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## RESEARCH LETTER

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## Key Points:

- Sequestration efficiency from North Atlantic
- Sequestration efficiency may be related to the mode Fe supply
- Mode of Fe supply needs to be considered in models

## Supporting Information:

- Readme
- Le\_Moigne\_et\_al\_GRL\_sup\_June12.docx

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## Sequestration efficiency in the iron-limited North Atlantic: Implications for iron supply mode to fertilized blooms

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**Abstract** Estimates of the amount of carbon sequestered in the ocean interior per unit iron (Fe) supplied, as quantified by the sequestration efficiency ( $C_{effx}$ ), vary widely. Such variability in  $C_{effx}$  has frequently been attributed to estimate uncertainty rather than intrinsic variability. Here we derive new estimates of  $C_{effx}$  for the subpolar North Atlantic, where Fe stressed conditions have recently been demonstrated. Derived values of  $C_{effx}$  from across the region, including areas subject to atypical external Fe fertilization events during the year of sample collection (2010), ranged from 17 to 19 kmol C (mol Fe<sup>-1</sup>). Comparing these estimates with values from other systems, considered in the context of variable bloom durations in the different oceanographic settings, we suggest that apparent variability in  $C_{effx}$  may be related to the mode of Fe delivery.

### 1. Introduction

Iron (Fe) availability has been shown to control phytoplankton growth in the so-called high nitrate low chlorophyll (HNLC) regions [Blain *et al.*, 2007; Boyd *et al.*, 2004; de Baar *et al.*, 2005; Pollard *et al.*, 2009; Smetacek *et al.*, 2012] including the Southern Ocean, equatorial Pacific, and subpolar North Pacific. More recently, some oceanic regions characterized by marked seasonal chlorophyll peaks (blooms), including the Irminger and Iceland Basins (hereafter IRB and IB, respectively) of the high latitude North Atlantic (HLNA), [Nielsdottir *et al.*, 2009; Ryan-Keogh *et al.*, 2013; Sanders *et al.*, 2005] have also been suggested to experience a degree of Fe stress. Within all these regions, Fe deficiency potentially contributes to incomplete utilization of surface macronutrients. Subsequent subduction of these unused macronutrients in regions of deep water formation, including the Southern Ocean or the HLNA, represents an inefficiency in the biological carbon pump [Marinov *et al.*, 2008; Nielsdottir *et al.*, 2009; Sarmiento and Orr, 1991]. Consequently, oceanic Fe availability has been invoked as a potential control on atmospheric CO<sub>2</sub> [Martin *et al.*, 1990], with for example, higher aerosol deposition to the glacial Southern Ocean hypothesized to have partly contributed to glacial/interglacial CO<sub>2</sub> cycles [Jickells *et al.*, 2005; Martinez-Garcia *et al.*, 2014; Ridgwell and Watson, 2002].

Quantitative understanding of linkages between variability in external Fe inputs and carbon cycling in different oceanic settings requires an understanding of the relationship between Fe supply and carbon sequestration, as encapsulated in the sequestration efficiency ( $C_{effx}$ ). To date, estimates of  $C_{effx}$  (defined as the ratio of carbon exported per unit of Fe supplied) from field programs have varied widely (~1.2 to 154 kmol C (mol Fe<sup>-1</sup>) [Boyd *et al.*, 2007; de Baar *et al.*, 2005; Morris and Charette, 2013]. The mode of Fe supply has previously been suggested as a mechanistic driver of such variability in  $C_{effx}$  [Boyd *et al.*, 2007; Chever *et al.*, 2010]. However, in the absence of any observed systematic basis for the reported >2 order of magnitude range in  $C_{effx}$ , these differences may also reflect uncertainties in calculations [Morris and Charette, 2013], including incomplete accounting for Fe sources or differing approaches for estimating C export. With the exception of values derived for Fe fertilized blooms around (sub-) Antarctic island systems, such as reported for the Kerguelen Ocean and Plateau compared Study (KEOPS) and Crozet natural iron bloom and export experiment (CROZEX) studies [Blain *et al.*, 2007; Pollard *et al.*, 2009], no estimates of  $C_{effx}$  have yet been derived for highly productive natural oceanic systems. Here we report new estimates for  $C_{effx}$  for the HLNA and attempt to synthesize these into a growing understanding of potential controls on this variable in the global ocean.

