 0.13)	0.45 (± 0.20)	0.29 (± 0.09)	0.47 (± 0.14)
$\text{FeT lith.comp} = \text{FeL}$ (wt. %) ¹	3.07 (± 1.35)	3.56 (± 1.43)	4.79 (± 0.96)	3.83 (± 1.27)

¹Neglecting three samples from each station that deviate most widely from average Fe_{L} .

pyritized highly reactive Fe at those stations (average Fe_{HR} and FeP contents are shown in table 2). The remaining fractions of highly reactive and pyritic iron must be derived from lithogenous iron [equations (6) and (8)].

The average lithogenous iron content from the model for euxinic Black Sea sediments (3.8 ± 1.3 wt. %, table 8) is consistent with the global average for continental-margin and deep-sea sediments (table 6) and other literature values (Poulton and Raiswell, 2002). But the model results indicate that lithogenous iron delivered to deep-basinal, euxinic environments of the Black Sea is more "reactive" than in the other settings considered here. The average value of the parameter K (fraction of lithogenous iron that is highly reactive to sulfidization) for the combined euxinic data is 0.56 ± 0.08 . In contrast, the average K value for continental-margin and deep-sea sediments is 0.26 ± 0.09 (table 3). Moreover, as noted by Raiswell and Canfield (1998) and discussed previously, the expected maximum $\text{Fe}_{\text{HR}}/\text{FeT}$ for those sediments is about 0.4. As well, average K values for Black Sea marginal sediments (0.17 ± 0.12) and turbidites (0.30 ± 0.09) are less than those for euxinic sediments (table 6).

In summary, the results of the mass-balance model of iron sources for euxinic Black Sea sediments indicate that (1) about 40 percent of the highly reactive iron is derived from imported components and (2) iron in the lithogenous component must account for the rest of the highly-reactive fraction and thus is unusually reactive. In other words, the enrichment of highly reactive iron in euxinic Black Sea sediments is attributable to both lithogenous-decoupled and lithogenous-coupled sources. We evaluate possible mechanisms for those sources in the following sections.

IMPORTED IRON COMPONENTS DECOUPLED FROM LITHOGENOUS SOURCES

Proposals for the source of lithogenous-decoupled imported iron to the deep Black Sea basin (and perhaps other basins) involve mobilization of reactive iron components from the continental margin and their transport to the deep basin. Currents at about the depths of the suboxic zone and the sulfide interface have lateral velocities of about 0.5 cm s^{-1} (Buesseler and others, 1991); those currents provide a potential mechanism for the supply of dissolved and suspended particulate iron from the basin margin to the interior (Kempe and others, 1990; Wijnsman and others, 2001).

Imported Iron Extracted by the Chemocline

Raiswell and others (2001) suggested that iron oxides are reduced and dissolved from margin sediments where the anoxic, iron-bearing zone of the water column

impinges on the margin floor. Dissolved iron can then be transported by advection and diffusion within the suboxic/anoxic iron-rich part of the water column and re-distributed to deep-basin regions. Dissolved iron profiles in the deep-basin water column (Brewer and Spencer, 1974; Haraldsson and Westerlund, 1988) suggest that the depth zone where dissolved iron exceeds dissolved sulfide is less than 100 meters (see fig. 1). Iron extraction effects along the margin could operate over a somewhat larger depth range due to short-term oscillations of the chemocline of up to 60 to 80 meters (Bryantsev and others, 1988; Kempe and others, 1990; Lyons and others, 1993; Anderson and others, 1994) assisted by shoaling (but see Tugrul and others, 1992; Anderson and others, 1994). The fine particulate layer in the Black Sea water column, extending over a zone of up to 300 meters from just above the chemocline (see Brewer and Spencer, 1974; Kempe and others, 1990), may also be a source of particulate iron extracted from marginal sediments by chemocline processes as described (see also below).

Steady-state mass-balance requires that the overall rate at which imported iron is deposited in the deep basin be equal to the overall rate at which lithogenous-decoupled iron is released from the continental margin. The flux (rate per unit area) of imported iron to deep-basin sediments is calculated by:

$$J(\text{Fe}_{\text{ihr}})_{\text{deep basin}} = J(\text{total sed.})_{\text{deep basin}} * 10^{-2} * \text{Fe}_{\text{ihr}} \quad (23)$$

where $J(\text{Fe}_{\text{ihr}})_{\text{deep basin}}$ is the flux of imported iron to deep-basin sediments, $J(\text{total sed.})_{\text{deep basin}}$ is the flux of total sediment to the deep-basin, and Fe_{ihr} = imported total iron content in weight percent. The total-sediment flux to the deep-basin is given by:

$$J(\text{total sed.})_{\text{deep basin}} = \omega * \rho * (1 - \varphi) \quad (24a)$$

where ω is the sedimentation rate, ρ is the density of sediment grains, and φ is the bulk sediment porosity. Sedimentation rates for the deep basin are in the range 0.013 to 0.028 cm yr^{-1} (Arthur and others, 1994; Hay, 1998; Pilskaal and Pike, 2001). We use $0.02 \pm 0.007 \text{ cm yr}^{-1}$ for the mean and standard deviation. We assume a sediment-grain density of $2.6 \pm 0.1 \text{ g cm}^{-3}$ and a bulk-sediment porosity of 0.86 ± 0.04 (Wijsman and others, 2001). The average flux of total sediments to the deep basin is thus

$$J(\text{total sed.})_{\text{deep basin}} = 7,300 (\pm 3,300) \mu\text{g cm}^{-2} \text{ yr}^{-1} \quad (24b)$$

