Reactive iron enrichment in sediments deposited beneath euxinic bottom waters: constraints on supply by shelf recycling

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Abstract: Modern and ancient euxinic sediments are often enriched in iron that is highly reactive towards dissolved sulphide, compared to continental margin and deep-sea sediments. It is proposed that iron enrichment results from the mobilization of dissolved iron from anoxic porewaters into overlying seawater, followed by transport into deep-basin environments, precipitation as iron sulphides, and deposition into sediments. A diagenetic model shows that diffusive iron fluxes are controlled mainly by porewater dissolved iron concentrations, the thickness of the surface oxygenated layer of sediment and to a lesser extent by pH and temperature. Under typical diagenetic conditions (pH < 8, porewater Fe2+ = 10^-6 g cm^-3) iron can diffuse from the porewaters in continental margin sediments to the oxygenated overlying seawater at fluxes of 100-1000 lag cm^-2 a^-1. The addition of reactive iron to deep-basin sediments is determined by the magnitude of this diffusive flux, the export efficiency (e) of recycled iron from the shelf, the ratio of source area (S) to basin sink area (B) and the trapping of reactive iron in the deep basin. Values of e are poorly constrained but modern enclosed or semi-enclosed sedimentary basins show a wide variation in S/B ratios (0.25-13) where the shelf source area is defined as sediments at less than 200 m water depth. Diffusive fluxes in the range 100-1000 µg cm^-2 a^-1 are able to produce the observed reactive iron enrichments in the Black Sea, the Cariaco Basin and the Gotland Deep for values of e × S/B from 0.1-5. Transported reactive iron can be trapped physically and/or chemically in deep basins. Physical trapping is controlled by basin geometry and chemical capture by the presence of euxinic bottom water. The S/B ratios in modern basins may not be representative of those in ancient euxinic/semi-euxinic sediments but preliminary data suggest that e × S/B in ancient euxinic sediments has a similar range as in modern euxinic sediments.

Recent studies of the Black Sea and the Cariaco Basin (Canfield et al. 1996; Raiswell & Canfield 1998; Wijsman et al. 2001; Wilkin & Arthur 2001; Lyons et al. 2003) have shown that their deep-basin sediments, deposited under euxinic bottom waters, are enriched in iron that is highly reactive towards sulphide compared to oxic continental margin and deep-sea sediments. Similar highly reactive iron enrichments are also found in ancient well-laminated black shales with ages ranging from Jurassic to Proterozoic (Schieber 1995; Raiswell & Canfield 1998; Raiswell et al. 2001; Poulton & Raiswell 2002; Shen et al. 2002, 2003; Werne et al. 2002). It has been suggested that highly reactive iron enrichment results from the mobilization of iron from basin margin sediments, followed by lateral transport from the basin margin to the deep basin (e.g. Canfield et al. 1996; Lyons 1997; Raiswell & Canfield 1998; Wijsman et al. 2001). Wijsman et al. (2001) also demonstrated that the extent of highly reactive iron enrichment in Black Sea deep-basin sediments was within the range of iron release from oxic and dysoxic continental shelf sediments, as estimated from a model of diagenetic iron recycling and in situ measurements of iron fluxes. It was proposed that highly reactive iron is first dissolved from iron oxides during anoxic diagenesis of the shelf sediments, and then released as dissolved Fe2+ to the overlying seawater. A significant fraction of the dissolved iron is re-oxidized and redeposited into the marginal sediments, but some escapes and is transferred to the deep basin, where the dissolved iron is precipitated as iron sulphide and deposited.

Mass balance calculations for the Black Sea (Anderson & Raiswell 2004) also suggest that the recycling of highly reactive iron from the continental margin makes an important contribution (40 ± 20%) to the iron enrichment found in the deep-basin sediments. Anderson & Raiswell (2004) suggested that the remaining enrichment was due to enhanced reactivity of
lithogenous iron but were unable to demonstrate quantitatively the mechanism(s) of enrichment, i.e. chemocline extraction, microbial enhancement of iron silicate reactivity or fractionation of the riverine sediment flux. Wijsman et al. (2001) suggest that iron enrichment by mobilization from shelf sediments probably occurs in other basins and, consistent with this, Landing & Bruland (1987) and Saager et al. (1989), have reported the shelf mobilization and lateral transport of iron in the Pacific and Indian Oceans. These observations indicate that a detailed study of intrabasinal mobilization and transport would be valuable. It is the purpose of the paper to use a simple model of diagenetic iron mobilization and recycling to examine the factors which determine the extent of iron mobilization from basin margin sediments and enrichment in deep-basin sediments.

**Recognition of iron enrichment**

Anderson & Raiswell (2004) discussed two different approaches by which reactive iron enrichment may be identified, as is summarized here briefly. The first approach (Raiswell & Canfield 1998; Raiswell et al. 2001) uses the ratio of highly reactive iron (Fe$_{HR}$) to total iron (Fe$_T$), and the second the ratio of Fe$_T$ to Al (Werne et al. 2002; Lyons et al. 2003).

The first approach is based on the formation of pyrite in anoxic marine sediments, where dissolved sulphide produced by microbial sulphate reduction reacts with iron-bearing minerals (Berner 1970, 1984). Anoxic conditions can be established either within the water column or within the sediment. In these environments, sulphate-reducing bacteria oxidize organic matter to generate H$_2$S (Berner 1970, 1984), a fraction of which reacts with detrital iron minerals to form pyrite. The initial products are usually iron sulphide minerals, which are transformed to pyrite by reaction with dissolved sulphide (Rickard 1997; Richard & Luther 1997) and/or polysulphides (Goldhaber & Kaplan 1974; Rickard 1975; Luther 1991; Schoonen & Barnes 1991). Modern sediment studies (Canfield 1989; Canfield & Raiswell 1991; Canfield et al. 1992; Poulton et al. 2004) have shown that iron oxides (ferrihydrite, goethite, hematite and lepidocrocite) react rapidly with dissolved sulphide. However, only relatively small concentrations of silicate iron react even over timescales of millions of years (Canfield et al. 1992; Raiswell & Canfield 1996). In general (except in deep-sea sediments) the amounts of iron oxide buried into the zone of sulphate reduction are exceeded by the amounts of H$_2$S that are produced microbially. Thus, in many basin margin sediments, the concentrations of pyrite are limited by concentrations of iron oxide. The concentration of iron that is highly reactive towards dissolved sulphide (Fe$_{HR}$) is measured as the sum of the iron that is extracted by dithionite (FeD, iron present mainly as oxides with small concentrations of silicates; Raiswell et al. 1994) plus that which has already reacted with sulphide (FeP, iron present as pyrite or other sulphides). Use of the Fe$_{HR}$/Fe$_T$ ratio corrects for the dilution effects of biogenous sediment and represents the maximum proportion of lithogenous iron that can be pyritized in such sediments.

