The continental shelf benthic iron flux and its isotope composition

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Abstract

Benthic iron fluxes from sites along the Oregon–California continental shelf determined using in situ benthic chambers, range from less than 10 μmol m⁻² d⁻¹ to values in excess of ~300 μmol m⁻² d⁻¹. These fluxes are generally greater than previously published iron fluxes for continental shelves contiguous with the open ocean (as opposed to marginal seas, bays, or estuaries) with the highest fluxes measured in the regions around the high-sediment discharge Eel River and the Umpqua River. These benthic iron fluxes do not covary with organic carbon oxidation rates in any systematic fashion, but rather seem to respond to variations in bottom water oxygen and benthic oxygen demand. We hypothesize that the highest rates of benthic iron efflux are driven, in part, by the greater availability of reactive iron deposited along these river systems as compared to other more typical continental margin settings. Bioirrigation likely plays an important role in the benthic Fe flux in these systems as well. However, the influence of bottom water oxygen concentrations on the iron flux is significant, and there appears to be a threshold in dissolved oxygen (~60–80 μM), below which sediment–ocean iron exchange is enhanced. The isotope composition of this shelf-derived benthic iron is enriched in the lighter isotopes, and appears to change by ~3% (δ⁵⁶Fe) during the course of a benthic chamber experiment with a mean isotope composition of ~2.7 ± 1.1% (2 SD, n = 9) by the end of the experiment. This average value is slightly heavier than those from two high benthic Fe flux restricted basins from the California Borderland region where δ⁵⁶Fe is ~3.4 ± 0.4% (2 SD, n = 3). These light iron isotope compositions support previous ideas, based on sediment porewater analyses, suggesting that sedimentary iron reduction fractionates iron isotopes and produces an isotopically light iron pool that is transferred to the ocean water column. In sum, our data suggest that continental shelves may export a higher efflux of iron than previously hypothesized, with the likelihood that along river-dominated margins, the benthic iron flux could well be orders of magnitude larger than non-river dominated shelves. The close proximity of the continental shelf benthos to the productive surface ocean means that this flux is likely to be essential for maintaining ecosystem micronutrient supply.

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1. INTRODUCTION

Within bioturbated or physically mixed continental shelf and slope marine sediments, the cycling of iron can play an important role in carbon degradation (Froelich et al., 1979; Aller et al., 1986; Canfield and Des Marais, 1993; Thamdrup et al., 1994; Thamdrup, 2000). In such locations, the high rates of electron transport, which are typically associated with carbon oxidation, rely on multiple electron transport pathways, with much of this electron transport taking place within the upper few centimeters of the sediment package. Carbon oxidation may thus generate a dissolved pool of reduced iron within the sediment package which can be transported to the overlying water column via fluid advection and diffusion (Aller, 1998, 2004). This process is likely to be an important route for trace metal supply to the biologically productive waters typical of the continental shelf (Johnson et al., 1999; Elrod et al., 2004, 2008; Lam et al., 2006; Nishioka et al., 2007). This benthic–pelagic exchange can be quantified indirectly from porewater profiles.
or directly from benthic incubation chamber experiments (e.g., Klinkhammer et al., 1982; Heggie et al., 1986; Archer and Devol, 1992; Johnson et al., 1992; Reimers et al., 1992; Berelson et al., 2003). However, because these environments are physically and chemically dynamic, and because sediments rather than the more easy-to-sample muds often dominate shelf environments (de Haas et al., 2002), it is difficult to quantify a global iron flux from these settings.

In this manuscript we present benthic incubation chamber data from muddy sites along the Oregon and California continental margin (Fig. 1) to estimate the magnitude of the benthic iron flux in these regions and the isotope composition of that benthic flux. Our work places a primary emphasis on continental shelf sediments neighboring two river systems of the Pacific Northwest—the Umpqua River of southern Oregon and the Eel River of northern California. For comparison, we also discuss previously published and new results from the central-to-southern California shelf and Borderland Basin systems. Collectively these data suggest that sediments on continental shelves, particularly systems neighboring high sediment discharge rivers (e.g., the Eel River) have a higher rate of iron sedimentary efflux than more typical continental margin settings (e.g., Elrod et al., 2004). The key characteristics that differentiate the margin systems discussed here are the reactive iron delivery from the continent, organic carbon rain rate, and the activity of macrobenthos, and consequently the mode of benthic–pelagic solute exchange (i.e., advective versus diffusive). Our thesis regarding the high benthic efflux of iron is consistent with previous observations of higher dissolved iron concentrations in surface waters on the broader shelves off northern California compared to central and southern California (Chase et al., 2005a). Of particular importance with respect to global processes, the high continental iron efflux at the northern shelf sites occurs in the face of relatively high dissolved bottom water oxygen concentrations (60–140 μM at our northern shelf sites compared to typically ≤10 μM in the San Pedro and Santa Monica Basins; Elrod et al., 2004).

Furthermore, our data show that the benthic iron flux at all of our sites is enriched in the lighter isotopes of iron, probably reflective of isotope fractionation during iron reduction and iron recycling in the sediments as well as in the bottom waters (Severmann et al., 2006, 2008; Staubwasser et al., 2006). We have observed distinct differences in the isotope compositions of the benthic iron efflux over the course of the benthic chamber incubation experiments that can be related to the depositional regime of these different shelf systems. A key finding presented here implicates the importance of reactive solid phase delivery via rivers for iron release within sediments, which may lead to a large advective or diffusive metal transport to the ocean.

1.1. Iron geochemistry

Despite its high crustal abundance, iron has a low solubility under the oxidizing conditions typical of the contemporary ocean, often resulting in low iron concentrations in the upper ocean (Martin and Fitzwater, 1988; Martin and Gordon, 1988; Martin et al., 1989, 1991; Cullen, 1991; Kuma et al., 1996; Johnson et al., 1997; Coale et al., 1998). Such low surface ocean iron concentrations can limit ocean fertility with this “iron limitation” being most notably expressed within the high nutrient low chlorophyll (HNLC) regions of the open ocean (references as above). Here, iron supply is restricted because of low iron inputs by atmospheric deposition and upwelling (Duce and Tindale, 1991; Johnson et al., 1997; Archer and Johnson, 2000; Fung et al., 2000; Jickells and Spokes, 2001; Cassar et al., 2007).

In contrast to the open ocean, however, coastal systems are proximal to a rich source of iron, as well as other micronutrients, i.e., the continent. Notwithstanding this proximity, coastal systems can also be limited by iron availability (Pakulski et al., 1996; Hutchins and Bruland, 1998), and even where production may not be limited by available iron, ecosystem structure can be influenced by iron availability (Brand et al., 1983; Brand, 1991; Sunda and Huntsman, 1995; Hutchins et al., 1999; Crawford et al., 2003; Leblanc et al., 2005).