Estimates of total imported iron contents for deep-basin euxinic sediments are given in table 8. The corresponding imported-iron fluxes are:

$$\text{Sta. 9: } J(\text{Fe}_{\text{ihr}})_{\text{deep basin}} = 55 (\pm 27) \mu\text{g cm}^{-2} \text{ yr}^{-1} \quad (25a)$$

$$\text{Sta. 14: } J(\text{Fe}_{\text{ihr}})_{\text{deep basin}} = 42 (\pm 25) \mu\text{g cm}^{-2} \text{ yr}^{-1} \quad (25b)$$

$$\text{Sta. 22: } J(\text{Fe}_{\text{ihr}})_{\text{deep basin}} = 21 (\pm 11) \mu\text{g cm}^{-2} \text{ yr}^{-1} \quad (25c)$$

$$\text{Combined: } J(\text{Fe}_{\text{ihr}})_{\text{deep basin}} = 38 (\pm 28) \mu\text{g cm}^{-2} \text{ yr}^{-1} \quad (25d)$$

The overall rate of imported iron deposition is the product of the flux times the area of the euxinic basin, which is about 73 percent of the total area of the Black Sea (Sorokin, 1983; Wijsman and others, 2001).

The flux of dissolved iron released from continental-margin source regions by the reduction-dissolution mechanism of Raiswell and others (2001), $J(\text{Fe}_{\text{diss.}})_{\text{source area}}$, can be estimated from a modification of equation 23:

$$J(\text{Fe}_{\text{diss.}})_{\text{source area}} = J(\text{lith. comp.})_{\text{cont. margin}} * \text{init.}(\text{Fe}_{\text{HR}})_{\text{cont. margin}} * r \quad (26)$$

where $J(\text{lith. comp.})_{\text{cont. margin}}$ is the flux of the lithogenous component of total sediments on the continental margin, $\text{init.}(\text{Fe}_{\text{HR}})_{\text{cont. margin}}$ is the initial highly reactive

iron content of the continental margin, and r is the fraction of initial highly reactive iron that is dissolved and liberated from oxic/dysoxic shelf sediments. First, we calculate the flux of total sediments following equation (24a). Sedimentation rates on the continental margin of the Black Sea are in the range 0.11 to 0.22 cm yr^{-1} (Winguth and others, 2000). We adopt 0.17 ± 0.04 cm yr^{-1} for the mean and standard deviation. We assume the same values for sediment-grain density and bulk-sediment porosity as for deep-basin sediments. The corresponding average flux of total sediments to the continental margin is thus:

$$J (\text{total seds.})_{\text{cont. margin}} = 62,000 (\pm 23,000) \mu\text{g cm}^{-2} \text{yr}^{-1} \quad (27)$$

We obtain the flux of lithogenous sediment by correcting the total-sediment flux for the biogenous flux. The results in table 4 suggest the biogenous fraction of marginal sediments is 0.28 ± 0.16 , corresponding to a lithogenous fraction of 0.72 ± 0.16 . Accordingly, the flux of lithogenous sediment to the continental margin is:

$$J (\text{lith. comp.})_{\text{cont. margin}} = 45,000 (\pm 19,000) \mu\text{g cm}^{-2} \text{yr}^{-1} \quad (28)$$

The initial highly reactive iron content of the continental margin is calculated from the product $\text{init. } (\text{Fe}_{\text{HR}}/\text{FeT})_{\text{cont. margin}} * \text{init. } (\text{Fe}_{\text{L}})_{\text{cont. margin}}$, where $\text{init. } (\text{Fe}_{\text{HR}}/\text{FeT})_{\text{cont. margin}}$ is the initial ratio of highly reactive to total iron and $\text{init. } (\text{Fe}_{\text{L}})_{\text{cont. margin}}$ is the initial lithogenous iron content. We assume that $\text{init. } (\text{Fe}_{\text{HR}}/\text{FeT})_{\text{cont. margin}}$ was 0.23 ± 0.09 , a value set higher than the measured ratio (0.17 ± 0.12) to compensate for the loss of Fe_{HR} by diagenetic mobilization and transport to deep basinal sediments (see table 9 and explanatory text). Likewise, we assume that $\text{init. } (\text{Fe}_{\text{L}})_{\text{cont. margin}}$ was 3.0 ± 1.2 weight percent, compared to the measured value of 2.8 ± 1.2 weight percent. For those values, we obtain $\text{init. } (\text{Fe}_{\text{HR}})_{\text{cont. margin}} = 0.7 \pm 0.4$ weight percent. The fraction of highly reactive iron in the marginal source area that is reduced, dissolved, and liberated is unknown. If 100 percent of the highly reactive iron was liberated and transported to the deep basin (that is, $r = 1.00$, a most unlikely situation), then from equation 26 the maximum flux of dissolved iron from the source area is:

$$\begin{aligned} \text{max. } J (\text{Fe}_{\text{diss.}})_{\text{source area}} &= 45,000 (\pm 19,000) \mu\text{g cm}^{-2} \text{yr}^{-1} * 0.007 (\pm 0.004) * 1.00 \\ &= 310 (\pm 220) \mu\text{g cm}^{-2} \text{yr}^{-1} \end{aligned} \quad (29)$$