The second approach for the recognition of highly reactive iron enrichments in euxinic sediments is through changes in the Fe$_T$/Al ratio (Werne et al. 2002; Lyons et al. 2003). This approach assumes that values of Fe$_T$/Al higher than base-line values (i.e. the Fe$_T$/Al ratio in lithogenous sediments deposited in shelf environments) are due solely to the addition of Fe$_{HR}$. Use of the Fe$_T$/Al ratio also eliminates the effects of dilution by biogenous sediment, but small changes in the Fe$_{HR}$/Fe$_T$ fraction may be difficult to identify within a large Fe$_T$ content.

This paper uses elevated Fe$_{HR}$/Fe$_T$ ratios to identify highly reactive iron enrichment. The base-line for recognizing enrichment was suggested by Raiswell & Canfield (1998) who found that an Fe$_{HR}$/Fe$_T$ ratio of 0.4 represented the maximum value for a geographically widespread compilation of oxic continental margin and deep-sea sediments; the average Fe$_{HR}$/Fe$_T$ ratio for those sediments is 0.26 (± 0.09). However, this approach may fail to detect iron enrichments imposed on local detrital sediment fluxes that have an Fe$_{HR}$/Fe$_T$ ratio below the threshold (Fe$_{HR}$/Fe$_T$ = 0.4) and in principle it is better to identify reactive iron enrichments by comparison with shelf sediments within the same basin. Werne et al. (2002) and Lyons et al. (2003) use this approach for the detection of reactive iron enrichments via Fe$_T$/Al ratios. This approach assumes that there is relatively little fractionation of iron within the basin, and thus the composition of lithogenous components deposited in shelf and deep basin sites are identical (but see Wijsman et al. 2001; Anderson & Raiswell 2004).

**Approach**

A schematic model of intrabasinal iron mobilization and transport from margin to deep-basin sediments is shown in Figure 1. Iron
enrichment requires a diagenetically mobilized source, a transportation mechanism and a deep-basin sink (Wijsman et al. 2001). First, iron must be reduced in the margin sediments and then released to the overlying seawater. This process requires margin sediments that contain sufficient organic C to become anoxic and undergo microbial reduction of iron oxides to produce dissolved Fe\(^{2+}\) usually by direct reduction (e.g. Canfield 1989):

\[
\text{CH}_2\text{O} + 4\text{FeOOH} + 8\text{H}^+ \rightarrow \text{CO}_2 + 4\text{Fe}^{2+} + 7\text{H}_2\text{O}.
\]

Iron reduction is followed closely by microbial sulphate reduction in most continental margin sediments (e.g. Canfield & Raiswell 1991):

\[
2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S},
\]

and the dissolved sulphide precipitates the iron reduced by microbial reduction. The rapid reaction between dissolved sulphide and dissolved Fe\(^{2+}\) (plus solid iron oxides) buffers dissolved sulphide at low concentrations until the reactive iron oxides are exhausted. The porewaters are then dominated by dissolved sulphide. Thus a depth profile through typical continental margin sediments shows a layer of iron-rich porewaters overlying a layer of dissolved sulphide-rich porewaters (Canfield & Raiswell 1991). Dissolved iron can diffuse from the upper layer into the overlying seawater. Here the dissolved iron may be oxidized and redeposited into the sediments, but dissolved iron that escapes oxidation may become available for transport to the deep basin. Anderson & Raiswell (2004) suggest that the iron oxides formed by the oxidation of Fe\(^{2+}\) after release to seawater may not all be redeposited into the shelf sediments and may be transported to the deep basin sediments. There is independent evidence for this process in the Black Sea, where Murray et al. (1995) have shown that the oxidation of sulphide at the oxic/anoxic interface requires the transport of Mn and iron oxides from the basin margins to the deep basin.

Secondly, the iron must be transported to the deep basin. In the Black Sea, currents at the depths of the suboxic zone and the sulphide interface have lateral velocities of about 0.5 cm s\(^{-1}\) (Buessler et al. 1991) and are able to transport dissolved and particulate iron to the deep basin (Kempe et al. 1990; Wijsman et al. 2001). Thirdly, the iron must be precipitated by reaction with dissolved sulphide in the water column and then deposited into the deep-basin sediments. In the deep basin of the Black Sea, eddy diffusion (Brewer & Spencer 1974; Lewis & Landing 1991) is an effective mechanism for mixing the upper dissolved iron-rich water with the lower sulphide-rich water, thus allowing the precipitation of iron sulphides in the water column and their deposition into sediments. Sediment trap data (Honjo et al. 1987; Muramoto et al. 1991; Canfield et al. 1996), pyrite S isotope composition (Calvert et al. 1996; Lyons 1997) and pyrite framboïd size distributions (Wilkin & Arthur 2001) confirm that iron sulphides are precipitating in the Black Sea water column. Consistent with this, the water column is supersaturated with iron sulphides at depths below approximately 120–180 m (Landing & Lewis 1991). The Black Sea micro-laminated Unit I sediments deposited under euxinic conditions are remarkably uniform and laminae can be traced for distances of more than 1000 km over the deep basin floor (Lyons 1991;
Iron released from the margin must be dispersed evenly over the entire area of the deep basin. Iron enrichments generated by recycling from the shelf clearly require that transport mechanisms similar to those observed in the Black Sea are a typical feature of other modern and ancient euxinic depositional environments. Studies of other modern basins may clarify whether such mechanisms are common but this may be difficult to substantiate in ancient sediments. Nonetheless provided transport mechanisms are available then the extent of enrichment in the deep basin is determined by: (1) the rate of iron release from the margin; (2) the fraction of the released iron which escapes the shelf; (3) the ratio between the margin source area and the area of the deep-basin sink; (4) the extent to which recycled iron is trapped in the deep-basin sink; and (5) the relative significance of the recycled iron compared to the background clastic (lithogenous) supply.