One principal difference between the iron cycle of coastal systems as compared to the ocean interior is that for coastal systems it is believed that sediments are an important iron source to the overlying water column (Crook and Hunter, 1998; Hutchins and Bruland, 1998; Hutchins et al., 1999; Johnson et al., 1999, 2001; Anderson and Raiswell, 2004; Elrod et al., 2004; Raiswell and Anderson, 2005; Raiswell, 2006; Elrod et al., 2008; Lohan and Bruland, 2008), whereas dust and glacial erosion might play a more prom-

Fig. 1. Map of our three study areas along the California and Oregon continental margin (basemap created using the USGS map generator Map-It at http://woodshole.er.usgs.gov/mapit/).
inent role in the remote oceanic regions of the central oceans and the Southern Ocean (Jickells et al., 2005; Mahowald et al., 2005, 2009; Cassar et al., 2007). The paradigm that dust is the principal source of reactive iron to the surface ocean in remote regions is increasingly being challenged, however, and several studies have highlighted the important role of coastal sediments as an iron source far beyond the immediate vicinity of the shallow shelf environments (Elrod et al., 2004; Lam et al., 2006; Nishioka et al., 2007; Lam and Bishop, 2008; Raiswell et al., 2008). Continental weathering supplies coastal regions with particulate iron, largely via river transport (for a recent review see Poulton and Raiswell, 2002). Once it is delivered to the coastal zone, terrestrial material makes its way to the seabed where it can be acted upon by physical, chemical, and biological processes (Fig. 2, and Colbert, 2004; Wetz et al., 2006). Under one scenario, physical resuspension of fine particulate sediment provides a source of iron that can be accessed by surface biota following its vertical transport to the euphotic zone (Hutchins et al., 1998; Chase et al., 2005b). An extension of that idea asserts that terrestrial iron undergoes repetitive oxidation-reduction steps within the benthos before a fraction of it is re-injected into the bottom water, thereby creating a biologically-accessible dissolved and fine particulate iron reservoir (Fig. 2, and Johnson et al., 2001; Poulton and Raiswell, 2002). This repetitive recycling is imposed upon iron because of the constant interplay between iron oxide reduction coupled to organic matter mineralization and iron oxidation coupled to advective supply of oxygenated bottom water. Bioirrigation or other physical mixing processes likely dominate exchange at the sediment–ocean boundary (Aller, 1980b, 2001; Canfield and Des Marais, 1993; Thamdrup et al., 1994). During upwelling events the combined dissolved and fine particulate iron fraction can be delivered to the overlying water column, as the benthic boundary layer communicates with the surface ocean (Fig. 2). This process can thus lead to elevated dissolved and fine particulate iron concentrations within the water column overlying the continental shelf (Chase et al., 2005a; Elrod et al., 2008; Lohan and Bruland, 2008).

2. STUDY SITES

A considerable amount of iron diagenesis research has focused on deltaic systems dominated by large rivers (e.g., Aller, 1998; McKee et al., 2004); part of the emphasis for this manuscript is on sites proximal to small rivers. We present results from two cruises in 2007 along the southern Oregon and northern California shelf (herein called BIF-I and BIF-II cruises, where BIF stands for Benthic Iron Flux). The BIF-I cruise took place in April/May and the BIF-II cruise in September. Our BIF study sites are the northern continental shelf (70–200 m water depth) adjacent to the outflow of the Eel and Umpqua Rivers (Fig. 1). This general region of the Pacific Northwest is one known for having relatively small river basins, but elevated sediment transport to the ocean (Griggs and Hein, 1980). The Eel River in particular is a system with an exceptionally high terrigenous sediment delivery, having an annual load of \( \sim 1.5–2.5 \times 10^{10} \) kg yr\(^{-1}\), making this system the largest terrigenous sediment source on the US West Coast (Milliman and Syvitski, 1992; Wheatcroft and Sommerfield, 2005). The outer shelf to upper slope of this margin accumulates
solutions at rates of 0.2–1.4 cm yr\(^{-1}\), with an area-normalized rate of 0.4 cm yr\(^{-1}\) (Sommerfield and Nittouer, 1999; Wheatcroft and Sommerfeld, 2005). This region of sediment accumulation accounts for approximately one third of all the sediment discharged by this system (Wheatcroft et al., 1997; Wheatcroft and Borgeld, 2000).

Although the Eel River represents the largest sediment source to the region (Wheatcroft and Sommerfield, 2005), much of that sediment (two thirds) appears to be transported elsewhere along the margin, presumably down the continental slope and canyon (Wheatcroft, 2000). The shelf near the Umpqua River also retains a significant fraction of its sediment (Wheatcroft and Sommerfield, 2005), but this system is smaller than the Eel. Both rivers deliver fresh, highly reactive material to the shelf bed as the climate of the Pacific Northwest is wet, and major flood events are common to this system. Sediments in this shelf region are typically bioturbated down to several tens of centimeters depth (Wheatcroft and Sommerfield, 2005; Wheatcroft, 2006) with bioirrigation as a major pathway for solute exchange, which was confirmed by the frequent encounter of macrofauna during processing of sediment cores. The final two aspects of our study site choices have to do with (1) the timing of upwelling, and (2) the possibility for late-season hypoxia. In terms of upwelling, the Pacific Northwest margin is characterized by the upwelling season typically being well under way by June (Bakun, 1973). Although much less is known about the occurrence of hypoxia in the region, it is possible that low oxygen conditions on the shelf may be a regular event—at least along the Oregon margin (Service, 2004; Chan et al., 2008). In some regards our selected sites are unusual in that they represent shelf areas where sediment is accumulating; however, these sites offer an opportunity for assessing the benthic iron efflux to this region’s coastal zone. In comparison to our Pacific Northwest continental shelf sites, we also discuss previously published data from Monterey Bay (Berelson et al., 2003; Elrod et al., 2004), and present new data for samples collected from Morro Bay in July 2001 (McManus et al., 2003; Hammond et al., 2004) (Fig. 1). The terrigenous sediment delivery flux at these central California shelf sites is likely to be smaller compared to the Pacific Northwest BIF sites, but as with the BIF sites, both of the central California shelf sites are quite likely to be occupied by macrofauna, and bioirrigation is a dominant pore water transport process. We also present both new and previously published data (McManus et al., 1997; Elrod et al., 2004) from two California Borderland Basin sites (San Pedro and Santa Monica Basins) for comparison of their iron fluxes and isotope compositions to those measured along the two shelf areas (see Table 1 for station overview).

### 3. METHODS

The benthic incubation chambers used in this work have been described previously (Berelson and Hammond, 1986; Berelson et al., 2003). Briefly, each “benthic lander” contains three PVC chambers with an approximate volume of 7 ± 1 l and is stirred by a rotating paddle (7 RPM). Each chamber draws six samples (200 ml) during incubation at preprogrammed time intervals. To assess chamber volume we introduce a spike of CsCl into each chamber. Upon recovery, samples are stored in various types of collection tubes before processing for analysis of pH, \(^{14}C\)O\(_2\), oxygen, and trace metals. Trace metal samples are filtered through 0.45 μm filters with Polyethersulfone membrane (Whatman® GD/X Syringe filters), which is operationally defined here as the total dissolved fraction, and trace metal samples are acidified to pH ~1.7 with purified HCl. Samples for oxygen analysis (8 ml) were collected and stored in valved, glass ampoules. Dissolved oxygen was analyzed on board ship within an hour of lander recovery using an optode (PreSens GmbH, Regensburg, Germany), which typically has an uncertainty of ±1 μM.

Sediment cores were retrieved using a multi-corer (Barnett et al., 1984) and immediately placed into a cold room for further processing at in situ temperature (~4 °C). Sediment pore fluids were obtained by centrifugation. For this technique sediments were placed in centrifuge tubes under a nitrogen atmosphere. After centrifugation, porewater samples were filtered using 0.45 μm filters with Polyethersulfone membrane. Wet sediments for two cores recovered during BIF-I (Eel River 70 m site and Umpqua River 105 m sites) were analyzed for their operationally defined highly reactive iron contents using 1 M hydroxylamine-HCl solution in 25% v/v acetic acid (Chester and Hughes, 1967; Poulton and Canfield, 2005). Extractions were performed at room temperature over 48 h, and this procedure has been shown to extract easily reducible iron oxides (ferrihydrite and lepidocrocite).