## 2. Methods for Ancillary Data and Export Fluxes

Sampling took place from 4 July to 10 August 2010, on board the RRS *Discovery* cruise D354 as part of the Irminger Basin Iron Study (IBIS) program. Inorganic nutrients and particulate organic carbon (POC) and nitrogen (PON) were sampled and analyzed as previously described [Le Moigne *et al.*, 2013b; Sanders and Jickells, 2000]. POC and PON export fluxes were subsequently calculated using the  $^{234}\text{Th}$  “small-volume” technique [Pike *et al.*, 2005]. Briefly, vertical profiles of  $^{234}\text{Th}$  activity (integrated to a depth of 100 m) were converted to estimates of downward  $^{234}\text{Th}$  flux using a one dimensional steady-state model [Buesseler *et al.*, 1992]. Extraction efficiencies for  $^{234}\text{Th}$  were  $90.6 \pm 6.7\%$  [Le Moigne *et al.*, 2013a, 2012]. Observed  $^{234}\text{Th}$ :POC and  $^{234}\text{Th}$ :PON ratios for large ( $>53 \mu\text{m}$ ) particles collected using in situ Stand Alone Pumping Systems (SAPS) deployed for 1.5 h at a single depth beneath the mixed layer were then used to convert  $^{234}\text{Th}$  fluxes to POC/N fluxes. Approximately 1500–2000 L of seawater was filtered using  $53 \mu\text{m}$  mesh filters (Nitex), with swimmers manually removed following filtration. Particles were then rinsed off the filters using Th-free seawater as prepared following [Le Moigne *et al.*, 2013b], and the particle suspensions were split and analyzed for  $^{234}\text{Th}$ , POC, and PON as described in Le Moigne *et al.* [2013b]. Maiti *et al.* [2012] suggested that high flow rates may lead to particle disintegration. The pump rates we used were about two times larger than those used by Maiti *et al.* [2012]; however, the surface area of our filters was around 4 times larger [Le Moigne *et al.*, 2013b]. Therefore, the velocity of seawater through the filter was around half of that used by Maiti *et al.* [2012]. Dissolved iron was determined following procedures reported by Painter *et al.* [2014].

## 3. Results and Discussion

### 3.1. The High Latitude North Atlantic in 2010

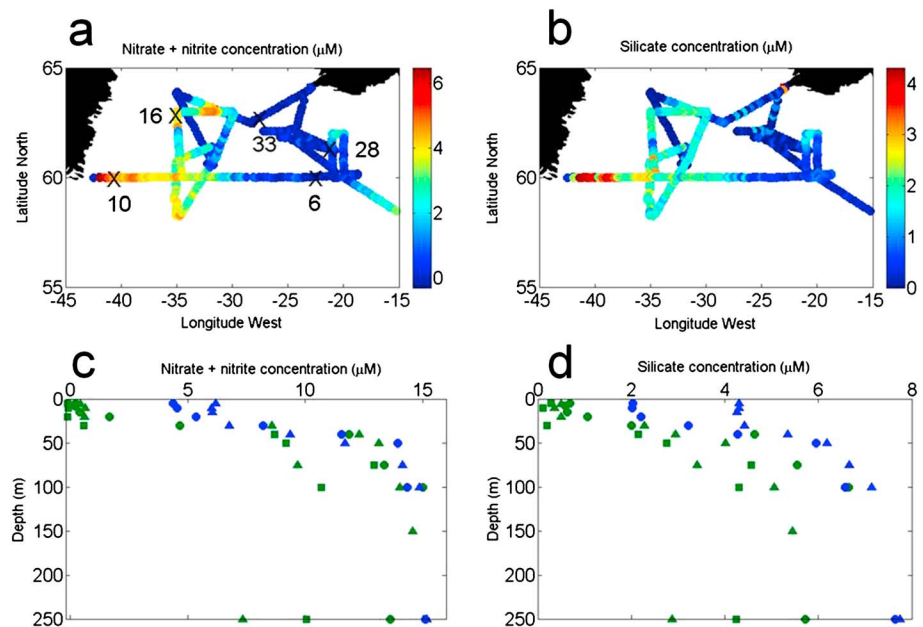
Biogeochemical cycles in the HLNA were perturbed during 2010 as a result of aerosol Fe deposition to the IB from the eruption of the Icelandic volcano Eyjafjallajökull [Achterberg *et al.*, 2013]. In addition, winter mixed layer depths prior to our cruise were shallower than average in the IRB, while the summer euphotic zone ( $40 \pm 5 \text{ m}$ ) and mixed layer depths ( $28 \pm 8 \text{ m}$ ) represented typical conditions for both the IB and IRB [Henson *et al.*, 2013; Painter *et al.*, 2014]. Consequently, inputs of Fe from deep winter convection were also likely up to fourfold higher in the IB ( $37,500 \text{ nmol m}^{-2}$ ) relative to the IRB ( $10,000 \text{ nmol m}^{-2}$ ) [Painter *et al.*, 2014].