A useful starting point is to identify the extent of iron enrichment associated with the Fe/hr/FeT ratios observed in modern and ancient euxinic sediments and then estimate the magnitude of Fe/hr flux which would need to be supplied by recycling to produce such enrichments. Anderson & Raiswell (2004) show that Fe/hr/FeT ratios in the Black Sea average 0.70 ± 0.19, and similar values have been found by Poulton & Raiswell (2002) for ancient euxinic sediments. We shall assume that these Fe/hr/FeT ratios are obtained solely by the addition of recycled iron to a background lithogenous flux, $J$(lith.) (in units of g cm$^{-2}$ a$^{-1}$) with FeT$_{\text{lith.}}$ = 4.0% (Raiswell & Canfield 1998) and an (Fe/hr/FeT)$_{\text{lith.}}$ ratio of 0.26 (see above). The flux of additional Fe/hr, defined as $J$(aHR), required to yield a particular value of Fe/hr/FeT is:

$$J(aHR) = FeT_{\text{lith.}} \times J(\text{lith.}) \times [Fe_{hr}/FeT - (Fe_{hr}/FeT)_{\text{lith.}}].$$

Figure 2 shows the benthic flux of recycled iron which must be added to a background sedimentation rate of lithogenous material to produce sediments with Fe/hr/FeT ratios of 0.5, 0.7 and 0.9 at varying sedimentation rates.

Quantifying iron release from the basin-margin sediments by diagenetic recycling

A diagenetic model for diffusive iron recycling

A general one-dimensional diagenetic equation for a solute in porewater can be written to describe the effects of diffusion, advection, adsorption and reaction on variations in solute concentration with time (Berner 1980; Boudreau 1996). A simplified version of this equation has been used by Boudreau & Scott (1978) to describe the flux of dissolved Mn$^2+$ from a reduced porewater through an oxygenated layer of sediment to the sediment–water interface. This equation:

$$D_s \frac{d^2C}{dx^2} - k_1(C - C_i) = 0$$

can be used to estimate the analogous diffusive flux of Fe$^{2+}$, where $x$ is the depth (cm) below the sediment–water interface, $D_s$ (cm$^2$ s$^{-1}$) is the diffusion coefficient corrected for tortuosity effects and $C$ is the porewater concentration of Fe$^{2+}$ (g cm$^{-3}$). It is assumed that: (i) steady state diagenesis occurs; (ii) there are no changes in porosity and $D_s$ with depth; (iii) the effects of advection are small relative to diffusion and
reaction; and (iv) Fe\(^{2+}\) is removed only by oxidation which occurs at a rate given by \(k_1(C - C_s)\), where \(C_s\) is the saturation concentration of Fe\(^{2+}\) (g cm\(^{-3}\)) with respect to Fe(OH)\(_3\) and \(k_1\) is the first order rate constant (s\(^{-1}\)) for Fe\(^{2+}\) oxidation. This model (Fig. 3) envisages that transport processes maintain a negligible concentration of Fe\(^{2+}\) above the sediment-water interface, below which there exists a thin zone of oxygenated sediment where solid phase iron oxides are present. There is a gradient in Fe\(^{2+}\) through this zone from the sediment-water interface to the base of the oxygenated layer. Porewaters below the oxygenated layer are reducing and maintain a uniform Fe\(^{2+}\) concentration with time. Boudreau & Scott (1978) show that the diffusive flux of Fe\(^{2+}\) in g cm\(^{-2}\) s\(^{-1}\) is then given by:

\[
\begin{align*}
J(\text{Fe}^{2+}) &= \frac{\varphi(D_{k_1})^{0.5}C_p}{\sinh \left(\frac{k_1}{D_{k_1}}^{0.5}L\right)}.
\end{align*}
\]

where \(\varphi\) is the porosity (assumed constant at 0.85), \(C_p\) is the porewater concentration of Fe\(^{2+}\) (g cm\(^{-3}\)) and \(L\) (cm) is the thickness of the oxygenated layer. The infinite dilution diffusion coefficient (\(D_{\infty}\)) for Fe\(^{2+}\) is derived from Boudreau (1996) as \(D_{\infty} = (3.31 + 0.15 T - 10^{-6}\) \(\text{cm}^2\text{s}^{-1}\)). The corrections for tortuosity are derived from Ullman & Aller (1982) who give \(D_s = D_{\infty} \frac{F}{\varphi}\), where \(\varphi\) is the porosity and the formation factor \(F\) is approximated as \(1/\varphi^m\) and \(m = 2.5\) to \(3.0\) for muddy sediments. Simplifying thus approximately produces:

\[
D_s = D_{\infty} \varphi^{-0.7}
\]

and hence

\[
D_s = \varphi^{1.7} (3.31 + 0.15 T \text{°C}) 10^{-9}.
\]

The oxidation of reduced iron can occur chemically or be catalysed biologically. Chemical oxidation may be retarded by the presence of humics and other natural organic species (Theis & Singer 1974) but is very rapid and is believed to predominate over biological oxidation (Nealson 1997; Santschi et al. 1990), which probably only occurs under acid conditions (Kristensen 2000). The chemical oxidation kinetics of Fe\(^{2+}\) in seawater have been studied by many workers (e.g. Stumm & Morgan 1980; Davison & Seed 1983; Roekens & van Grieken 1983; Millero et al. 1987) and there is general agreement that the rate law can be expressed as:

\[
\frac{d[\text{Fe}^{II}]}{dt} = -k[\text{Fe}^{II}][\text{O}_2]^{0.5}\left[\text{OH}^\cdot\right]^2.
\]

Millero et al. (1987) have derived the following expression for \(k\) (mol\(^{-3}\) kg\(^{-1}\) min\(^{-1}\)):

\[
\log k = 21.56 - 1545/T - 3.29I^{0.5} + 1.52I.
\]

Where \(T\) is temperature in kelvin and \(I\) is the ionic strength. Table 1 shows values of log \(k\) from 0–20 °C, assuming \(I = 0.723\) for seawater. Equation (4) can be modified to derive an apparent first order rate constant \(k_1\), where:

\[
\frac{d[\text{Fe}^{II}]}{dt} = -k_1[\text{Fe}^{II}]
\]

and

\[
k_1 = k[\text{O}_2]^{0.5}\left[\text{OH}^\cdot\right]^2.
\]

Values of \(k_1\) (s\(^{-1}\)) are given in Table 1 for the appropriate oxygen concentrations (Benson & Krause 1984) to achieve saturation at the specified temperature, and for varying pH (using the apparent Kw for seawater from Millero 2001). The results in Table 1 show that it is necessary to define values of temperature, pH and bottom water O\(_2\) concentrations in order to make reasonable estimates of \(k_1\) for shelf sediments. Furthermore Equation (3) shows that fluxes of Fe\(^{2+}\) from shelf sediments also depend on porewater Fe\(^{2+}\) concentrations (\(C_p\)) and the thickness of the oxygenated layer (\(L\)) in addition to \(k_1\). Some reasonable limits are derived for these variables below.