In this communication we report the dissolved oxygen, total dissolved iron and organic carbon respiration rates from the benthic incubation chambers. In addition, the iron isotope composition of a number of benthic incubation samples is presented. Total dissolved iron concentrations from the BIF-I and BIF-II lander samples were measured by isotopic dilution (ID) using enriched \(^{57}\)Fe spike. Sample purges were sampled using Nitriloacetic Acid (NTA) Superflow resin, following the protocol described in Lohan et al. (2005). For this procedure an aliquot of H\(_2\)O\(_2\) was added to the acidified sample (pH 1.7) before passing it through a small in-line column containing 0.2 ml of the NTA resin. After removing the salt-matrix with ultra-pure water, samples were eluted with 2 M HNO\(_3\). Analyses of purified ID samples were conducted on an Axiom high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) at Oregon State University, average reproducibility was ±1% based on replicate analyses. In addition to the ID method, samples from BIF-II, Morro Bay and the Borderland basins were also analyzed by developing a standard curve using Sc and Ge as internal monitor. Analysis of 10-fold diluted samples (no pre-concentration) was performed on an Agilent 7500ce quadrupole ICP-MS equipped with a collision cell at the University of California Riverside, average reproducibility for this method was ±7%. Comparison of ID versus standard calibration on select samples from BIF-II show good agreement between the two methods (average reproducibility ±11%) Obvious outliers that do not reproduce within our expected range, most likely due to contamination during or after sampling, were
Table 1
Station overview and flux data summary.

<table>
<thead>
<tr>
<th>Site name and sampling depth (approx.)</th>
<th>Lats</th>
<th>Longs</th>
<th>Date</th>
<th>Number of chambers</th>
<th>Bottom water diss. O₂ (µM)</th>
<th>Bottom water diss. Fe (nM)</th>
<th>Dissolved O₂ flux (mmol m⁻² d⁻¹)</th>
<th>Dissolved Fe flux (µmol m⁻² d⁻¹)</th>
<th>Carbon oxidation rate (mmol m⁻² d⁻¹)</th>
</tr>
</thead>
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<tr>
<td><strong>Northern Shelf. BIFI+II</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eel River shelf 70 m</td>
<td>40°</td>
<td>48.0</td>
<td>-124°</td>
<td>Apr-07</td>
<td>81</td>
<td>45.0</td>
<td>-5.1 ± 0.4</td>
<td>No lander deployment</td>
<td></td>
</tr>
<tr>
<td>Eel River shelf 70 m</td>
<td>40°</td>
<td>57.0</td>
<td>-124°</td>
<td>Apr-07</td>
<td>2</td>
<td>93</td>
<td>-8.0 ± 2.0</td>
<td>12 ± 4</td>
<td></td>
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<tr>
<td>Eel River shelf 70 m</td>
<td>40°</td>
<td>57.0</td>
<td>-124°</td>
<td>Apr-07</td>
<td>1</td>
<td>83</td>
<td>-6.5 ± 0.7</td>
<td>97 ± 11</td>
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<tr>
<td>Eel River shelf 70 m</td>
<td>40°</td>
<td>57.0</td>
<td>-124°</td>
<td>Apr-07</td>
<td>2</td>
<td>94</td>
<td>-5.2 ± 0.2</td>
<td>332 ± 30</td>
<td></td>
</tr>
<tr>
<td>Umpqua River shelf 105 m</td>
<td>43°</td>
<td>56.0</td>
<td>-124°</td>
<td>Apr-07</td>
<td>2</td>
<td>60</td>
<td>-6.1 ± 0.6</td>
<td>97 ± 11</td>
<td></td>
</tr>
<tr>
<td>Umpqua River shelf 105 m</td>
<td>43°</td>
<td>56.0</td>
<td>-124°</td>
<td>Apr-07</td>
<td>2</td>
<td>78</td>
<td>-6.5 ± 1.0</td>
<td>55 ± 18</td>
<td></td>
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<tr>
<td>Umpqua River shelf 105 m</td>
<td>43°</td>
<td>55.5</td>
<td>-124°</td>
<td>Apr-07</td>
<td>2</td>
<td>64</td>
<td>-3.3 ± 1.3</td>
<td>52 ± 19</td>
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<td>Umpqua River shelf 190 m</td>
<td>43°</td>
<td>55.2</td>
<td>-124°</td>
<td>Apr-07</td>
<td>3</td>
<td>60</td>
<td>-4.7 ± 0.4</td>
<td>21 ± 8</td>
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<td><strong>Central California shelf</strong></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Morro Bay 100 m</td>
<td>35°</td>
<td>17.9</td>
<td>-120°</td>
<td>Jul-01</td>
<td>2</td>
<td>112</td>
<td>n/d</td>
<td>26 ± 43</td>
<td></td>
</tr>
<tr>
<td>Morro Bay 200 m</td>
<td>35°</td>
<td>17.9</td>
<td>-121°</td>
<td>Jul-01</td>
<td>1</td>
<td>64</td>
<td>n/d</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>Monterey Bay 100 m</td>
<td>36°</td>
<td>44.8</td>
<td>-121°</td>
<td>Mar-94</td>
<td>6</td>
<td>133</td>
<td>n/d</td>
<td>6 ± 2</td>
<td></td>
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<tr>
<td>Monterey Bay 100 m</td>
<td>36°</td>
<td>44.8</td>
<td>-121°</td>
<td>Nov-95</td>
<td>3</td>
<td>153</td>
<td>n/d</td>
<td>11 ± 4</td>
<td></td>
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<tr>
<td><strong>California Borderland Basins</strong></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>San Rdsro Basin 900 m</td>
<td>33°</td>
<td>35.7</td>
<td>-118°</td>
<td>Jul-01</td>
<td>3</td>
<td>3</td>
<td>n/d</td>
<td>568 ± 215</td>
<td></td>
</tr>
<tr>
<td>Santa Monica Basin 900 m</td>
<td>33°</td>
<td>44.3</td>
<td>-118°</td>
<td>Jul-01</td>
<td>3</td>
<td>4</td>
<td>n/d</td>
<td>412 ± 81</td>
<td></td>
</tr>
<tr>
<td>Santa Monica Basin 900 m</td>
<td>33°</td>
<td>44.3</td>
<td>-118°</td>
<td>Jul-03</td>
<td>n/d</td>
<td>n/d</td>
<td></td>
<td>2 ± 1</td>
<td></td>
</tr>
</tbody>
</table>

a This study.
b Hammond et al. (2004) (lander data except Fe); McManus et al. (2003) (pore water Fe data); this study (lander Fe data).
d This study (lander data); McManus et al. (1997) (porewater Fe data, cores collected in March 1994).
e Brod et al. (2004) (lander data); this study (porewater Fe data, cores collected in July 2003).
f Errors for all calculated fluxes are 1-SD based on multiple chambers.
excluded from the data presented here. The means of the initial sample draws for the two BIF cruises are 28 ± 16 and 38 ± 13 nM for BIF-I and II, respectively. These values typically represent the sample draw approximately 1 h into the experiment and are assumed to represent a reasonable estimate of the iron concentration within the benthic boundary layer. In addition, bottom water samples were collected ~10 m above the seafloor with Niskin bottles (BIF-I cruise only), and concentrations were determined by a flow injection technique following Lohan et al. (2006) (analysis courtesy of Chris Holm, OSU). This method, which is modified after Measures et al. (1995), uses NTA resin for on-line sample pre-concentration and catalytic spectrophotometric detection with N,N-dimethyl-p-phenylenediamine dihydrochloride (FI-NTA-DPD). Analysis of NASS-5 (seawater certified reference material from the National Research Council of Canada) by the same technique gave a measured value of 3.4 ± 0.4 nM compared to the certified reference value of 3.7 ± 0.6 nM. Mean bottom water concentration during our cruise was 58 ± 8 nM, i.e. slightly higher than the initiallander draws.