Volcanic Fe inputs during May 2010 to the IB potentially resulted in enhanced macro-nutrient drawdown, with low observed nitrate ( $<1 \mu\text{M}$ ) during summer 2010 in the IB [Achterberg *et al.*, 2013; Ryan-Keogh *et al.*, 2013], while concentrations remained relatively high ( $3\text{--}5 \mu\text{M}$ ) and comparable with previous observations in the IRB [Sanders *et al.*, 2005] (Figures 1a and 1c). Silicate was also strongly depleted in the IB ( $<1 \mu\text{M}$ ) relative to IRB ( $1\text{--}4 \mu\text{M}$ ) (Figures 1b and 1d). Correspondingly, nutrient enrichment experiments demonstrated clear evidence of Fe limitation in the IRB during summer, while Fe stress was much less severe under the low macronutrient conditions encountered in the IB [Ryan-Keogh *et al.*, 2013]. Furthermore, phytoplankton Fe:C uptake ratios calculated using radiotracer incorporation techniques [Poulton *et al.*, 2010; Twining *et al.*, 2004] averaged  $0.9 (\pm 0.6)$  and  $4.1 (\pm 1) \mu\text{mol mol}^{-1}$  during summer in the IRB and IB, respectively (C. M. Moore and A. J. Poulton, unpublished data), comparable with observations of Fe-limited temperate taxa ( $\sim 2\text{--}10 \mu\text{mol mol}^{-1}$ ) [Sunda and Huntsman, 1995] and, for the IRB, Fe-limited taxa isolated from chronically low Fe environments [Strzepek *et al.*, 2012].

By the time of our summer sampling, chlorophyll-a (Chl-a) concentrations in the IB had decreased following the spring bloom [Ryan-Keogh *et al.*, 2013]. In contrast, a marked bloom ( $\sim 1\text{--}4 \mu\text{g l}^{-1}$ ) was still underway in the central IRB, potentially as a result of anomalous hydrographic forcing [Henson *et al.*, 2013]. Conditions in the post-bloom western IRB [Ryan-Keogh *et al.*, 2013] were similar to those within the classical Fe-limited systems, with relatively low Chl-a concentrations ( $<1 \mu\text{g l}^{-1}$ ) and residual nitrate ( $>4 \mu\text{M}$ ). Hereafter, we thus restrict discussion of the IRB to this western region [Ryan-Keogh *et al.*, 2013]. Consequently, we compare carbon export measurements for two stations in the IRB (stations 10 and 16, hereafter lower Fe input, –Fe) and three stations in the IB (stations 6, 28, and 33, hereafter higher Fe input, +Fe) (Figure 1).

### 3.2. Carbon Export

In order to derive  $C_{\text{eff},x}$  estimates of both carbon export and Fe input fluxes are required. Following our previous work [Pollard *et al.*, 2009], seasonal nutrient deficits were combined with estimates of the  $^{234}\text{Th}$ -based C and N