This source flux could be generated in the suboxic/anoxic part of the water column where dissolved Fe exceeds dissolved sulfide. Fe_{HR} can be extracted where this zone of the water column intersects the seafloor. This zone is about 100 meters thick (see above) and occurs at a depth of more than 100 meters below the redox interface. Deuser (1974) showed the relationship between basin area and water depth in the Black Sea. His results suggest that the depth zone where reduction and dissolution of iron oxides may occur (about 100 - 200 m) occupies only about 3 percent of the total-basin area. Thus, a flux of dissolved iron from 3 percent of the basin is distributed (assumed to be uniformly) over the entire deep-basin floor, which occupies 73 percent of the total-basin area (Sorokin, 1983; Wijsman and others, 2001). Accordingly, the "basin-equivalent" flux for this source is:

$$\begin{aligned} \text{basin equiv. } J (\text{Fe}_{\text{diss.}})_{\text{source area}} &= (0.03/0.73) * 310 (\pm 220) \mu\text{g cm}^{-2} \text{yr}^{-1} \\ &= 13 (\pm 9) \mu\text{g cm}^{-2} \text{yr}^{-1} \end{aligned} \quad (30)$$

Comparing the result from equation (30) to those of equations (25) suggests that the maximum potential reduction/dissolution source from the continental margin ($13 \mu\text{g cm}^{-2} \text{yr}^{-1}$) is small relative to the average imported flux of highly reactive iron to the deep basin ($38 \mu\text{g cm}^{-2} \text{yr}^{-1}$). Oscillations in the chemocline would not significantly change this comparison. Thus, the reduction-dissolution mechanism cannot alone

TABLE 9

Calculated composition of the lithogenous component of Black Sea deep-basinal euxinic sediment and possible sources for those sediments

	$(\text{Fe}_{\text{HR}}/\text{FeT})_{\text{lith.comp.}}$	$(\text{Fe}_{\text{PR}}/\text{FeT})_{\text{lith.comp.}}$	$(\text{Fe}_{\text{U}}/\text{FeT})_{\text{lith.comp.}}$	$\text{FeT}_{\text{lith.comp.}}$ = Fe_{L} (wt. %)
Black Sea euxinic sediments				
Sta. 9	0.68±0.05	0.28±0.10	0.04±0.22	3.1±1.4
Sta. 14	0.56±0.09	0.28±0.07	0.16±0.18	3.6±1.4
Sta. 22	0.36±0.07	0.23±0.07	0.41±0.09	4.8±1.0
Combined	0.56±0.08	0.25±0.04	0.19±0.25	3.8±1.3
Black Sea marginal sediments (table 4)	0.17±0.12	0.29±0.23	0.54±0.28	2.8±1.2
Black Sea marginal sediments prior to Fe_{HR} transport to the deep basin (see text for explanation)	0.23±0.12	0.27±0.22	0.50±0.27	3.0±1.2
Continental margin and deep-sea sediments (table 3)	0.26±0.09	0.26±0.12	0.48±0.13	4.0±1.0
Danube River particulates (Poulton and Raiswell, 2002)	0.42±0.05	0.24±0.02	0.35±0.04	5.8±0.1
World mean riverine particulates (Poulton and Raiswell, 2002)	0.43±0.03	0.25±0.01	0.31±0.02	4.8±0.2

account quantitatively for the transfer of highly reactive iron to deep-basin sediments, although it may be a minor contributory source.

Imported Iron Extracted by Diagenetic Recycling

Wijsman and others (2001) suggested that iron oxides recycled in microbial iron reduction during early diagenesis of marginal sediments are a potential source of highly reactive iron to the deep basin of the Black Sea (their fig. 5). Much of this iron is re-oxidized at the sediment-water interface, but a fraction escapes the sediment and enters the water column. This fraction decreases as the bottom-water oxygenation levels increase; nonetheless, as much as 10 percent may escape even in well-oxygenated waters. In the chemocline model, this flux of dissolved iron can be transported to the basinal regions provided that it enters the anoxic, iron-rich portion of the water column. However, in the diagenetic recycling model discussed here, a fraction of the dissolved (ferrous) iron is oxidized to colloidal (ferric) iron oxides that remain suspended during transportation (for example, in the fine particulate layer; see also below). Those iron oxides would be reduced again when they enter the anoxic, iron-rich zone of the water column in the deep basin.

The flux of iron from margin to basin by the recycling mechanism of Wijsman and others (2001) depends on the fraction of highly reactive iron deposited on the margin that is liberated. The extent of iron liberation varies inversely with bottom-water oxygen concentration. Wijsman and others (2001) report oxygen concentrations from their Black Sea margin sites ranging from 350 μM at Sta. 13 on the Dneister Delta to 126 μM at Sta. 19 on the shelf edge; the average and standard deviation are 250 ± 23 μM . From their model of iron recycling, the corresponding extent of iron liberation is 0.38 ± 0.20 . In other words, 38 ± 20 percent of the highly reactive iron initially deposited in margin sediments is transformed to dissolved ferrous iron and suspended iron oxides and is available for transport to the deep basin. The flux of dissolved and particulate iron from the margin by this recycling mechanism is the product of the extent of liberation (0.38 ± 0.20) and the flux of highly reactive iron to the margin [see equations (26) and (29)]:

$$\begin{aligned} J(\text{Fe}_{\text{HR}})_{\text{cont. margin}} &= (0.38 \pm 0.20) * 310 (\pm 220) \mu\text{g cm}^{-2} \text{yr}^{-1} \\ &= 120 (\pm 100) \mu\text{g cm}^{-2} \text{yr}^{-1} \end{aligned} \quad (31)$$