Iron isotope measurements were made on a Thermo Finnigan High Resolution Multi-Collector ICP-MS (Neptune) at the University of California, Santa Cruz, and at the Woods Hole Oceanographic Institution Plasma Laboratory. Porewater and lander samples were purified using two different protocols. Porewater samples were purified following a standard anion exchange protocol (e.g., Beard et al., 2003), where an appropriate volume of porewater (previously acidified to pH <2 for preservation) was mixed with trace metal grade concentrated HCl to give a final molarity of 6 M HCl for the sample-acid mix. Following the initial processing through a large (0.6 ml) ion exchange column, purified samples were dried down, re-dissolved in 0.2 ml of 6 M HCl and processed through a second, smaller column with a 0.2 ml resin volume. Lander samples were purified and pre-concentrated using NTA resin and following the same procedure described above for iron concentration measurements. Following this initial purification step, samples were processed through a small ion exchange column (same as above) to remove any naturally occurring copper in the samples. The limited quantity of isotope data for the benthic chamber experiments is in part governed by the quantity of iron necessary for isotope analyses, the low iron concentrations at the start of the experiments, and the small sample volumes available from each sample draw.

To monitor matrix interference effects during isotope analysis we prepared an in-house seawater sample by spiking 1–10 ml of trace metal free seawater with a small amount of iron with known isotope composition. Trace metal free seawater was obtained by passing open ocean surface water through Chelex-100 resin. The ratio of iron to seawater matrix in our synthetic sample matched the lowest iron to seawater ratio in our porewater and lander samples. The measured isotope composition of our synthetic seawater samples was analytically indistinguishable from the pure iron standard reference material (Table S1, Electronic Annex).

Following the procedure of Arnold et al. (2004), purified samples were introduced into the mass spectrometer as 0.2–2 ppm iron solutions, mixed with equal amounts of copper standard of known isotope composition (NIST-976 copper isotope standard), which was measured simultaneously for mass bias correction. Sample isotope ratios were normalized to the average of two bracketing standards. Isotope ratios of \(^{56}\text{Fe}/^{54}\text{Fe}\) and \(^{57}\text{Fe}/^{54}\text{Fe}\) are reported using standard delta notation. Measured ratios are normalized relative to igneous rocks, which have an average iron isotope reference material IRMM-014 is \(-0.09\%\) for \(^{56}\text{Fe}\). The average analytical precision and the external precision for \(^{56}\text{Fe}\) (2 SD) are very similar at 0.13\% and 0.10\% respectively. Several standard reference materials of known isotope composition, including IRMM-014 (an international iron isotope standard), SDO-I (a black shale standard reference material) BIR-I (a basalt standard reference material) and an in-house porewater reference standard (made from natural porewater samples, iron concentration ~55 \(\mu\)M) were measured routinely for each sample batch.

Organic carbon respiration rates were estimated from the efflux of respiratory CO\(_2\). Measurements were made on 1–3 ml of chamber water using a UIC coulometer and standards provided by Scripps Institute of Oceanography (CO\(_2\)CRMS). In general, this estimate is not as precise as our other flux estimates. Some of this lack in precision derives from the \(\sum\text{CO}_2\) measurement, which had a large uncertainty during our BIF-I and BIF-II cruises in part because we are measuring a small change in \(\sum\text{CO}_2\) against a large background signal. However, the estimated respiratory CO\(_2\) flux is also limited by our lack of an accurate estimate for carbonate dissolution (or precipitation) rates in these settings. Thus our estimates of carbon oxidation rates are generally presented with a large uncertainty, and we look to the dissolved oxygen uptake fluxes to further develop the electron transport background for our discussion.

For all experiments presented, analytical precision is not likely the limiting factor governing our confidence in the benthic flux estimates. Contamination of samples, either with ambient bottom water or some other unknown contaminant introduced during handling, and our estimation of chamber volume and leakage all influence our confidence in any particular value or flux estimate. Benthic lander experiments are inherently fraught with a host of potential sampling artifacts that have been extensively discussed in the literature (see e.g., Rutgers van der Loeff et al., 1984; Sundby et al., 1986; Tengberg et al., 2005). For example, oxidation effects during chamber deployment and recovery are unavoidable and may cause an underestimation of the actual flux. However, we note that these oxidation effects essentially mimic processes that would otherwise occur in the water column as the benthic efflux is exposed to oxygenated bottom water. In addition, the heterogeneity of flux values at any given site produce an average flux with an uncertainty that tends to be as large or larger than the uncertainty deriving from any analytical uncertainty (Hammond et al., 1996). Despite these limitations, benthic chamber experiments remain one of our most dependable tools to shed light on the solute exchange between the sediments and the water column (Tengberg et al., 2005).
4. RESULTS

4.1. Incubation chamber results

Iron concentrations in the benthic incubation chambers from all sites generally show an increase with time (Fig. 3) with a range in iron flux from essentially zero iron flux (one chamber from Morro Bay) to a high flux exceeding \( \approx 500 \mu \text{mol m}^{-2} \text{d}^{-1} \) in the low oxygen environments of the Santa Monica and San Pedro Basins (Table 1). In total, these observations imply a net transport of iron from the sediments to the overlying water column along the continental margin (Elrod et al., 2004), with a particularly high benthic iron flux from the shelf region around the Eel River and the Borderland Basins. In addition, both nitrate (not shown) and dissolved oxygen within the incubation chambers exhibit a decrease in concentration with time (Fig. 4) and \( \Sigma \text{CO}_2 \) increases, which is consistent with the high rates of organic carbon oxidation in all of these settings. Evidence for oxygen consumption along with nitrate reduction
is prevalent not only throughout this study but it is a general feature of this continental margin (Reimers et al., 1992; Berelson and Stott, 2003), as is the observation of a significant iron benthic flux (Elrod et al., 2004).

When examined as a whole, the BIF-I benthic incubations suggest a non-linear increase in total dissolved iron as the experiments progress (Fig. 3). We will discuss this feature later; however, it is important to note here that to estimate the initial benthic flux—i.e., the change in concentration over time during the first 2–5 h of the experiment—we chose those data that best approximate a linear relationship between concentration and time as representative of the benthic flux. Samples that were excluded from the fit for flux calculations are in parentheses in the data appendix (Table S1). This approach effectively makes our estimates of the benthic flux minimum estimates. In contrast to the BIF-I experiments, during BIF-II the two Umpqua River sites suggest an approximately linear change in iron concentration with time. However, both Eel River sites show a curved profile with an increasing benthic iron flux with time, much like that observed during BIF-I (Fig. 3).