Surface waters in the present oceans range from approximately 2 °C in the polar seas to approximately 28 °C in the equatorial regions (Chester 2000). The models used here have a slightly lower range (0–20 °C) in order to account for dealing with cooler bottom waters at depths down to 200 m (see below). The observed pH of porewaters in modern shelf sediments undergoing anoxic diagenesis is usually between 7 and 8 (e.g. Boudreau & Canfield 1988). This relatively small range in pH is a consequence of the combined effects of iron reduction and sulphate reduction, and has been modelled by Ben-Yaakov (1973), Gardner (1973) and Boudreau & Canfield (1993). These models are consistent with field data in indicating that pH varies only between approximately 7 and 8, with the lower values occurring where greater proportions of sulphide accumulate in
Table 1. Variation in the apparent first-order rate constant ($k_1$) for Fe$^{2+}$ oxidation in seawater with temperature and pH

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$pK_w$</th>
<th>$\log k$</th>
<th>Sat. $O_2$ (µM kg$^{-1}$)</th>
<th>$k_1$ (sec$^{-1}$) at varying pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>pH 7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>pH 7.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>pH 8</td>
</tr>
<tr>
<td>0</td>
<td>14.3</td>
<td>14.2</td>
<td>348</td>
<td>$2.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>5</td>
<td>14.1</td>
<td>14.3</td>
<td>307</td>
<td>$6.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>10</td>
<td>13.8</td>
<td>14.4</td>
<td>275</td>
<td>$2.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>20</td>
<td>13.4</td>
<td>14.6</td>
<td>226</td>
<td>$2.4 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Values of $k_1$ assume saturation with respect to the atmospheric oxygen. Data for $pK_w$ from Millero (2001), $\log k$ from Millero et al. (1987) and oxygen saturation concentrations from Benson & Krause (1984).

the porewaters (as opposed to being precipitated as iron sulphide). A pH range of 7–8 is used here to accommodate the observed and model ranges of pH. A literature survey (Fig. 4) of porewater Fe$^{2+}$ concentrations (averaged over depths of 10–30 cm below the surface oxidized layer) in anoxic shelf sediments shows that values of $10^{-6}$ to $10^{-5}$ g cm$^{-3}$ are common, and this range is used in the present models. Relatively high porewater dissolved iron concentrations are found in suboxic sediments where sulphate reduction is suppressed. For example, values as high as $10^{-4}$ g cm$^{-3}$ are observed, in depositional environments such as the Amazon inner shelf (Aller et al. 1986) where physical reworking regenerates iron oxides and allows iron reduction (rather than sulphate reduction) to dominate sediment diagenesis. Aller et al. (1986) point out that reworking on this scale promotes the export of colloidal iron oxides.

Lower values of $k_1$ produce slower rates of oxidation (in turn enhancing escape through the oxygenated layer) and the variations in $k_1$ with temperature and pH are shown in Figure 5a. A temperature change of 10 °C produces a change of about one order of magnitude in $k_1$, as does a change of 0.5 pH. A decrease in bottom water

![Fig. 4](image-url)  
**Fig. 4.** Mean porewater dissolved iron concentrations (averaged over depths of 10–30 cm below the surface oxygenated layer). Data from Aller (1977), Elderfield et al. (1981), Trefry & Presley (1982), Chanton (1985), Sorensen & Jorgensen (1987), Canfield (1989), Canfield et al. (1993), Thamdrup et al. (1994), Thamdrup & Canfield (1996), Haese et al. (2000), Deflandre et al. (2002), Krom et al. (2002).  

![Fig. 5](image-url)  
**Fig. 5.** Variations in the first order rate constant ($k_1$) for iron oxidation (a) as a function of temperature at pH 7, 7.5 and 8, (b) with dissolved oxygen concentrations.
O$_2$ concentrations from saturation produces a substantial decrease in $k_1$ (Fig. 5b), with concentrations at 1% saturation producing a decrease in $k_1$ of two orders of magnitude. Thus variations in temperature, pH and bottom water O$_2$ concentrations are clearly capable of producing substantial variations in $k_1$, and thus also in the flux of recycled iron from the sediment. Equation (3) also shows that variations in $C_p$ produce equivalent variations in the flux of recycled iron from the sediment.

Model results: validation, implications and constraints

The estimated diffusive fluxes of recycled iron from Equation (3) can be validated to a limited extent by comparison with more sophisticated diffusion–advection–reaction models (e.g. Wang & Van Cappellen 1996; Wijsman et al. 2002; Berg et al. 2003). Such models take account of the rates of all the main carbon mineralization reactions (aerobic respiration, denitrification, manganese oxide reduction, iron oxide reduction, sulphate reduction and methanogenesis) together with the effects of oxidation on porewater and solid phase species (by O$_2$, iron and manganese oxides) and the precipitation of iron sulphones. In general, these models show that there is extensive redox cycling of iron in the upper few centimetres of sediment, in contrast to the single oxidation pathway modelled here. The model of Wijsman (2001) and Wijsman et al. (2002) predicts that the Black Sea shelf sediments generate a diffusive iron flux of approximately 7 nmol cm$^{-2}$ day$^{-1}$ (equivalent to 140 µg cm$^{-2}$ a$^{-1}$) for bottom waters saturated with O$_2$ (Wijsman et al. 2001). Wijsman (2001) gives data for one shelf station (pH = 7.2, $C_p$ = 3 × 10$^{-6}$ g cm$^{-3}$, $\phi$ = 0.88, $T$ = 5.8 °C and $L$ = 0.42 cm) that can be used in Equation (3) to derive a flux of 425 µg cm$^{-2}$ a$^{-1}$. Some discrepancies of a similar magnitude (up to a factor of 3) occur in comparisons with calculated diffusive fluxes from other sites (McManus et al. 1997; Elrod et al. 2004). Thus the simple model presented here should be regarded principally as identifying the main variables that affect diffusive recycling of iron and the flux estimates should only be used semi-quantitatively, as here in examining iron recycling in a basinal context.

Friedl et al. (1998) and Friedrich et al. (2002) also report benthic flux measurements for the shelf sediments of the Black Sea which range from 0.5–184 nmol cm$^{-2}$ day$^{-1}$ and average 46 nmol cm$^{-2}$ day$^{-1}$ (excluding one unusually high value of 1633 nmol cm$^{-2}$ day$^{-1}$). The average is equivalent to 920 µg cm$^{-2}$ a$^{-1}$. However the benthic flux measurements may be elevated because the benthic chambers became depleted in O$_2$ which significantly decreases the rate of re-oxidation in the surface layer and thus enhances the benthic flux (see above). McManus et al. (1997) and Elrod et al. (2004) also report benthic flux measurements of iron from sites on the California continental margin. The data show two significant features. First, shallow-water bioirrigated sites (99 m depth) with well-oxygenated bottom waters (101–185 µM kg$^{-1}$) have benthic flux measurements in the range 2–22 µg cm$^{-2}$ a$^{-1}$ that are on average 75 times higher than predicted by diffusion flux estimates based on porewater dissolved iron concentrations (Elrod et al. 2004). Ferro et al. (2003) have observed experimentally that bioirrigation maintains porewater iron at low levels and thus results in low estimates of diffusive fluxes. Together these data suggest that bioirrigation decreases porewater dissolved iron by transporting iron to the overlying waters, producing low diffusive fluxes that are augmented by bioirrigation fluxes.