Assuming that the source area for diagenetic recycling and release of iron is the entire continental margin, 27 percent of the basin area, then the “basin-equivalent” flux from this source is:

$$\begin{aligned} \text{basin equiv. } J(\text{Fe}_{\text{HR}})_{\text{cont. margin}} &= 140 (\pm 120) \mu\text{g cm}^{-2} \text{yr}^{-1} * [0.27/0.73] \\ &= 44 (\pm 38) \mu\text{g cm}^{-2} \text{yr}^{-1} \end{aligned} \quad (32)$$

We derived previously (equation 25d) that the accumulation flux of imported highly reactive iron in combined deep-basin sediments is $38 (\pm 28) \mu\text{g cm}^{-2} \text{yr}^{-1}$, or a margin-equivalent source flux of $100 (\pm 80) \mu\text{g cm}^{-2} \text{yr}^{-1}$ ($= 38 \pm 28 * 0.73 / 0.27$). Comparing the source flux to the accumulation flux suggests that diagenetic iron recycling on the continental margin is an adequate source for sustaining the accumulation of imported highly reactive iron in deep-basin sediments. Wijsman and others (2001) reached the same conclusion starting from somewhat different assumptions about the basin and margin fluxes of reactive iron. Our calculations suggest that 80 to 90 percent of the potential flux of reactive iron from the margin is deposited in the deep sea. The remainder is presumably redeposited on the shelf as iron oxides, compensating in part for the net transfer of highly reactive iron to the deep basin.

The critical factors which control the amount of reactive iron imported to the deep basin area are the re-mobilization flux of iron from the shelf area, the efficiency

with which this iron is exported and fixed in the deep basin, and the ratio of the shelf source area to the deep basinal sink. Shelf sediments will be most effective sources when the near-surface oxic layer is thin or absent. Under those conditions, the trapping of dissolved iron (released during anoxic diagenesis) by precipitation as oxides is minimized. Iron fluxes from the inner Mississippi delta have been estimated as about $1000 \mu\text{g cm}^{-2} \text{yr}^{-1}$ by Trefry and Presley (1982). Iron fluxes from Black Sea shelf sediments are of a similar magnitude (10 to $3800 \mu\text{g cm}^{-2} \text{yr}^{-1}$ with a mean of $940 \mu\text{g cm}^{-2} \text{yr}^{-1}$; Friedl and others, 1998). Wijsman and others (2001) suggested that much of this iron will be re-deposited on the shelf and will not reach the deep basin area, whereas our results suggest that most (80 - 90%) of the liberated iron is transported to the deep basin. In any case, the iron that is exported from the shelf will be re-distributed over the deep basin area. In the Black Sea the ratio of shelf source area (< 200m depth) to the deep basinal sink is 0.27 / 0.73 or 0.37 (see earlier). The comparable global ratio of shelf area to deep basin for the major oceans is 0.075. Given similar iron mobilization rates from their shelf areas, and similar export efficiencies, anoxic basins like the Black Sea will receive more imported iron to their deep basinal areas than the world oceans simply because of the higher ratio of shelf source area to the deep basinal sink area.

The dispersed iron flux to deep-sea sediments in the world oceans is termed "authigenic" and is considered to be derived from iron dissolved in seawater, supplied either from land or released during near-surface diagenesis (Chester, 2000). Measured authigenic fluxes of iron into deep-sea sediments range up to $3 \mu\text{g cm}^{-2} \text{yr}^{-1}$ (Krishnaswami, 1976; Thomson and others, 1984). This flux could be derived from shelf source areas generating iron at about $1000 \mu\text{g cm}^{-2} \text{yr}^{-1}$, exporting at a net efficiency of 4 percent, and re-distributing the exported iron globally to be diluted over deep basin sediments at a shelf : basin ratio of 0.075. We conclude that the iron mobilization mechanisms of Wijsman and others (2001) are indeed widespread, but that their significance in the Black Sea derives from the comparatively large shelf source area compared to the deep-basin sink area.

ENHANCED IRON REACTIVITY OF LITHOGENOUS SEDIMENT

The results of our mass-balance model of iron sources suggests that about 60 percent of reactive-iron enrichment in euxinic Black Sea sediments is due to unusually reactive iron in the lithogenous component of the sediment. Enhanced reactivity could arise either because the lithogenous material arriving in the deep basin was relatively enriched in reactive iron, or because anoxic or euxinic conditions in the water column enhanced the reactivity of the lithogenous iron. Some insight into the nature of the processes that produce enhanced reactivity is gained by estimating the iron-pool ratios and contents of the lithogenous fraction in the euxinic Black Sea sediments and comparing those values to composition of possible sources of deep-basinal sediments (table 9).