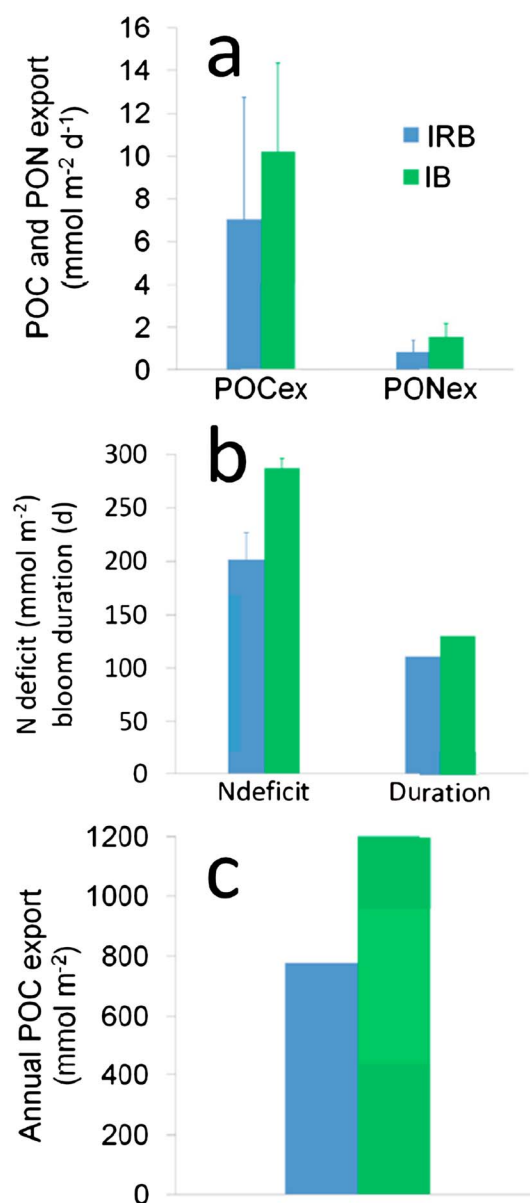
**Figure 1.** Nutrients in the high-latitude North Atlantic. (a) Map of surface water nitrate + nitrite concentrations ( $\mu\text{M}$ ) during summer 2010. Carbon export stations are indicated for reference, 10 and 16 are the high nitrate stations while 06, 28, and 33 are the low nitrate stations. (b) Map of surface water silicate concentrations ( $\mu\text{M}$ ) during summer 2010. (c) Nitrate + nitrite concentration ( $\mu\text{M}$ ) profiles at high (blue filled, triangles: st10; circles: st16) and low (green filled, circles: st6; triangles: st28, squares: st33) nutrients stations. (d) Silicate concentration ( $\mu\text{M}$ ) profiles at, st6, 10, 16, 28, and 33, symbols are in Figure 1c (see Table S1, S2, and text in supporting information for full description).

export fluxes [Buesseler *et al.*, 1992; Le Moigne *et al.*, 2013b]. Dividing the observed inorganic N deficit (Figure 2a) with thorium-derived estimates of downward N flux, then multiplying the resultant estimates of export duration by the thorium-derived daily organic carbon fluxes (Figure 2b) (see supporting information), we determined annually integrated POC export estimates of 780 and 1330  $\text{mmol m}^{-2}$  in the IRB (–Fe) and the IB (+Fe), respectively (Figure 2c, range for both +Fe and –Fe given in Table 1). Excess C export between the Fe-replete (IB) and Fe-limited (IRB) area (Figure 2c) was thus 550  $\text{mmol m}^{-2}$ , similar to a previous estimate for the Crozet region [Morris and Charette, 2013; Pollard *et al.*, 2009], but lower than that for the KEOPS experiment [Blain *et al.*, 2007].

### 3.3. Sources of New Iron

In keeping with prior work [Blain *et al.*, 2007; Pollard *et al.*, 2009], we consider new sources of Fe to the system when deriving  $C_{\text{eff}}$ , while acknowledging that recycled Fe was likely important in supporting additional recycled production [Boyd and Ellwood, 2010]. As summarized in Table 1, we considered five potential sources of new Fe to the IB and IRB during 2010 (see supporting information for detailed derivations), namely: (1) typical (i.e., non volcanic) atmospheric deposition [Achterberg *et al.*, 2013], (2) additional volcanic atmospheric Fe flux to the IB as a result of the Eyjafjallajökull eruption [Achterberg *et al.*, 2013; Painter *et al.*, 2014], (3) upward vertical diffusive flux [Painter *et al.*, 2014], (4) convective winter mixing flux [Painter *et al.*, 2014], and (5) horizontal Fe flux from the adjacent continental shelves. The latter may include material originating from benthic supplies from continental shelves [Elrod *et al.*, 2004] and direct runoff from rivers and glacial melt [Bhatia *et al.*, 2013; Hawkings *et al.*, 2014].

Horizontal fluxes were estimated by considering surface water Fe concentrations away from shelf regions, ridges, or major currents in both the IB and the IRB following previously approaches [Bucciarelli *et al.*, 2001; Planquette *et al.*, 2007; Rijkenberg *et al.*, 2012] (see supporting information), considering two main sources to the IB (Icelandic shelf and Reykjanes ridge) and three main sources to the IRB (Greenland shelf, the Reykjanes ridge, and the Eastern Greenland Current). Overall, elevated dissolved and particulate iron (DFe and PFe) concentrations (Figures S2 and S3) observed close to the Iceland and Greenland shelves did not persist into