Secondly, Elrod et al. (2004) show that deeper water sites with oxygen-depleted bottom waters (< 100 µM kg$^{-1}$) have benthic fluxes in the range 0.2–37 µg cm$^{-2}$ a$^{-1}$ that are roughly in agreement with estimated diffusive fluxes. However, exceptions occur for the highest benthic flux measurements which are significantly smaller (by a factor of > 10) than the estimated diffusive fluxes. Elrod et al. (2004) suggest that dissolved iron was re-oxidized in the sediment rather than being transported into the benthic chamber. It is also possible that iron was released but re-oxidized and precipitated from seawater in the benthic chamber without being collected and measured. In the absence of the chamber such iron might have been transported away from the site and some fraction exported from the shelf (see later). Overall the benthic flux measurements show that iron fluxes can be significant but are clearly influenced by processes that are poorly-understood. These are further reasons to regard the present model as semi-quantitative (see earlier).

The model partially accommodates the effects of bioirrigation and bioturbation through their effects on $C_p$ and $L$. High rates of iron reduction require the rapid redox cycling of iron which is aided by bioirrigation and bioirrigation (Canfield et al. 1993; Thamdrup 2000; Ferro et al. 2003). These processes transport iron oxides down into the reduced zone by particle mixing and transport reduced iron upwards by
particle mixing, diffusion and irrigation. The overall effect is to maintain porewater dissolved iron at low levels (Ferro et al. 2003) and thus our use of mean observed porewater values accommodates the effect of bioturbation and bioirrigation on the diffusive benthic fluxes but does not account for any additional fluxes resulting from bioirrigation.

Figure 6 shows the model estimates of recycled iron fluxes as a function of the thickness of the oxygenated layer ($L = 0.1$–$10$ cm). Smaller values of $L$ approach the thickness of the benthic boundary layer ($400$–$1200 \mu$m in coastal marine sediments; Kristensen 2000) and would thus be unrealistic. The three graphs in Figure 6 have been derived for pH values of 8.0, 7.5 and 7.0, assuming bottom waters saturated with $O_2$ at the designated temperatures ($T = 0$, $10$ and $20$ °C) of each plot. All three graphs use a value of $C_p = 10^{-8}$ g cm$^{-3}$ (see Fig. 2). Equation 3 shows that the diffusive flux varies directly with $C_p$ and using $C_p = 10^{-5}$ g cm$^{-3}$ simply produces an order of magnitude increase in the diffusive flux. Figure 6 shows that the diffusive flux of recycled iron increases sharply for decreasing values of $L$ but approaches a maximum as $L$ becomes relatively small. The graphs for pH 7 and 7.5 show similar maximum fluxes of 100–1000 µg cm$^{-2}$ a$^{-1}$ are reached for $L < 1$ cm at any temperatures from 0–20 °C. However, the graph for pH 8 only approaches maximum values of 1000 µg cm$^{-2}$ a$^{-1}$ for $L < 0.1$ cm and $T = 0$ to 10 °C. Diffusive fluxes of recycled iron are clearly very sensitive to variations in $L$ for any given $C_p$.

Diffusive iron fluxes are not directly affected by bottom-water oxygenation concentrations. Figure 7 shows that diffusive fluxes of recycled iron remain uniform as bottom-water oxygen concentrations decrease from saturation. However, bottom-water oxygen levels are likely to affect the thickness of the oxygenated layer ($L$). Jorgensen & Boudreau (2001) show that values of $L$ decrease with increasing rates of organic C mineralization (and thus vary seasonally in many shelf sediments). Hence lower bottom-water oxygen levels will also tend to decrease $L$, for any given mineralization rate. Conversely, bioturbation and bioirrigation act to increase the volume of oxic sediment by a factor of 1–3 (Kristensen 2000) and thus increase $L$ (which may be of irregular thickness). Nonetheless, the thickness of the oxygenated zone is often only a few millimetres in shelf sediments (Jorgensen & Boudreau 2001). Figure 6 suggests that maximum diffusive iron fluxes from shelf sediments with fully oxygenated bottom waters will typically be in the range 100–1000 µg cm$^{-2}$ a$^{-1}$ for porewater $C_p$ values of $10^{-6}$ g cm$^{-3}$. Note, however, that steady-state conditions require that the addition of reactive iron by sedimentation at least equals the loss by mobilization to overlying seawater. The mean reactive iron content of continental margin sediments is 0.83 ± 0.21% (Raiswell & Canfield 1998). Sediments with this composition that deposit at rates of 0.012 ± 0.003 and 0.12 ± 0.03 g cm$^{-2}$ a$^{-1}$ are potentially capable of supplying reactive iron fluxes of 100–1000 µg cm$^{-2}$ a$^{-1}$.

**Fig. 6.** Variations in the diffusive flux of diagenetically recycled iron with oxygenated zone thickness ($L$ cm) for $Fe^{2+} = 10^{-6}$ g cm$^{-3}$, temperatures of 0, 10 and 20 °C, at pH 7, 7.5 and 8.
Fig. 7. Variations in the diffusive flux of diagenetically recycled iron with bottom-water oxygen concentrations for $L = 0.1$ cm, $\text{Fe}^{2+} = 10^{-6}$ g cm$^{-3}$, pH 7.5 and a temperature of $0$ °C.

respectively, provided all the deposited reactive iron is recycled.