For the lithogenous component of any given sediment or suite of sediments, iron mass-balance requires that $\text{Fe}_{\text{HRlith.comp.}} + \text{Fe}_{\text{PRlith.comp.}} + \text{Fe}_{\text{Ulith.comp.}} = \text{Fe}_{\text{Tlith.comp.}} = \text{Fe}_{\text{L}}$ and hence $(\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}})_{\text{lith.comp.}} + (\text{Fe}_{\text{PR}}/\text{Fe}_{\text{T}})_{\text{lith.comp.}} + (\text{Fe}_{\text{U}}/\text{Fe}_{\text{T}})_{\text{lith.comp.}} = 1$. The ratio $(\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}})_{\text{lith.comp.}}$ for Black Sea euxinic sediments is equal to the model parameter K (see table 8), the slope of Fe_{HR} versus Fe_{T} (fig. 2). Since Fe_{PR} and Fe_{U} are derived entirely from lithogenous iron, their proportions in the total sediment (table 2), which is diluted by Fe_{irr} and biogenous components, are the same as those in the lithogenous component. The resulting $(\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}})_{\text{lith.comp.}}$, $(\text{Fe}_{\text{PR}}/\text{Fe}_{\text{T}})_{\text{lith.comp.}}$, and $(\text{Fe}_{\text{U}}/\text{Fe}_{\text{T}})_{\text{lith.comp.}}$ ratios, together with Fe_{L} and estimates of the other iron-pool contents, are presented in table 9. Sediments deposited on the margin are the most obvious source for deep-basinal sediments. The compositions of Black Sea marginal sediments at present (see table 4) and prior to the diagenetic mobilization and transport of highly reactive iron from the margin to the deep basin are also shown in

table 9. In calculating the composition prior to Fe_{HR} transfer, we assumed a net flux of Fe_{HR} from marginal sediments ($100 \pm 80 \mu\text{g cm}^{-2} \text{yr}^{-1}$, see above) to account for the flux of Fe_{HR} to deep-basinal sediments. Combining this net flux with the flux of lithogenous sediment to the margin yields a net loss of 0.2 weight percent Fe_{HR} and FeT from marginal sediments. We added that value to the present contents of Fe_{HR} and FeT and calculated iron-pool ratios and contents prior to Fe_{HR} transfer. The estimated composition of Black Sea marginal sediments prior to Fe_{HR} transfer is virtually the same as mean composition of continental margin and deep-sea sediments, which is also given in table 9.

The composition of modern Danube River particulates is also shown in table 9 (Poulton and Raiswell, 2002). The sample was taken near the headwaters of the Danube in southwestern Germany, about 2,800 km upstream from its entry into the Black Sea. Particle fluxes prior to the construction of dams on the major rivers into the Black Sea in 1970 - 72 (Milliman and Meade, 1983) indicate that the Danube supplied three times more sediment than the combined fluxes of the other major rivers (Dnester, Dneiper, Bug, Irmak and Riona). Dams constructed on the Danube have reduced the sediment flux by approximately half (Mikhailova and Levashova, 2001) and have resulted in a finer suspended sediment fraction (Marjonovic and others, 1995). Nonetheless, the composition of Danube particulates is quite similar to the mean composition of world riverine particulates (table 9).

Although the uncertainties are large, we can make one important conclusion from the results on table 9: The $\text{Fe}_{\text{HR}}/\text{FeT}$ ratio of the lithogeneous component of combined Black Sea euxinic sediments is significantly higher than that ratio in possible sources for those sediments. In the following sections we consider chemical, microbial, and physical processes that may account for enhanced reactivity of lithogenous iron in Black Sea euxinic sediments as well as other features of the results in table 9.

Chemical Enhancement of Reactivity

The presence of unusually reactive iron in the lithogenous fraction of euxinic sediments may suggest that mechanisms for enhancing the reactivity of the lithogenous material are associated with encountering dissolved sulfide in the bottom waters. However, the following evidence argues that abiotic chemical mechanisms for enhancing reactivity due simply to water column exposure to dissolved sulfide are unlikely to be effective.

Sedimentary iron minerals divide mainly into two pools with very different reactivities towards dissolved sulfide. One pool, consisting of ferrihydrite, lepidocrocite, goethite, and hematite, reacts quickly with dissolved sulfide (Canfield and others, 1992) and is readily pyritized in both euxinic conditions (in the water column or during diagenesis) and in sediments deposited from oxygenated bottom waters (during diagenesis only). By contrast, the other pool, iron soluble in HCl and present mainly as silicates plus magnetite, reacts extremely slowly with dissolved sulfide. In the Black Sea, suspended lithogenous debris is scavenged and incorporated into larger aggregates with average sinking times of $115 \pm 70 \text{ m day}^{-1}$, which are comparable to those found in other marine environments (Hay and others, 1990). Such settling times are only sufficient to allow the sulfidization of iron oxides (half lives < 30 days with respect to sulfidization; Canfield and others, 1992) but not iron silicates (half lives of approximately 10^5 to 10^6 years; Canfield and others, 1992; Raiswell and Canfield, 1996). Hence, sulfidic deep waters of the Black Sea bottom are unable to sulfidize more lithogenous iron than would also react during anoxic diagenesis in oxic/dysoxic sediments.

Microbial Enhancement of Reactivity

Transformation of a portion of recalcitrant iron-bearing phases (silicates and crystalline oxides represented by Fe_{PR} and Fe_{U}) to highly reactive components

(dissolved iron or iron oxides) by microbial activity in the water column is a potential mechanism for enhancing the reactivity of lithogenous iron. The extent of required iron reactivity enhancement in the deep-basinal sediments of the Black Sea can be estimated from mass-balance considerations. Given that the lithogenous iron content, Fe_L , is $3.8 (\pm 1.3)$ weight percent and $Fe_{HR}/FeT_{lith.comp.}$ (K) is $0.56 (\pm 0.08)$ (table 9), and that the average K value of marine sediments is $0.26 (\pm 0.09)$ (table 3), then the corresponding concentration of “enhanced” Fe_{HR} is $(0.56 - 0.26) \times 3.8 = 1.1 (\pm 0.6)$ weight percent.