The northern continental shelf environments display quite high benthic fluxes compared to the central California shelf and previously reported iron fluxes in this region (Berelson et al., 2003; Elrod et al., 2004), but they are similar to fluxes reported by Lohan and Bruland (2008) for hypoxic shelf waters near large rivers. The highest benthic iron fluxes, however, were measured in the low oxygen settings of the San Pedro and Santa Monica basins (Fig. 3 and Table 1). Our estimates for these two basins are much higher than estimates from Elrod et al. (2004) for the same locations. We note, however, that the bottom water oxygen concentrations (3–4 μM) during sample collection for this study (Hammond et al., 2004) were lower than the values reported in Elrod et al. (2004), who measured oxygen concentrations of 9–10 μM during their sampling campaign. It is plausible that this difference in dissolved oxygen could drive large differences in the iron flux if the presence of higher oxygen concentrations in this basin effectively limited the flux of iron. The contrast between our data and that of Elrod et al. (2004) suggests that our high benthic flux does not represent a steady state feature of these basins and that fluxes in these settings can be highly variable.

The iron concentrations at the two central California shelf sites off Morro Bay are in the same range as the lowest estimates from our northern shelf data and previously published data from Monterey Bay (Fig. 3). One chamber from Morro Bay 100 m exhibits an iron flux that is essentially zero, and the other chamber from this station exhibits a non-linear concentration increase with time. The Morro Bay 200 m site has a higher benthic iron flux; however, we do not have an initial point for this chamber and this flux could therefore be non-linear as well. In sum, these values are consistent with the Oregon and northern California margin.

In addition to the iron concentration data, we also present iron isotope compositions of the dissolved benthic iron flux. Both the BIF-I chambers we measured from the Eel River 125 m site suggest that as the total dissolved iron concentration increases, the δ56Fe increases to progressively heavier isotope compositions relative to the initial point (Fig. 5). The first measured δ56Fe value for the red chamber from this site (Table S1) has an iron isotope composition of −5.0 ± 0.1‰ (2 SD), and linear extrapolation of this value to the initial stage of the experiment suggests that the initial iron flux might have had an isotope composition as low as ~−6‰. These values are among the lightest reported for natural samples, yet they are comparable to those measured for sediment porewaters from the mixing zone of a subterranean estuary, where precipitation of Fe-oxyhydroxides causes the residual dissolved Fe(II) to shift to values as low as −5‰ (Rouxel et al., 2008).

For the remaining deployments we measured only the experiment end points for their isotope composition (Table S1); therefore, it is not possible to make inferences whether similar trends are apparent for the other sites. However, all experiment end points converge on a mean iron isotope composition of −2.7 ± 1.1‰ (2 SD).

Benthic chamber isotope compositions from experiments conducted in the San Pedro and Santa Monica Basins have a slightly more negative isotope composition compared to the experiment end points from the northern
diffusion across the sediment–water interface, thus under these circumstances the source of the iron-rich fluid could be well below the sediment–water interface (Aller, 2001). The porewater iron isotope profile from the Santa Monica Basin shows a trend similar to that observed at northern shelf sites, with light values of −3‰ near the sediment surface and values between −1‰ and −2‰ at depth (Fig. 7).

5. DISCUSSION

5.1. The continental shelf iron flux

Our estimate of the benthic iron flux off the Eel River for the April/May 2007 period (≈330 μmol m⁻² d⁻¹) is the highest of the Pacific Northwest shelf sites, and is also the highest flux for any of the shelf sites we have measured (i.e., including Monterey Bay and Morro Bay). Furthermore, for the two stations near the Umpqua River and the 125 m station on the Eel River shelf we measured higher benthic iron fluxes during the April/May sampling period compared to those measured in September (Table 1). In the case of the 125 m Eel River station the flux decreased by more than one order of magnitude between May and September. The shallower (90 m) Eel River station exhibits little difference in the flux between the two sampling periods. Also, we do not have data from our third Eel River station (120 m) for both cruises.

One possible explanation for the apparent spatial and temporal difference in iron flux is that it may be related to the higher availability of reactive iron near the Eel River shelf compared to the Umpqua River shelf (i.e., spatial difference), and during spring as compared to September (i.e., temporal difference, see also Elrod et al., 2008). In terms of the spatial difference this rationale follows from the idea that the Eel River likely has higher sediment discharge as compared to the Umpqua. In terms of the temporal differences, the principle is that the winter and spring river discharge can deliver a significant reactive iron input to the shelf bed and that the remobilization of this iron is greatest during the high production period that follows the high
river discharge period (Fig. 2, and Colbert, 2004; Wetz et al., 2006; Elrod et al., 2008). Central to these ideas is the point made by Wetz et al. (2006) that the coastline-normalized riverine discharge decreases by >65% from Oregon to Northern and Central California. In short, there is ample evidence to suggest that there is a significant input of riverine particulate material in the winter and spring in these regions. Consistent with the hypothesis that reactive iron availability affects the magnitude of the benthic iron efflux, we have measured significantly higher concentrations of highly reactive iron in the sediments below 5 cm from the Eel River shelf compared to sediments from the Umpqua Rivers shelf (Fig. 8). We only measured highly reactive iron contents during the spring and cannot assess directly whether a depletion of reactive iron has occurred over the summer season. However, porewater iron concentrations during late summer are similar to or even slightly higher than spring porewater concentrations, suggesting that highly reactive iron is not depleted. In fact, mass balance calculations based on an average highly reactive iron contents of 0.5 wt.% (Fig. 8), and a mass accumulation rate that assumes a constant sedimentation rate of 0.4 cm yr$^{-1}$, an average downcore porosity of 0.7 and a sediment density of 2.6 g cm$^{-3}$, suggests that the sedimentary reactive iron delivered to the self can support an annual average benthic iron flux of $\geq 600 \mu$mol Fe m$^{-2}$ d$^{-1}$, i.e. an order of magnitude higher than most of our measured spring and summer iron fluxes (Table 1). The apparent excess of sedimentary

Fig. 6. Low porewater iron concentrations at the central California shelf station coincide with low benthic iron flux, whereas seasonal differences, e.g. at the 125 m Eel River station, are not reflected in the porewater concentrations. Morro Bay data are from McManus et al. (2003), Monterey Bay data are from Elrod et al. (2004), Santa Monica Basin data for March 1995 are from McManus et al. (1997), all other data are from this study.
reactive iron argues against its diminished availability over the summer exerting a major control on the seasonal variation in benthic iron flux.

With respect to geographic variations in sedimentary reactive contents, we observe that pore fluid iron concentrations are generally higher for the Eel River shelf compared to the Umpqua River shelf, consistent with the higher benthic iron fluxes measured near the Eel as well as the generally higher dissolved iron concentrations seen in the incubation chambers (Table 1 and Figs. 3 and 9). In contrast to these sites, which both have relatively high porewater iron concentrations, the porewater iron concentrations from Monterey Bay are quite low by comparison (Fig. 6 and Elrod et al., 2004), as is the benthic iron flux. Thus, to first order we observe high porewater iron concentrations (implying higher reactive iron contents) at shelf sites where iron fluxes are larger than the general oceanographic iron flux versus carbon oxidation relationship (Fig. 9a and Elrod et al., 2004). However, this broad generalization is unlikely to be true in detail, as other factors will certainly influence the transport of iron across the sediment–seawater boundary. For example, one of the influential factors that could affect exchange is the sediment irrigation rate because this process rather than diffusion, likely dominates transport in shelf environments (Aller, 1980a, 2001; Berelson et al., 2003). Another important example, as will be examined below, is the bottom water oxygen concentration. In short, we would not expect a simple relationship between the porewater concentrations and the large seasonal changes we observe in the benthic flux simply because variations in oxygen availability would tend to influence the iron flux as well (Sundby et al., 1986; Pakhomova et al., 2007).