**Figure 2.** Annual carbon export in the Iceland and Irminger basins. (a) POC and PON export fluxes integrated at 100 m ( $\text{mmol m}^{-2} \text{d}^{-1}$ ), (b) nitrogen budget (nitrogen deficit  $\text{mmol m}^{-2}$ , and bloom duration, days, see main text for explanation), and (c) annual carbon export ( $\text{mmol m}^{-2}$ ). Errors (standard deviation) are also given in Table 1.

the central basins and hence horizontal inputs were minor, albeit still somewhat uncertain (Table 1). Horizontal fluxes and similar minor vertical diffusive fluxes were scaled up by multiplying daily fluxes by 100 days (the estimated bloom duration), and this showed that both were ultimately minor contributors to overall annual new Fe inputs (Table 1), which were dominated by the winter convective supply [Nielsdottir *et al.*, 2009; Painter *et al.*, 2014]. In total, the annual input of new Fe to the IB ( $0.041\text{--}0.044 \text{ mmol m}^{-2}$ ) was estimated to be  $\sim 4$  times larger than the input to the IRB ( $0.011 \text{ mmol m}^{-2}$ ), principally due to higher convective and volcanic fluxes (Table 1). Both these Fe input estimates are comparable with reported values from the KEOPS ( $0.001\text{--}0.023 \text{ mmol m}^{-2}$ ) and CROZEX ( $0.016\text{--}0.076 \text{ mmol m}^{-2}$ ) studies [Morris and Charette, 2013] (Figure 3a).

### 3.4. Sequestration Efficiency

Values of  $C_{\text{eff}}$  in the IB and IRB were  $\sim 30$  and  $\sim 65 \text{ kmol C (mol Fe)}^{-1}$ , respectively (Table 2), further confirming that the IB experienced Fe fertilization (values of  $C_{\text{eff}}$  were calculated separately for the two basins rather than as the difference between the two basins, see supporting information). Consistently with previous studies [Blain *et al.*, 2007; Pollard *et al.*, 2009], we also calculated the apparent efficiency of the excess export resulting from the enhanced flux of new Fe to the IRB ( $C_{\text{eff}(x)}$ ) (supporting information), yielding values of  $17\text{--}19 \text{ kmol C (mol Fe)}^{-1}$ , close to the CROZEX ( $17 \text{ kmol mol}^{-1}$ ) but lower than KEOPS ( $154 \text{ kmol mol}^{-1}$ ) values (Table 2, note hereafter we use the corrected values [Chever *et al.*, 2010; Morris and Charette, 2013] for KEOPS which include an additional source of Fe not considered in the seminal study [Blain *et al.*, 2007]). All these estimates are considerably higher than those from three artificial Fe fertilizations experiments ( $1.2\text{--}6.5 \text{ kmol mol}^{-1}$ , locations, and references given in Table 2).

Previous studies discussing such ranges in estimates for  $C_{\text{eff}(x)}$  have tended to focus on the comparability and validity of the methods used to construct Fe and C budgets [Blain *et al.*, 2007; Chever *et al.*, 2010; Morris and Charette, 2013; Pollard *et al.*, 2009], presumably based on the inherent assumption that the variability in  $C_{\text{eff}(x)}$  was too large to be ascribed to natural factors.

### 3.5. Mode of Fe Supply

Here we focus on an alternative hypothesis, namely that, as previously suggested [Boyd *et al.*, 2007; Chever *et al.*, 2010], the observed range may instead be driven by differences related to the mode of Fe supply. Three distinct modes of Fe supply characterize the various experiments. (1) In the shallow waters of the Kerguelen plateau (500 m deep [Blain *et al.*, 2007])  $C_{\text{eff}(x)}$  was large at intermediate levels of Fe inputs during