Microbial reduction of ferric iron in oxides and silicates is a potential mechanism for enhancing iron reactivity. Experimental studies have shown that a fraction of the FeIII in magnetite and smectite can be microbially reduced under anoxic conditions (Stucki and others, 1987; Kostka and Nealon, 1995; Kostka and others, 1999). The magnetite content of deep-basinal Black Sea lithogenous sediments is probably too low to make a noticeable contribution to highly reactive iron (see Canfield and Berner, 1987). Smectite comprises about 40 percent of the clay fraction of the Unit 1 deep basin sediments in the Black Sea (Muller and Stoffers, 1974), which probably makes up the major component of the lithogenous fraction. Let us assume that this smectite has a typical FeIII content of $2.6 (\pm 2.0)$ weight percent (mean of 101 smectites, Weaver and Pollard, 1973). For these estimates, the smectite FeIII content of the lithogenous component is $0.40 \times 2.6 = 1.0 (\pm 0.8)$ weight percent. Thus, all of the smectite FeIII would have to be reduced (and sulfidized) to account for the enhanced reactivity of lithogenous iron in the deep basin. In addition, Kostka and others (1999) reported that similar amounts of smectite FeIII were extracted by microbial oxidation and by dithionite extraction. From equation (7) and the results in table 8, we calculate that the lithogenous FeD content of deep-basin sediments is about 0.3 weight percent. If microbial reduction extracted a comparable amount of FeIII from smectite, then this process could contribute to, but not account completely for enhanced reactivity of lithogenous iron. However, microbial reduction of FeIII in smectite would only be able to contribute to reactive iron enhancement if microbially extracted iron was more reactive towards dissolved sulfide than dithionite-extractable iron (FeD). In addition, microbial reduction of iron in smectites, and a corresponding enhancement in iron reactivity, should occur to some extent in any anoxic environment.

Microbial oxidation of recalcitrant ferrous iron in silicates and oxides is another possible mechanism for enhancing the reactivity of lithogenous iron. Bacteria and Archaea can utilize ferrous iron as an electron donor under oxic conditions. Although this metabolism is considered to operate primarily at low pH, there is increasing evidence to indicate that those microbes play a role in iron recycling and CO_2 fixation at neutral pH under suboxic to anoxic (but not sulfidic) conditions (Emerson and Moyer, 1997; Emerson and others, 1999; Straub and others, 2001). Thus, there is a range of environments within the Black Sea water column where microbial oxidation of ferrous silicates and oxides might occur. Unfortunately, there is little information on the link between the decomposition of iron silicates and the growth of iron-oxidizing microbes (Santelli and others, 2001).

However, recent batch dissolution experiments indicate that iron-oxidizing bacteria were able to release $10 \mu\text{g/g}$ of Fe from basaltic glass in 25 days under oxic conditions (K. Edwards, WHOI, personal communication, 2003). These rates were about 20 times faster than in abiotic controls. We estimated previously that the concentration of enhanced Fe_{HR} is about 1 weight percent, or $10^4 \mu\text{g/g}$. This concentration would require that the rates of dissolution observed in the above experiments be sustained for 70 years, which is about 30 times larger than the minimum time required for lateral currents (0.5 cm s^{-1} ; see earlier) to transport suspended material from the shelf to the deep basin. More detailed experiments are needed to establish the controls on rates of iron release by iron-oxidizing bacteria, and

demonstrate effective dissolution rates from minerals from iron-bearing minerals. Additionally, our observations suggest that such rates are higher in dysoxic/euxinic basins than in oxic/dysoxic basins. In summary, microbial activity may enhance the reactivity of lithogenous iron in euxinic Black Sea sediments. However, current results suggest that the extent of enhancement may not be quantitatively significant.

Physical Processes for Enhancement of Reactivity

Enhanced reactivity of lithogenous iron in deep-basin sediments could result if the lithogenous flux to the Black Sea is fractionated to produce a Fe_{HR} -enriched component during transport across the shelf into the deep basin. In addition, sediment fractionation provides a mechanism for changing the total lithogenous iron content, as well as iron-pool ratios, from the source (riverine particulates) to various sinks (continental margin and deep basin). Those changes are suggested from the results in table 9.

Lithogenous sediments that are discharged into the Black Sea are partitioned between the continental margin and the deep basin. If sediment fractionation is the primary mechanism for iron partitioning between the margin and basin, then the composition of the discharge input (distinct from riverine particulates) can be calculated from simple mass-balance. To do so, we must first estimate the relative proportion of lithogenous input that is deposited in each environment. This parameter is a function of lithogenous fluxes to and relative areas of the margin and the basin. The lithogenous flux to the margin was estimated to be $45,000 (\pm 19,000) \mu\text{g cm}^{-2} \text{yr}^{-1}$ (eq 28). The lithogenous flux to the basin is the product of the total flux, $7,300 (\pm 3,300) \mu\text{g cm}^{-2} \text{yr}^{-1}$ (eq 24b), and the fraction of total sediment that is lithogenous, f . We assume that f is $0.36 (\pm 0.09)$, the average value for Stations 9 and 14 corrected for biogenous and imported-component fluxes (see table 2). The corresponding value of the lithogenous flux to the basin is $2,600 (\pm 1,200) \mu\text{g cm}^{-2} \text{yr}^{-1}$. The relative areas of the margin and basin are 0.27 and 0.73, respectively. Accordingly, the fraction of lithogenous input to the Black Sea that is deposited in the deep basin, q , is:

$$q = \frac{2,600 * 0.73}{2,600 * 0.73 + 45,000 * 0.27} = 0.05 (\pm 0.02) \quad (33)$$

Thus, our results suggest that only about 5 percent of the lithogenous sediment entering the Black Sea is deposited in the deep basin; the remaining 95 percent is deposited on the continental shelf.