Factors influencing the flux of Fe$_{HR}$ to deep basins

Evidence from modern sediments

In addition to the gross flux of iron from shelf sediments derived above, the flux of highly reactive iron to deep-basin sediments is dependent on the escape efficiency of iron from the shelf source region and the relative sizes of the source generating ($S$) and basin sink ($B$) areas (and by their spatial interrelationships). The escape efficiency, $\varepsilon$, can be defined as:

$$\varepsilon = \frac{J(nHR)}{J(gHR)},$$

(6)

where $J(gHR)$ is the gross flux of Fe$_{HR}$ from source sediments and $J(nHR)$ is the net flux of Fe$_{HR}$ from source sediments to the deep basin. The net flux from the source is determined by the Fe$_{HR}$ flux into deep-basin sediments (given by $J(aHR)$ in Equation (1)), and the source (shelf): basin area ratio, $S/B$:

$$J(aHR) = (S/B) \times J(nHR).$$

(7)

Combining Equations (6) and (7) gives:

$$J(aHR) = \varepsilon \times (S/B) \times J(gHR).$$

(8)

The evaluation of iron fluxes in the Black Sea by Wijsman et al. (2001) and Anderson & Raiswell (2004) permits the estimate of the escape efficiency for that basin. The diagenetic model of Wijsman et al. (2001) yields a gross flux of recycled iron [$J(gHR)$] from the Black Sea shelf sediments over the range 7–22 nmol cm$^{-2}$ day$^{-1}$ (equivalent to 140–440 μg cm$^{-2}$ a$^{-1}$) with the higher values occurring in oxygen-depleted bottom waters. Based on the composition of one deep-basin core, Wijsman et al. (2001) estimated an additional highly reactive iron flux to the deep basin [$J(aHR)$] of 0.82–2.75 nmol cm$^{-2}$ day$^{-1}$ (16–35 μg cm$^{-2}$ a$^{-1}$). Given that the relative areas of the shelf ($S$) and deep basin ($B$) are 27% and 73%, respectively, then by rearranging Equation (7) the net flux of Fe$_{HR}$ from the shelf is $J(nHR) = J(aHR) / (S/B) = 44–150$ μg cm$^{-2}$ a$^{-1}$. The corresponding escape efficiency is approximately 30%. Anderson & Raiswell (2004) used different assumptions in the Wijsman et al. (2001) diagenetic model to derive a gross flux of recycled iron from the shelf of 140 ± 120 μg cm$^{-2}$ a$^{-1}$. Based on their evaluation of Fe$_{HR}$ enrichment in three deep-basin sediment cores, Anderson & Raiswell (2004) estimated that the flux of recycled iron to the deep basin is 38 ± 28 μg cm$^{-2}$ a$^{-1}$. Using the same $S/B$ ratio, the required net flux from the shelf is 120 ± 100 μg cm$^{-2}$ a$^{-1}$, corresponding to an escape efficiency of 80–90%. We can take a third approach to estimate the gross flux of recycled iron from the Black Sea shelf. The average dissolved oxygen concentration at the margin sites reported by Wijsman et al. (2001) is 250 ± 23 μM (quoted by Anderson & Raiswell 2004). Using this value the diagenetic model of Wijsman et al. (2001) gives an average gross flux of recycled iron of 220 ± 40 μg cm$^{-2}$ a$^{-1}$. Assuming the basal flux of Anderson & Raiswell (2004) the corresponding escape efficiency is about 50%, intermediate between the two previous estimates. These differing estimates of $\varepsilon$ indicate that $\varepsilon \times S/B$ for the Black Sea ranges from 0.1 to 0.3.

The spatial relationships between the source-generating and basin-sink areas also influence the extent of reactive iron enrichment in deep-basin sediments. Anderson & Raiswell (2004) define the source area of the Black Sea basin as being those sediments at depths of < 200 m. These sediments are anoxic below the sediment-water interface and have the potential to recycle iron diagenetically because their overlying waters are non-sulphidic. The top 95 m of the Black Sea water column are oxic or suboxic (Murray et al. 1989; Jorgensen et al. 1991) and below this depth there is approximately a further 100 m depth of waters that contain dissolved iron but which are undersaturated with respect to iron sulphides (Brewer & Spencer 1974; Lewis & Landing 1991; Landing...
& Lewis 1991). However, deeper waters are saturated with FeS and high dissolved sulphide concentrations maintain low concentrations of dissolved iron. Porewaters in sediments beneath these euxinic waters have little source potential. Thus, the Black Sea basin source area is constrained by oceanographic variables that determine the depths below which euxinicity occurs. This is also likely to be true for ancient black shales.

The capacity of the source area to mobilize iron may also vary between different types of sediment and with the degree of oxygenation of the bottom waters (see earlier). The Black Sea sediments at < 200 m depth (Muller & Stoffers 1974; Wijsman 2001) comprise a mixture of sand, silt and clay sediment with variable proportions of carbonate (< 50%) and organic C (< 5%). In some areas these sediments support suboxic diagenesis with elevated concentrations of porewater dissolved iron (Lyons et al. 1993). As described earlier, the fluxes of recycled iron from the shelf sediments have been measured directly using benthic chambers (Friedl et al. 1998; Friedrich et al. 2002) and indirectly via a diagenetic model (Wijsman et al. 2001). Both methods show considerable variation between localities across the shelf. Accurate basinal-scale estimates of recycled iron clearly require that measurements by either method are made at a range of shelf locations that encompasses the main sediment types and depositional environments in order to obtain an integrated value for the benthic flux over the entire source area.

Anderson & Raiswell (2004) conclude that iron enrichments in the Black Sea are readily discernible partly because of a favourable (i.e. high) ratio of the source area to the deep basinal sink area. However, Lyons et al. (2003) have shown that euxinic sediments on the margins of the Cariaco Basin show little (or no) iron enrichments in contrast to the marked enrichments in the euxinic central basin. This is attributed to rapid sedimentation at the margins (up to 0.8 cm a\(^{-1}\)) where lithogenous supply dilutes the iron enrichment in contrast to the more slowly deposited sediments (approximately 0.05 cm a\(^{-1}\)) in the central basin. Consistent with this, Table 2 shows the ratio of the source shelf area (S defined as sediments at < 200 m depth which is typically the limit of surface water mixing) to the remaining deeper area (B) for a range of modern enclosed and semi-enclosed basins. The S/B ratios in Table 2 do not imply that these areas are capable of exhibiting source-sink characteristics nor that iron enrichments occur in their deep-basinal areas. However, they demonstrate that the Black Sea does not have an unusually favourable S/B ratio, and that other enclosed and semi-enclosed basins have comparable or larger S/B

Table 2. Ratios of shelf area (< 200 m depth) to deep (> 200 m) basin area in modern basins (from Dietrich et al. 1980 except as indicated*)