Although the reported fluxes for our study are higher than previously reported for the Oregon–California margin, and are indeed comparatively high for open-ocean sites (e.g., Elrod et al., 2004) they are not anomalous for restricted basins with limited bottom water renewal (Sundby et al., 1986; Skoog et al., 1996; Friedl et al., 1998; Warnken et al., 2001; Friedrich et al., 2002; Pakhomova et al., 2007). Results from our study, specifically the high fluxes measured for the Eel River shelf, emphasizes the point made by the table and figure 7.
in Elrod et al. (2004) that their estimate for the shelf contribution to the global ocean iron budget ($2.2 \times 10^9$ mol y$^{-1}$) needs to be considered a minimum. Placing a more specific value on that flux is difficult; however, it is worth noting that in some locations at least a portion of this flux can be detected hundreds to thousands of kilometers from the ocean–continent boundary (Elrod et al., 2004; Lam et al., 2006; Nishioka et al., 2007; Lam and Bishop, 2008; Raiswell et al., 2008), making benthic iron flux an important delivery vector to the global ocean.

5.2. Relationship of chamber iron to dissolved oxygen

One of the more striking relationships that arise from our data is the non-linear iron concentration versus time relationship as the incubation experiments evolve. This relationship appears to be related to the depletion of oxygen during the experiments (Fig. 4). Essentially it appears that as oxygen decreases below a particular range, which seems to be centered around $60–80$ µmol (Fig. 10), the sediment package becomes sufficiently reducing that the flux of iron can increase. This observation implies a coeval relationship between the availability or remobilization of reactive iron in any one location and the bottom water oxygen concentration. The expression of this relationship is at least implied for the 125 m Eel River site where the spring flux is much greater than all of the other sites, yet the September flux is puzzlingly low. Here the bottom water oxygen contents for September are greater ($125$ µM) than for the spring period ($94$ µM). At the Umpqua River sites both time periods have oxygen concentrations of $60–80$ µM (Table 1) but the spring Fe fluxes are roughly twice the fall flux.

The importance of oxygen on the benthic iron flux certainly has been discussed prior to this work (Balzer, 1982; Sundby et al., 1986; Pakhomova et al., 2007; and references therein), and may also partially explain the low fluxes at the Monterey Bay site, as this site was reported to have much higher bottom water oxygen concentrations that ranged between $100$ and $185$ µM (Elrod et al., 2004). Thus although we believe that the presence of reactive iron and, more specifically, high pore water iron concentrations, is an important component to the high benthic iron flux, the influence of dissolved oxygen certainly cannot be ignored (Sundby et al., 1986; Pakhomova et al., 2007).

This point of the importance of dissolved oxygen is also apparent in the Morro Bay sites. Here the lower flux occurs at a Shallower site (100 m) having a bottom water oxygen concentration of $112$ µM (Hammond et al., 2004), whereas the high iron flux is at a deeper shelf site (200 m), with a lower organic carbon oxidation rate, but a bottom water oxygen concentration that is roughly half that of the shallower site ($64$ µM, Hammond et al., 2004). Another important difference between the two Morro Bay stations is the higher porewater iron contents at the 200 m site compared to the shallower 100 m site (Fig. 6).

The San Pedro and Santa Monica Basin sites provide additional data regarding the importance of oxygen on iron benthic fluxes. These sites differ significantly in a number of respects from the shelf sites. An important distinction between the Borderland Basin sites and the other shelf sites is that in these low oxygen basins the transport across the sediment–seawater boundary is likely dominated by diffusive rather than advective transport (i.e., bioirrigation). This difference means that critical oxygen levels could well
play a more prominent role in restricting or enhancing iron transport across that boundary. During the period when these basins were sampled for this work, oxygen contents were quite low (3–4 μM, Hammond et al., 2004). These basins are intermittently flushed (Berelson, 1991) and exhibit sedimentary characteristics of temporal oxygen variability (Hagadorn et al., 1995; Stott et al., 2000), thus oxygen can be consumed over time following a flushing period or event, which would allow the oxygen penetration depth to shoal and reducing conditions expand over time. This would have the net effect of remobilizing oxidized iron close to the sediment–water boundary, and likely lead to high variability in the benthic flux measured in this basin. Prior data from this region also showed higher fluxes compared to the other continental margin sites (Fig. 9a, and Elrod et al., 2004); however, the iron fluxes from that study were lower than those reported here while the reported bottom water oxygen content was higher (9–10 μM, Elrod et al., 2004).

Overall the benthic iron flux values presented in this study show a reasonably good correlation with bottom water oxygen (Fig. 9b). The improved correlation compared to the iron flux versus carbon oxidation relationship (Fig. 9a) suggests that oxygen is a more dominant variable with respect to benthic iron flux, at least in coastal sediments that have an excess of reactive iron. It is unlikely, however, that a single parameter can be considered as a master variable that operates across a broad range of marine settings.

### 5.3. Iron isotope composition of the benthic flux

Porewaters from bioturbated continental margin sediments near Monterey Bay have previously shown iron isotope compositions to be light relative to average weathering flux (Severmann et al., 2006). The porewater values generally range between −1‰ and −3‰ with the lightest compositions near the sediment–water boundary. These porewater iron isotope compositions imply that if there is a substantial benthic iron flux along continental margins, and that iron originates from near the sediment water interface, then the water column iron would be isotopically light. Our new porewater data reaffirm that indeed the near-surface porewater isotope compositions are light and our benthic incubation chamber data clearly suggest that the benthic flux is also light (Figs. 5 and 7).

The positive correlation between δ⁵⁶Fe and iron concentrations in the BIF porewaters (Fig. 11) suggests that the isotope compositions are driven not just by the effect of iron reduction, but also, at least in part, by the fractional removal of iron into isotopically heavier oxyhydroxide phases (Bullen et al., 2001; Rouxel et al., 2008). Teutsch et al. (2005) offer an alternative explanation and suggest that sorption of Fe(II) onto iron oxide/hydroxide particles is the primary control on the dissolved iron isotope compositions. Irrespective of the removal mechanism, the pertinent observation with respect to our BIF porewater and chamber isotope compositions is that partial removal of a Fe(II) by oxidation or sorption onto freshly precipitated oxyhydroxides would drive the residual dissolved iron pool to lower δ⁵⁶Fe values.

The effect of partial re-oxidation of dissolved iron on the isotope compositions is evident in the BIF-I chamber data from the Eel 125 m site, where δ⁵⁶Fe values increase steadily with decreasing oxygen concentrations and increasing iron concentration in the chamber (compare Figs. 3–5). One interpretation of the higher δ⁵⁶Fe values as the incubation experiment progresses is that an increasingly smaller proportion of Fe(II) is re-oxidized at this site. However, the absence of such a correlation in the chamber data from the California Borderland Basin sites, where the isotope
consistent with the porewater data in this report and in Severmann et al. (2006). Although not apparent in the bulk porewater profile, infaunal pumping (Fig. 12b). Because chamber oxygen concentrations in our northern shelf station experiments (Eel and Umpqua River shelves) did not drop to zero, a thin but significant oxidized layer would have remained intact at the sediment–seawater boundary, and benthic pumping would have persisted. Within the burrows, however, the oxidized layer likely disappeared, effectively eliminating any diffusive barrier to the iron-rich pore fluids that are apparent in the ‘bulk’ porewater profiles at depths >5 cm (Fig. 6). Under low bottom water oxygen conditions the iron-rich water that would fill the anoxic burrows is transferred very effectively to the bottom water by infaunal pumping (Fig. 12b).