The composition of the lithogenous input can be evaluated from simple iron mass-balance relationships:

$$Fe_{\text{lith.comp.-input}} = q * Fe_{\text{lith.comp.-d.b.}} + (1 - q) * Fe_{\text{lith.comp.-c.m.}} \quad (34)$$

where Fe represents the concentration of any given iron pool in the lithogenous component or total lithogenous iron (Fe_L), the subscripts refer to the lithogenous component of the input, deep basin (d.b.), and continental margin (c.m.), and q is as defined above. Iron-pool ratios are calculated from concentrations. The resulting estimated composition of the lithogenous input to the Black Sea is $Fe_{HR}/Fe_T = 0.25 \pm 0.17$, $Fe_{PR}/Fe_T = 0.27 \pm 0.22$, $Fe_U/Fe_T = 0.48 \pm 0.27$, and $Fe_L = 3.0 \pm 1.3$. The composition of the lithogenous input differs markedly from that of modern Danube River particulates (table 9), notably in the lower Fe_{HR}/Fe_T ratio and the lower Fe_L content in the former. There are two possible explanations for this discrepancy. First, suspended sediments in the modern Danube flux have a higher Fe_{HR}/Fe_T ratio and Fe_L content than the "pre-dam" flux, which should correspond more closely to the time interval of accumulation of the marginal and deep-basin Black Sea sediments considered here. Second, Poulton and Raiswell (2002) point out that this discrepancy is global in scale, that is, the Fe_{HR}/Fe_T of riverine particulates is greater than the

$\text{Fe}_{\text{HR}}/\text{FeT}$ of lithogenous marine sediments (see table 9). Poulton and Raiswell (2002) suggest that the primary reason for this global discrepancy is the preferential trapping Fe_{HR} in estuaries, floodplains, salt marshes, tidal flats and other inner-shelf environments. The iron-pool data base for continental margins (table 3) does not include many sediments from inner-shelf environments, which are Fe_{HR} -enriched (such as the Amazon Delta, see Aller and others, 1986).

Sediment fractionation (size sorting) can be an effective mechanism for enhancing the reactivity of lithogenous iron in sediments delivered to the deep basin of the Black Sea provided that (1) Fe_{HR} is preferentially incorporated into the fine-grain fraction of the lithogenous input and (2) that fraction is preferentially transported across the shelf to the deep basin. The distribution of iron species in different fractions of riverine particulates indicates that Fe_{HR} is incorporated preferentially and $\text{Fe}_{\text{HR}}/\text{FeT}$ is relatively high in the finest fractions (see, for example, Horowitz and Elrick, 1987; Poulton, 1998). A likely mechanism for transporting fine, Fe_{HR} -rich sediments from discharge inputs to the deep basin is incorporation of those sediments into the suspended particulate layer in the Black Sea. That layer is located just above the oxic/anoxic interface. It is comprised mainly of fine-grained lithogenous material and is dispersed widely throughout the basin by lateral transport (Honjo and others, 1987; Hay and others, 1990; Kempe and others, 1990). A portion of the discharged fine sediment that remains in suspension and escapes trapping and deposition during transport through inner shore environments and the shelf (Hay and others, 1990) would constitute an Fe_{HR} -enriched lithogenous flux to the deep basinal area. There is evidence for fractionation of iron species in other river-coastal systems. Results from Stummeyer and others (2002) on the Ganges River delta and adjacent shelf suggest a significant increase in Fe_{HR} and corresponding decrease in Fe_{U} from estuarine sediments to distal shelf sediments.

In theory, therefore, the partitioning of lithogenous iron pools by sediment size between the continental margin and the deep basin of the Black Sea can account for enhanced reactivity of lithogenous components in euxinic sediments. However, this mechanism implies that the finest 5 percent of the lithogenous input to the Black Sea has an $\text{Fe}_{\text{HR}}/\text{FeT}$ ratio that is on average about two times higher than that of the total input, an enrichment level that is significantly higher than that reported between fine- and coarse-size fraction in riverine sediments (Poulton, 1998; Poulton and Raiswell, unpublished data). Moreover, although iron-pool fractionation has been reported in one other river-shelf setting (Stummeyer and others, 2002; see above), the results in table 4 show little if any significant change from delta areas to the shelf edge in the Black Sea. In addition, the extent of Fe_{HR} enrichment varies markedly among the different deep-basin sites, but there is no obvious explanation for such variation. Also, iron-pool fractionation between finer-grained pelagic sediment and coarser-grained neritic sediments should be expected to operate throughout the world ocean. However, the average iron-pool ratios in continental-margin and in deep-sea settings are virtually identical within the stated uncertainties (table 3). Perhaps the Black Sea system is unique in the extent to which (1) Fe_{HR} is partitioned into a fine fraction (2) and fine and coarse fractions are partitioned between the continental margin and the deep basin. Iron speciation results for the fine particulate layer and for sediment traps would be necessary to test those possibilities.