**Table 1.** Fe Inputs and Carbon Budget in Both Iceland and Irminger Basins (IB and IRB)

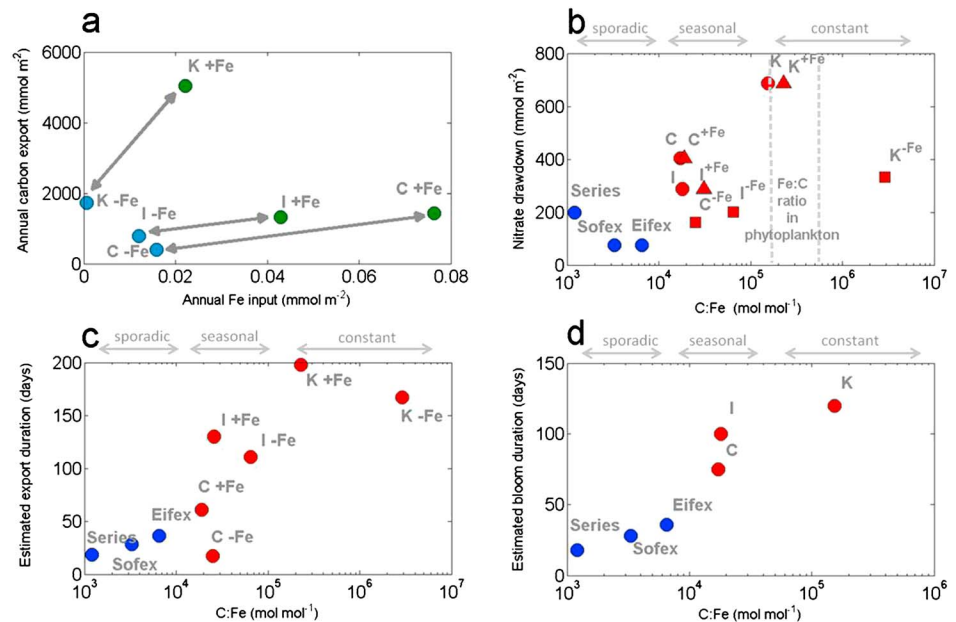
Annual Flux of Iron (nmol m <sup>-2</sup> )	IRB (-Fe)	IB (+Fe) Lower Limit <sup>b</sup>	IB (+Fe) Upper Limit <sup>b</sup>	Reference	Carbon Budget	IRB (-Fe)	IB (+Fe)
Atmospheric	(1168)	3478	6128	[Achterberg et al., 2013; Painter et al., 2014]	Nitrate drawdown (mmol m <sup>-2</sup> )	201 ± 25	287 ± 9
Vertical diffusive flux	160 <sup>a</sup>	250 <sup>a</sup>	250 <sup>a</sup>	[Painter et al., 2014]	Daily POC ex (mmol m <sup>-2</sup> d <sup>-1</sup> )	7.0 ± 5.7	10.2 ± 4.1
Winter mixing	10,000	37,500	37,500	[Painter et al., 2014]	Daily PON ex (mmol m <sup>-2</sup> d <sup>-1</sup> )	0.8 ± 0.6	1.5 ± 0.6
Horizontal Fe	15 <sup>a</sup>	4.5 <sup>a</sup>	4.5 <sup>a</sup>		Bloom duration (days)	111	130
Total	11,343	41,232	43,882		Annual POCex (mmol m <sup>-2</sup> )	778	1331
Total (in mmol m <sup>-2</sup> )	0.011	0.041	0.044		Range <sup>c</sup> (lower and upper limits)	682–769	1266–1449

<sup>a</sup>This was multiplied by 100 days to reflect the duration of the bloom (see text in supporting information). Values in brackets are measured “background” fluxes [Painter et al., 2014] (see text in supporting information).

<sup>b</sup>The lower and upper limit of Fe flux to the IB reflect the sensitivity analysis on the modeled volcano iron deposition given in Achterberg et al. [2013].

<sup>c</sup>Calculated as [Pollard et al., 2009].

the KEOPS study, with continued supply Fe throughout the year through a combination of diapycnal mixing across a vertical gradient over the shallow shelf and a northwestward flow from Heard islands past the eastern side of the Kerguelen plateau [Chever et al., 2010]. Hence, the Fe stocks above the plateau did not appear to vary much over the duration of the bloom [Blain et al., 2008; Chever et al., 2010]. (2) Conversely, in the deep waters of the productive HLNA and the fertilized region of the CROZEX bloom, the main supply of