In the porewater isotope profile, the oxidized surface layer coincides with the lowest porewater δ^{56}Fe values (Fig. 7a), as has previously been observed in other continental margin sediments (Severmann et al., 2006). Although not apparent in the bulk porewater profile, infaunal

boundary is constant, and that the proportion of iron that is re-oxidized in the benthic boundary layer also remains constant. The data collected at the BIF study sites forces a reanalysis of these assumptions, and there are (at least) two plausible explanations for how progressively decreasing bottom water oxygen concentrations may affect the iron flux from the sediments, and both of them are consistent with the benthic chamber iron trends.

5.4. Effects within the sediments

The first explanation concerns the effect that decreasing oxygen concentrations would have on benthic infauna activity, the sediment oxygen penetration depth, and consequently the rate of solute exchange. The curvature observed in some of the chamber iron concentrations may be considered as a transition from small to large fluxes as porewater iron diffuses across the oxidized surface layer in the sediments. The oxygen penetration depth in the sediments was calculated from the initial bottom water oxygen concentrations and the flux of oxygen into the sediments (Table 1, following the approached used in Cai and Reimers, 1995) and was found to vary between 0.2 and 0.4 cm for our BIF stations (Table 2). The time it would take for an iron molecule to diffuse a distance of 0.2 to 0.4 cm through surface sediments with an average porosity of 0.9 at 10 °C (based on the Stokes–Einstein equation) is 5–20 h, which overlaps with the time frame during which we have the observed the transition from small to large flux at these stations. Sites with shorter oxygen penetration depth show this increase in iron flux earlier, and it is intriguing that the diffusion time scale corresponds with the timing of change in the magnitude of the flux.

Decreasing bottom water oxygen will also affect the depth of oxygen penetration into the sediments and the activity of benthic organisms. The conventional wisdom is that asphyxiation of benthic infauna will shut down the advective transport and significantly decrease the rate at which dissolved species are released from the sediments (Aller, 1980b, 2001; Rutgers van der Loeff et al., 1984). In the case of iron (and other redox-sensitive species), however, a progressive shoaling of the oxygen penetration depth could also dramatically increase the diffusive iron flux into the bottom water (Fig. 12). Because chamber oxygen concentrations in our northern shelf station experiments (Eel and Umpqua River shelves) did not drop to zero, a thin but significant oxidized layer would have remained intact at the sediment–seawater boundary, and benthic pumping would have persisted. Within the burrows, however, the oxidized layer likely disappeared, effectively eliminating any diffusive barrier to the iron-rich pore fluids that are apparent in the ‘bulk’ porewater profiles at depths >5 cm (Fig. 6). Under low bottom water oxygen conditions the iron-rich water that would fill the anoxic burrows is transferred very effectively to the bottom water by infaunal pumping (Fig. 12b).

In the porewater isotope profile, the oxidized surface layer coincides with the lowest porewater δ^{56}Fe values (Fig. 7a), as has previously been observed in other continental margin sediments (Severmann et al., 2006). Although not apparent in the bulk porewater profile, infaunal
burrows are probably lined by a similar low $\delta^{56}$Fe porewater boundary layer. Under the initial conditions of relatively high bottom water oxygen, all porewater iron must overcome this oxidized boundary before it exits the sediments. As the burrows become increasingly anoxic, iron diffuses more freely into the water contained within the burrows and the isotope composition progressively shifts to heavier $\delta^{56}$Fe values, approaching that of the deeper porewater pool (Fig. 7). The deep burrows provide a pathway for rapid transfer of the deeper sourced high [Fe]-high $\delta^{56}$Fe porewater pool to the overlying water, consistent with a change in benthic chamber iron isotope compositions from very light to progressively heavier values. In the California Borderland Basin sites, in contrast, bioturbation is likely limited to the upper few millimeters and deep bioirrigation by macofauna is absent or at least highly reduced compared to the shelf environment as evidenced by laminations in some locations within the basin (Stott et al., 2000). Consequently, the porewater iron flux is sourced from shallow sediment depth throughout the experiment, and the isotope composition does not change over time.

Under this scenario of decreasing bottom water oxygen concentrations, this situation may lead to an initial increase in solute exchange of redox-sensitive species, and yet may ultimately involve a reduction in advective transport when bioirrigating fauna become asphyxiated. With prolonged low bottom water oxygen concentrations, bioirrigation will eventually cease, and porewater iron would be increasingly titrated by sulfide as bacterial iron reduction is replaced by sulfate reduction. Previous flux studies from a shallow bay

Table 2

<table>
<thead>
<tr>
<th>Station</th>
<th>Oxygen penetration depth</th>
<th>Time to large Fe flux (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIF-I Eel River shelf 90 m</td>
<td>0.38</td>
<td>14.5</td>
</tr>
<tr>
<td>BIF-II Eel River shelf 90 m</td>
<td>0.35</td>
<td>17</td>
</tr>
<tr>
<td>BIF-I Eel River shelf 125 m</td>
<td>0.39</td>
<td>7</td>
</tr>
<tr>
<td>BIF-II Eel River shelf 125 m</td>
<td>0.43</td>
<td>20</td>
</tr>
<tr>
<td>BIF-I Umpqua River shelf 105 m</td>
<td>0.26</td>
<td>5</td>
</tr>
<tr>
<td>BIF-II Umpqua River shelf 105 m</td>
<td>0.25</td>
<td>–</td>
</tr>
<tr>
<td>BIF-I Umpqua River shelf 190 m</td>
<td>0.40</td>
<td>15</td>
</tr>
<tr>
<td>BIF-II Umpqua River shelf 190 m</td>
<td>0.27</td>
<td>17</td>
</tr>
</tbody>
</table>

Fig. 12. High initial bottom water oxygen concentrations establish an oxidized surface layer with isotopically light porewater iron; the oxic layer poses a barrier to rapid diffusion. Decreasing bottom water oxygen concentrations causes the worm holes to become anoxic, and porewater with high iron concentrations and heavier isotope composition is rapidly transferred into the bottom water through pumping by the benthic biota.
in the Black Sea have shown that sediments may even become a sink for iron as it is scavenged by porewater sulfide (Pakhomova et al., 2007); therefore, and because of the dynamics between the benthic biota and chemistry, it is unclear precisely how the magnitude of benthic-ocean exchange will be altered once lower oxygen concentrations become a persistent feature. However, based on our results, relatively small changes in bottom water oxygen concentration may promote large changes in the benthic Fe flux, but as oxygen concentration continues to decline, benthic Fe fluxes may also lessen.

5.4.2. Effects within the bottom water

A second explanation for the coupling between iron flux and bottom water oxygen relates to the affect of iron oxidation kinetics; it essentially concerns the fate of the dissolved iron flux after it leaves the sediments and mixes into the bottom or chamber water. The half-life \(T_{1/2}\) of dissolved iron within a chamber describes the rate at which Fe(II) is lost through oxidation; it can be estimated as a function of oxygen concentration, temperature and pH, and should be on the order of a few hours (Lohan and Bruland, 2008) under typical sea water, upper ocean conditions. During the seafloor incubation experiments, Fe(III) may be precipitated on the chamber walls, the sediment surface, or within the sample vials prior to filtration. As the experiments progress, the decrease in chamber oxygen concentration with time causes the iron \(T_{1/2}\) in the benthic chamber to progressively increase. The assumption is that the changes in chamber pH during incubation (as much as 0.2 pH units) are secondary to the oxidation rate as a function of oxygen concentration.