<table>
<thead>
<tr>
<th>Enclosed/semi-enclosed basins</th>
<th>Basin area (× 10⁶ km²)</th>
<th>S/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gulf of California</td>
<td>0.15</td>
<td>0.47/0.53 = 0.89</td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>0.39</td>
<td>0.99/0.01 = 99</td>
</tr>
<tr>
<td>Caspian Sea*</td>
<td>0.41</td>
<td>0.70/0.30 = 2.3</td>
</tr>
<tr>
<td>Black Sea*</td>
<td>0.42</td>
<td>0.27/0.73 = 0.37</td>
</tr>
<tr>
<td>Red Sea</td>
<td>0.45</td>
<td>0.42/0.58 = 0.72</td>
</tr>
<tr>
<td>Sea of Japan</td>
<td>1.01</td>
<td>0.23/0.77 = 0.30</td>
</tr>
<tr>
<td>East China Sea</td>
<td>1.20</td>
<td>0.81/0.19 = 4.3</td>
</tr>
<tr>
<td>Hudson Bay*</td>
<td>1.23</td>
<td>0.93/0.07 = 13</td>
</tr>
<tr>
<td>Gulf of Mexico*</td>
<td>1.29</td>
<td>0.48/0.52 = 0.92</td>
</tr>
<tr>
<td>Sea of Okhotsch</td>
<td>1.39</td>
<td>0.27/0.73 = 0.37</td>
</tr>
<tr>
<td>Bering Sea</td>
<td>2.26</td>
<td>0.46/0.54 = 0.85</td>
</tr>
</tbody>
</table>

**Marginal basins**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>S. Australian Basin*</td>
<td>1.53</td>
</tr>
<tr>
<td>Argentine Basin*</td>
<td>4.40</td>
</tr>
<tr>
<td><strong>World oceans</strong></td>
<td><strong>362</strong></td>
</tr>
</tbody>
</table>

\[
\text{S/B} = \frac{\text{Area of Shelf}}{\text{Area of Deep Basin}}
\]
ratios. The data also reflect present tectonic, sea-level and oceanographic conditions and are not necessarily representative of \( S/B \) ratios in enclosed or semi-enclosed basins in the geological record. The effective \( S/B \) ratio for any basin will be determined primarily by the depth at which euxinic bottom waters occur, which in turn limits the area of the remaining regions of the basin that have source potential.

The Baltic Sea is a comparable semi-enclosed basin to the Black Sea, although the deepest areas (the Gotland Deep and the Bornholm Deep) are not persistently anoxic/euxinic. The Bornholm Deep has oxygen-depleted bottom waters (0.1–1.0 ml \( O_2 \) l\(^{-1} \)) for periods of up to a few years, but the Gotland Deep is euxinic below 150 m depth for periods of at least 10 years (Boesen & Postma 1988). Recent studies of sediments of the Gotland Deep have been concerned mainly with their manganese enrichment (e.g. Burke & Kemp 2002) and analytical data for \( Fe_{HR} \) and \( Fe_T \) on the same samples are rare. Belmans et al. (1993) have analysed two Gotland Deep sediments which have a mean \( Fe/P/Fe_T = 0.7 \) (which approximates to \( Fe_{HR}/Fe_T \); see Poulton & Raiswell 2002). Boesen & Postma (1988) give a mean sedimentation rate of 0.02 cm a\(^{-1} \) for the Gotland Deep but rates in the deepest part of the basin vary greatly. Assuming that the mean sedimentation rate is equivalent to a mean sediment flux of 0.005 g cm\(^{-2} \) a\(^{-1} \), then the \( J(aHR) \) required to produce the observed \( Fe_{HR}/Fe_T \) ratio is obtained from Equation (1): \( J(aHR) = 0.04 \times 0.005 \text{ g cm}^{-2} \text{ a}^{-1} \times (0.70 - 0.26) = 88 \mu \text{g cm}^{-2} \text{ a}^{-1} \). This flux could be derived from a diffusive flux of recycled iron of 100–1,000 \( \mu \text{g cm}^{-2} \text{ a}^{-1} \) from shelf sediments with oxygenated bottom waters by any combination of \( \epsilon \) and the \( S/B \) ratio such that \( \epsilon \times S/B = 0.1 \) to 1. A detailed study of the Baltic shelf sediments that produced an integrated measure of the benthic recycled iron flux and, a comparison with the \( Fe_{HR}/Fe_T \) ratio in the deep euxinic sediments would provide valuable data for \( \epsilon \) and the \( S/B \) ratio for this basin.

The Cariaco Basin occupies a depression approximately 175 km long and 50 km wide located on the continental shelf north of Venezuela, and thus provides a useful contrast to the semi-enclosed basins of the Black Sea and the Baltic Sea. Water exchange with the Caribbean Sea is restricted by a series of sills with maximum depths of 120–140 m. Euxinic bottom waters exist from approximately 300 m depth to maximum depths of approximately 1400 m (Lyons et al. 2003). Sediment geochemical data in Lyons et al. (2003) allow a mean \( Fe_{HR}/Fe_T = 0.48 \) to be calculated for a core deposited at a depth of 900 m and at a sedimentation rate of 0.45 cm a\(^{-1} \). This sedimentation rate includes the deposition of approximately 30% calcareous and up to 30% opaline material (Raiswell & Canfield 1998; Lyons et al. 2003). Thus the deposition rate of lithogenous material is approximately 0.2 cm a\(^{-1} \). Assuming a lithogenous sediment flux of 0.05 g cm\(^{-2} \) a\(^{-1} \), then the \( J(aHR) \) required to produce the observed \( Fe_{HR}/Fe_T \) ratio of 0.48 is \( J(aHR) = 0.04 \times 0.05 \text{ g cm}^{-2} \text{ a}^{-1} \times (0.48 - 0.26) = 440 \mu \text{g cm}^{-2} \text{ a}^{-1} \). This flux could be derived from a benthic recycled iron flux of 100–1000 \( \mu \text{g cm}^{-2} \text{ a}^{-1} \) from shelf sediments with oxygenated bottom waters by any combination of \( \epsilon \) and the \( S/B \) ratio such that \( \epsilon \times S/B = 0.5–5 \) (a higher range than in the semi-enclosed basins of the Black Sea and the Baltic Sea). A more detailed study of the Cariaco Basin is required to identify the potential source area and produce an integrated measure of the benthic recycled iron flux over that area. The resulting estimates of \( \epsilon \) and the \( S/B \) ratio for this basin would provide a better comparison with the semi-enclosed basins of the Black Sea and the Baltic Sea.

**Evidence from ancient sediments**

Many ancient black shales accumulated in the deeper parts of epicontinental seas (Wignall 1994) rather than in enclosed or semi-enclosed basins such as those in Table 2. The spatial relationships between the source area and the basin sink area may be complex in these circumstances. Shallow seas which have become euxinic over substantial areas may have relatively low \( S/B \) ratios, especially where a narrow, essentially linear, shelf source area borders on a deeper euxinic basin. Present-day marginal basins may provide an indication of the \( S/B \) ratios of such ancient black shales that are iron-enriched. Table 2 shows the \( S/B \) ratios for the South Australian and Argentine Basins, which are well-defined areas of deep water adjacent to the continental shelf. The source areas are defined as being the coastal sediments deposited at depths of < 200 m that are laterally adjacent to the basin and, on this basis, these basins have \( S/B \) ratios of approximately 0.2. For comparison the \( S/B \) ratio of the world oceans is 0.08 (see Table 2).