**Figure 3.** Sequestration efficiency, annual carbon export, and nutrients drawdown for six artificial and natural Fe fertilization on the ocean. (a) Annual carbon export (mmol m<sup>-2</sup>) versus annual Fe input (mmol m<sup>-2</sup>), fertilized regions are in green circles, and non-fertilized regions are in blue circles. Experiment names and fertilized/non fertilized regions are indicated (I: IBIS; K: KEOPS; C: CROZEX). (b) Nitrate drawdown (mmol m<sup>-2</sup>) (inpatch – outpatch concentrations of nitrate multiplied by export integration depth for SERIES, EIFEX, and SOFEX) versus  $C_{effx}$  and  $C_{eff}$  (mol mol<sup>-1</sup>); red are naturally fertilized regions (circles:  $C_{effx}$ , triangles:  $C_{eff} + Fe$  regions, squares:  $C_{eff} - Fe$  regions), and blue circles are artificial fertilizations ( $C_{effx}$ ) (see Table 2). The mode of Fe supply is indicated on top of the panel as well as the Fe:C ratio in phytoplankton (reference in the main text). (c) Estimated export duration (days, given in [Pollard et al., 2009] for CROZEX and in Figure 2b for IBIS. KEOPS export duration was estimated in a similar fashion by dividing the daily downward fluxes of POC by the “seasonally integrated” downward fluxes of POC given in Blain et al. [2007]) (their Table 1). Bloom durations for KEOPS are 198 and 167 days, respectively, for + and -Fe regions) versus  $C_{eff}$  (mol mol<sup>-1</sup>); red circles are natural fertilized/non-fertilized regions, and blue circles are artificial fertilizations (see Table 2) concentrations (in μM, estimated from nutrients references given in Table 2 and Levitus [1982]) and annual carbon export (mmol m<sup>-2</sup>). (d) Bloom duration in the +Fe region (days) estimated from observed satellite-derived Chl-a time series (KEOPS [Blain et al., 2007]; CROZEX [Pollard et al., 2009]; IBIS [Achterberg et al., 2013], see Table S3 in supporting information) versus  $C_{effx}$ . Bloom duration for artificial experiments is assumed to be equal to the length of each experiment [Boyd et al., 2004; Buesseler et al., 2004; Smetacek et al., 2012].

**Table 2.** Carbon Sequestration Efficiency and Nutrient Drawdown

Area	Type of Fertilization	Nitrate Drawdown (mmol m <sup>-2</sup> ) <sup>d</sup>	Sequestration Efficiency ( $C_{effx}$ and $C_{eff}$ , kmol mol <sup>-1</sup> )	Reference
			$C_{effx}$	
HLNA	Natural	287	17.2–19.0	This study
Southern Ocean	Natural	687 <sup>b</sup>	154.0 <sup>a</sup>	[Blain et al., 2007]
Southern Ocean	Natural	404 <sup>c</sup>	17.2 <sup>a</sup>	[Pollard et al., 2009]
Southern Ocean	Artificial	75 <sup>e</sup>	6.5	[Smetacek et al., 2012]
Southern Ocean	Artificial	75 <sup>e</sup>	3.3	[Buesseler et al., 2004]
Subarctic Pacific	Artificial	200 <sup>e</sup>	1.2	[Boyd et al., 2004]
			$C_{eff}$	
HLNA	+Fe (IB)	given above	30.2–32.5	This study
	–Fe (IRB)	201	65.5	
Southern Ocean	+Fe	given above	227.3 <sup>a</sup>	[Blain et al., 2007]
(KEOPS Kerguelen)	–Fe	332 <sup>b</sup>	2,883.3 <sup>a</sup>	
Southern Ocean	+Fe	given above	18/8 <sup>a</sup>	[Pollard et al., 2009]
(CROZEX Crozet)	–Fe	161 <sup>c</sup>	25.0 <sup>a</sup>	

<sup>a</sup>Recalculated in [Morris and Charette, 2013].

<sup>b</sup>Nutrient data from KEOPS are presented in Mosseri et al. [2008].

<sup>c</sup>Nutrient data from CROZEX are presented in Sanders et al. [2007] (reference in supporting information).

<sup>d</sup>Nitrate drawdown in the upper panel of the table is given for the fertilized area or patch (+Fe).

<sup>e</sup>Nutrient drawdown was calculated as surface nutrient in-patch – surface nutrient out-patch multiplied by export integration depth.

Fe appears to be seasonal [Pollard et al., 2009] (Table 1). Hence, in both these regions, Fe might be expected to build up within the mixed layer during winter (a period of about 100 days). Once this mixed layer shoals in spring, the Fe pool can be used during the productive season until exhaustion [Nielsdottir et al., 2009; Planquette et al., 2007]. A similar situation is likely to characterize much of the Southern Ocean [Boyd et al., 2012; Tagliabue et al., 2014]. (3) Finally, during the artificial experiments, several tons of FeSO<sub>4</sub> were supplied to the surface ocean in one or several discrete seedings over a period of several weeks, resulting in a large loss of Fe due to the formation of insoluble Fe oxy-hydroxides [Boyd et al., 2000].