To demonstrate the influence of a change in the iron oxidation kinetics we generated a model where a constant initial iron flux was delivered to the chamber (height = 10 cm). The term ‘initial’ in this case refers to the primary benthic flux without taking into account anyoxic removal that may take place in the chamber or chamber sample storage vessel. At 2 h intervals the accumulated iron is subjected to a loss term such that

\[
C_t = C_0 \cdot e^{-\lambda t}
\]  

(1)

The iron concentration \(C_t\) at time \(t\) was calculated cumulatively for each time interval with a loss term defined by the time for iron accumulation and a decay term \(\lambda\), where

\[
\lambda = 0.69 / T_{1/2}
\]  

(2)

and

\[
T_{1/2} = 34.36 \cdot e^{(-0.242 \cdot \frac{\text{O}_2}{2})}
\]  

(3)

as defined by Lohan and Bruland (2008). A further correction in chamber data takes into account the time it took for sample recovery and processing, including a 5-h time delay between the last sample draw and shipboard filtration. The oxygen concentrations applied to each time step were based on measured oxygen profile for the chamber in question.

We applied this model to the results from the Eel River site at 125 m (Fig. 13). Our observations from two seafloor incubation experiments, are consistent with a model that assumes an initial iron flux of 1 mmol m \(^{-2}\) d \(^{-1}\) for BIF-I and 3 mmol m \(^{-2}\) d \(^{-1}\) for BIF-II, respectively. The two example chambers had different initial and final chamber oxygen concentrations, yet both were well fitted by the Lohan and Bruland (2008) formulation. This outcome suggests that a remarkably large rate of Fe(III) remobilization occurs within BIF sediments such that it generates an initial Fe(II) flux of 1–3 mmol m \(^{-2}\) d \(^{-1}\). The model output also shows that \(T_{1/2}\) likely increased from 1–3 to 8–11 h over the duration of the experiments. A longer \(T_{1/2}\) implies that relatively less dissolved Fe(II) is oxidized to Fe(III) and removed as iron-oxyhydroxide. The effect on the iron isotope composition is that the iron in the chamber will become increasingly heavier as the iron oxidation kinetics shift in favor of a relatively larger dissolved Fe(II) pool (Bullen et al., 2001; Rouxel et al., 2008). In the California Borderland Basin sites, the initial bottom water oxygen concentrations were very low, suggesting that \(T_{1/2}\) at the start of the experiments was already comparable to the duration of the incubation, and oxidative iron loss was minimal. Consequently, the isotope compositions of dissolved iron remained relatively constant during the experiment, even as the chambers turned anoxic.

Both processes (shoaling of the oxygen penetration depth and change in iron oxidation kinetics) would lead
to a progressive increase in the $\delta^{56}\text{Fe}$ values of the chamber dissolved iron, which makes it difficult to evaluate quantitatively which process is more important. The likelihood is that both processes occur simultaneously, which explains why there is not a single threshold value for the transition from linear to exponential increase in chamber iron concentrations (i.e., low to high flux regime). Rather, we observe that ‘iron breakthrough’ occurs at bottom water oxygen concentrations ranging from $\sim$60 to 80 $\mu$M, presumably depending on a range of factors, including depth of bioirrigation and porewater iron concentrations.

6. CONCLUSIONS AND IMPLICATIONS FOR PAST AND FUTURE COASTAL IRON CYCLING

The primary motivation for this study was to assess the magnitude of the benthic iron flux along the continental shelf, and to assess if it has a recognizable iron isotope signature that is distinct from other oceanic iron sources. As predicted from previous studies of porewater isotope compositions in shallow coastal sediments (Bergquist and Boyle, 2006; Severmann et al., 2006), we found that the benthic iron flux has a light isotope composition that makes it distinct from other continental weathering sources. The mean $\delta^{56}\text{Fe}$ value of this flux generally ranges between $-2.5\%_{\text{e}}$ and $-3.5\%_{\text{e}}$, although it is somewhat sensitive to bottom water oxygen concentrations, especially in sediments dominated by solute transport associated with bioirrigation. If a significant portion of this shelf iron flux makes it to the open ocean it is likely that it is identifiable by its light isotope composition. Further modification of the isotope composition may occur as the iron is transported off shore, although quantitative utilization of bioavailable iron by the biota in HNLC regions will likely preserve the isotope composition of the shelf source in the cells.

Our general thesis regarding the first order processes that regulate the benthic iron flux is summarized in the schematic diagram of Fig. 2. The general concept is that during the lower productivity period of winter, rivers discharge most of their particulate material, and some of that material will maintain residence along the continental shelf. During the more productive spring period, primary production is likely fueled in part by the upwelling of nutrient-rich near-shore waters (Fig. 2, bottom). This production then produces a pool of reactive organic material that settles to the seafloor and creates a sedimentary package that has sufficient reducing potential to mobilize the particulate metals. The combination of these ideas is partially borne out in the high “dissolvable” water column iron concentrations, which have been observed previously along the Oregon margin (Chase et al., 2005a), as well as along the central California margin (e.g., Elrod et al., 2008). Our specific interest here was focused on comparing eastern-boundary sites having high particulate river discharge (Eel and Umpqua Rivers) with regions of presumably lower particulate discharge (e.g., Monterey Bay). Our general hypothesis was that the higher supply of continental “reactive” iron in the region near the rivers would result in a higher benthic flux as compared to “average” continental margin regions. Although this idea maintains merit, it is also clear that other shelf regions (e.g., Morro Bay) may also produce high benthic iron fluxes and that there is considerable (over an order of magnitude) variation in continental shelf benthic fluxes. Part of this variability appears to be linked to variations in dissolved oxygen. For example, the Umpqua River region dissolved oxygen is generally lower than the areas around the Eel River, and this difference may help maintain the high benthic iron fluxes during both study periods.

Our experiments highlight the effect of variable bottom water oxygen on the magnitude of the benthic iron flux in the context of past and current environmental changes. It is quite likely that changes in coastal productivity and sea level have had, or will have, an impact on the coastal and likely also the oceanic iron cycle (Fig. 14). During the current interglacial or high sea level stand, the flux of iron is assumed to be relatively high from shelf and low-oxygen regions. During the low sea level stands typical of glacial periods, much of the continental shelf may have been better ventilated or partially exposed, thus benthic iron delivery from the shelves would have been minimized during these periods. In contrast, as sea level rises, more of the shelf could become depositional, and if these environments also

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig14.png}
\caption{Changing environmental conditions, such as sea-level stand, ventilation, or surface productivity are likely to affect iron cycling on continental shelves, with higher coastal benthic iron flux during high sea-level stands and expanded oxygen minimum zones. This change in coastal biogeochemical iron cycling may have implications for productivity further offshore if iron can be effectively transported to the open ocean.}
\end{figure}
become increasingly hypoxic the iron supply to the water column could also increase (Fig. 14, future scenario). If a feedback is established that further enhances production and carbon export, the oxygen minimum zone could also expand, as has been shown to be the case for low-latitude coastal upwelling zones (Paulmier et al., 2008; Stramma et al., 2008). This admittedly oversimplified model highlights the need for a firm biogeochemical framework to improve the accuracy of past interpretations and future predictions.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2010.04.022.

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