The Toarcian (early Jurassic) period was an interval of widespread black shale deposition (notably the Jet Rock and the Posidonia schiefer; Jenkyns 1988) in an epicontinental sea that covered much of Europe. These two sediments show different behaviour in respect
of their highly reactive iron contents (Raiswell & Berner 1985; Poulton & Raiswell 2002), which are more enriched in the Jet Rock (where highly reactive iron is also correlated with organic C) than in the Posidoniaischief. Poulton & Raiswell (2002) give a mean Fe$_{HR}$/Fe$_T$ = 0.66 for the Jet Rock, which was deposited at a rate of 0.007 cm a$^{-1}$ (McArthur et al. 2000), equivalent to approximately 0.07 cm$^2$ a$^{-1}$ of uncompacted sediment. Assuming a lithogenous sediment flux of 0.02 g cm$^{-2}$ a$^{-1}$, then the J(aHR) required to produce the mean Fe$_{HR}$/Fe$_T$ ratio of 0.66 is

\[ J(aHR) = 0.04 \times 0.02 \text{ g cm}^{-2} \text{ a}^{-1} \times [0.66 - 0.26] = 320 \mu \text{g cm}^{-2} \text{ a}^{-1}. \]

This flux could be derived from a benthic recycled iron flux of 100–1,000 µg cm$^{-2}$ a$^{-1}$ from shelf sediments deposited beneath oxygenated bottom waters by any combination of ε and the S/B ratio such that ε $\times$ S/B = 0.3–3. Estimates of ε varied from 0.3–0.8 (see earlier) which then suggests that S/B for the Jet Rock ranged approximately from 1–10. Better estimates of ε have the potential to provide a useful insight into the basinal configurations (and areas of euxinic bottom waters) in which the deposition of ancient black shales occurred.

Wignall (1994) has also shown that ancient black shales developed during the initial stages of transgression occur in topographic hollows. Transgressions are favourable periods for the development of topographically-controlled basins because the initial flooding can occur over incised river valleys (Wignall 1991, 1994) or irregular palaeo-relief surfaces shaped by combinations of glacial, erosive and tectonic processes (e.g. Luning et al. 2000). These hollows serve as traps for fine-grained sediment (such as colloidal iron oxides) and organic matter (Huc 1988) and the irregular topography inhibits bottom-water circulation so that the influx of organic matter increases oxygen demand and assists the development of euxicity (Wignall 1991, 1994). An irregular bottom topography which confines euxinic bottom waters to an area surrounded by oxic shelf sediments might also be characterized by relatively large S/B ratios, compared to those typically found in the enclosed and semi-enclosed basins listed in Table 2. A combination of these factors is likely to be responsible for the notably high levels of reactive iron that are found in many transgressive black shales (Wignall pers. comm.).

Ultimately, the mobilized iron exported from shelf areas will always tend to accumulate by physical trapping within the deeper areas of a basin, as does all fine-grained material, e.g. organic matter (Huc 1988). This will be true whether or not the deep-basin area is euxinic, and enclosed oxic deep basins might therefore show iron enrichments subject to the constraints of sedimentation rate and their S/B ratio. Note that anoxic, non-sulphidic basins may also physically trap reactive iron but the iron will tend to be dissolved and retained within the water column. Thus the sediments of the Orca Basin do not appear to show reactive iron enrichment (Raiswell & Canfield 1998). However, the existence of euxicity also provides a chemical trap for reactive iron which might otherwise be exported (provided the recycled iron can be brought in contact with the sulphidic waters and sedimented as iron sulphides). Export from the deep areas of an enclosed/semi-enclosed basin is unlikely but chemical trapping may be critical in preventing export from shallow topographic hollows surrounded by oxic shelf sediments. Source generating areas adjacent to euxinic basins may also exist in an oceanographic regime that prevents transport of recycled iron to the basinal sink area. Local oceanographic conditions (wind, currents, bottom topography) will dictate whether, and how effectively, the source and sink areas are connected.

Conclusions

Reactive iron enrichment in the Black Sea results at least partly from the diagenetic mobilization of iron from shelf sediments. A significant fraction of the mobilized iron is exported from the shelf and transported into the deep basin where precipitation of sulphides occurs. A diagenetic model has been used to show that iron can be mobilized from shelf sediments deposited from oxygenated bottom waters at rates of 100–1,000 µg cm$^{-2}$ a$^{-1}$ under typical diagenetic conditions (\(T = 0–20^\circ\text{C}, \text{pH} = 7–8\), porewater Fe$_{2+}$ = 10$^{-6}$ g cm$^{-3}$). These rates are essentially independent of pH and temperature provided the thickness of the oxygenated surface layer of the sediments is less than 1.0 cm. The mobilized iron may be either exported or redeposited on the shelf. In the Black Sea the export efficiency (ε) is at least 30% and may be as high as 80–90% but the exported iron is dispersed over a deep basal area (B) which is larger than the shelf generating area (S). In the Black Sea the ratio S/B = 0.37, for a shelf area confined to depths < 200 m, below which euxinic bottom waters occur and diagenetic mobilization of iron is impossible. The S/B ratio of the Black Sea is not unusually large compared to other modern basins which have S/B ratios ranging from 0.25–13 approximately for a shelf generating area at depths of
< 200 m. However, the critical factor that defines the shelf area is the depth at which euxinic bottom waters occur. In general, surface waters are well-mixed by wind and wave action to depths of approximately 200 m (Chester 2000) in the absence of sills or other constraints on circulation. Where such constraints exist, the S/B ratio of any particular basin may be reduced substantially. Estimates of $e \times S/B$ for modern euxinic sediments in the Black Sea (0.1–0.3), the Baltic (0.1–1), and the Cariaco Basin (0.5–5) appear possibly similar to those in ancient euxinic sediments (0.3 to 3.0 in the Jurassic Jet Rock), assuming that iron is mobilized from shelf sediments deposited from oxygenated bottom waters. Further studies of these modern euxinic basins are urgently needed to identify the range of variation in $e$ and the S/B ratio.

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References


Canfield, D.E., Lyons, T.W. & Raishwell, R. 1996. A
model for iron deposition to euxinic Black Sea sediments. American Journal of Science, 296, 818–834.


Thamdrup, B. & Canfield, D.E. 1996. Pathways of