IMPLICATIONS FOR IRON-BASED PALEOREDOX INDICATORS

The Degree of Pyritization (DOP) and the Indicator of Anoxicity (IA) identify euxinic sediments by unusually high concentrations of FeP and Fe_{HR} , respectively, relative to oxic/dysoxic sediments. The utility of those paleoredox indicators depends on the availability of relatively large amounts of highly reactive iron in euxinic environments. The results developed in this study suggest that the availability of highly

reactive iron to a deep euxinic basin may be controlled, at least in part, by processes operating external to that basin.

Our results suggest that about 40 percent of the highly reactive iron in euxinic Black Sea sediments is derived from the mobilization and transfer of dissolved Fe^{2+} and particulate iron oxides from continental shelves (Wijsman and others, 2001). As discussed previously, the addition of this lithogenous-decoupled, imported reactive iron to the total iron pool in euxinic Black Sea sediments is readily discernable because the shelf-to-basin area ratio is comparatively large. In an ancient euxinic system where the shelf-to-basin ratio was smaller, the influx of imported reactive iron to the basin, and hence the values of DOP and IA, would be reduced. Thus, imported highly reactive iron contents are quantitatively most significant where lithogenous fluxes are low (Raiswell and others, 2001) and are least significant when diluted by high lithogenous fluxes (which then result in low DOP and IA; Lyons, 1997, and Lyons and others, 2003). The remaining 60 percent of highly reactive iron in euxinic Black Sea sediments appears to be due to unusually high reactivity of lithogenous iron relative to modern oxic/dysoxic sediments. If enhanced reactivity is the consequence of microbial alteration of iron-bearing silicates (that is, Kostka and others, 1999) in an anoxic/euxinic water column, then we might expect a comparable enhancement in analogous ancient environments. If, on the other hand, enhanced reactivity is due to the preferential deposition of an Fe_{HR} -enriched lithogenous component generated during transport to and across the shelf, then the extent of reactivity enhancement in an ancient euxinic basin would have been a complex function of a variety of factors, including sediment-transport dynamics, dimensions (width) of the adjacent shelf, and the origin and composition of the riverine lithogenous influx to the shelf.

The above discussion implies that one should be cautious in applying a general threshold value of DOP or IA for euxinicinity. In the Black Sea, physical, chemical, and perhaps microbial processes have combined to produce a relatively high concentration of FeP and Fe_{HR} and hence high DOP and IA values in deep-basinal euxinic sediments. But a different combination of those processes (including rapid lithogenous delivery) operating in a comparable ancient depositional environment could result in FeP and Fe_{HR} concentrations, and corresponding DOP and IA values, that are only slightly higher than those in contemporaneous oxic-dysoxic sediments. Accordingly, DOP or IA values should be included with other evidence to interpret the redox state of ancient sedimentary environments.

CONCLUSIONS

The results presented in this paper show that the enrichment of highly reactive iron (Fe_{HR}) in euxinic Black Sea sediments is the result of two fundamentally different processes. The first process involves the deposition of iron sulfides, which were precipitated in the anoxic water column, and reactive iron oxides. The iron sequestered in those sulfide and oxide phases was imported from marginal depositional environments to the deep basin. The second process causes unusually high reactivity of iron in the lithogenous component of euxinic sediments, and hence high pyritic iron contents. Those "lithogenous-decoupled" and "lithogenous-coupled" processes were identified and evaluated quantitatively from the linear correlations between Fe_{HR} and FeP (sulfidized iron) with total iron, FeT . The most likely source of imported highly reactive iron is the microbial diagenetic mobilization of highly reactive iron in margin sediments (Wijsman and others, 2001). The estimated flux of dissolved iron and (re-oxidized) iron oxides from the margin is sufficient to sustain the flux of imported, highly reactive iron to the deep basin. The causes of enhanced reactivity of lithogenous iron in euxinic Black Sea sediments are uncertain. Possible mechanisms include the microbial alteration of recalcitrant iron-bearing silicates and oxides and the preferential deposition of fine-grained Fe_{HR} -enriched lithogenous sediments in the deep basin. However, there is at present no confirming evidence to support definitively any

particular mechanism of reactivity enhancement. The recognition that several processes contribute to highly reactive iron in euxinic Black Sea sediments has implications for the application of paleoredox indicators based on iron reactivity. Specifically, we suggest that the threshold values of the Degree of Pyritization (DOP) and the Indicator of Anoxicity (IA) for euxinic conditions in ancient sediments may be lower than those presently accepted.

Enrichment of highly reactive iron has been identified in other (but not all) modern anoxic basins (Raiswell and Canfield, 1998; Lyons and others, 2003) and in analogous ancient sediments (Raiswell and others, 2001; Werne and others, 2002). Highly reactive iron enrichments generally appear to be small and are thus difficult to recognize against high background fluxes of lithogenous Fe_{HR}-bearing sediment. However, it would be useful to determine whether significant highly reactive iron enrichments in other depositional environments are due to the same types of processes as those operating in the Black Sea. In addition, it would be informative to estimate the content of imported highly reactive iron from Fe/T/Al systematics in the Black Sea and other anoxic environments. Such information is necessary to evaluate the reliability of highly reactive iron enrichment as a diagnostic indicator of anoxic-euxinic conditions in the ancient sedimentary record. In addition, a more complete understanding of the interplay of lithogenous-decoupled and lithogenous-coupled sources of highly reactive iron should provide new insights into the cycling of iron and sulfur in marine sediments.

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