### 3.6. Implication for the Mode of Iron Supply in Fertilized Blooms

We suggest that it is likely that high  $C_{effx}$  values are associated with protracted blooms where Fe availability is maintained due to continuous Fe supply and perhaps also Fe complexation by organic ligands, sustaining continued C export over a prolonged period, rather than being rapidly lost through precipitation and scavenging. We test the association of high  $C_{effx}$  with prolonged blooms by comparing Fe supply modes to in situ estimates of nitrate uptake, duration of the export phase, and bloom duration (derived from satellite Chl-a time series, see supporting information Table S3). We acknowledge that estimates of the duration of export for the HLNA and CROZEX are not independent of the calculated seasonally integrated C export (and thus  $C_{eff(x)}$ ), as both are based on observed nitrate drawdown. However, nitrate drawdown and  $C_{effx}$  were independent variables in KEOPS and in the artificial Fe release experiments. Moreover, bloom durations derived from satellite Chl-a time series are independent of  $C_{effx}$  calculations in all cases and scaled well with estimated export durations (see Table S3 in supporting information). Overall, both  $C_{effx}$  and/or  $C_{eff}$  were correlated with bloom (or experiment) nitrate uptake (Figure 3b), export duration (Figure 3c), and bloom duration (Figure 3d). Moreover, the maximum estimates of  $C_{effx}$  and/or  $C_{eff}$  were comparable to the range of C:Fe ratios measured in Fe-replete phytoplankton cultures [Sunda and Huntsman, 1995], which could conceivably set the upper bound on  $C_{effx}$ . All the markedly lower estimates of  $C_{eff}$  to date thus appear to relate to situations where Fe supply was discontinuous (Figure 3).

Blooms characterized by a more continuous supply of Fe (KEOPS) thus appear to export carbon more efficiently per unit of Fe added over a complete seasonal cycle. Such an effect would be consistent with a low but continuous supply of Fe allowing efficient retention of Fe within the dissolved phase in the euphotic zone, likely through full complexation by organic ligands [Gledhill and Buck, 2012], or within the ecosystem itself. Indeed, biological uptake within such blooms could be envisaged to generate the gradients in bioavailable Fe at the periphery (either below or to the edges of the bloom), which would likely dictate the magnitude of Fe flux into the bloom region. Such a scenario is in marked contrast to the situation in

purposeful  $\text{FeSO}_4$  release experiments, where a large amount of Fe is supplied to a region with low pre-existing biomass. Orders of magnitude lower  $C_{\text{effx}}$  in such situations might be expected to result from loss of much of the pulsed excess Fe inputs [Boyd *et al.*, 2004; Buesseler *et al.*, 2004; Smetacek *et al.*, 2012] due to saturation of the available Fe complexing ligands sites and rapid transfer of Fe into colloidal ( $>200$  kDa) phases with subsequent particle scavenging alongside a limited capacity for the extant microbial community to take up the sudden large Fe excess [Bowie *et al.*, 2001; Boyd *et al.*, 2007]. Finally, in systems where the supply of Fe is seasonally dominated (CROZEX, IBIS), the bloom likely terminates when the Fe stock is used up [Boyd *et al.*, 2012; Nielsdottir *et al.*, 2009]. Consistent with such arguments, both the excess carbon export (+Fe minus –Fe carbon export) and excess Fe input (+Fe minus –Fe Fe input) for IBIS were about half that of CROZEX (552 versus 1041  $\text{mmol C m}^{-2}$  and 0.031 versus 0.062  $\text{mmol Fe m}^{-2}$ , respectively).

As outlined above, our estimates of  $C_{\text{effx}}$  are, by definition, based on new Fe inputs to the upper ocean. However, a large fraction of the total Fe used by phytoplankton is likely derived from regeneration, for example through grazing and viral lysis [Boyd *et al.*, 2012, 2005; Strzepek *et al.*, 2005]. Our simple explanation for the apparent relationship between  $C_{\text{eff(x)}}$  and bloom duration (Figure 3), as dictated by the period over which Fe is retained and/or resupplied to the system will, in reality, likely reflect a range of complex microbial recycling processes in the mixed layer [Boyd and Ellwood, 2010; Strzepek *et al.*, 2005]. Subsequent consequences for  $C_{\text{effx}}$ , as defined, will depend on the extent to which Fe or C/macronutrients are preferential remineralized within a system [Frew *et al.*, 2006; Twining *et al.*, 2014]. For example, if C is effectively remineralized at shallower depth than Fe, potentially due to (re-)scavenging of the latter [Frew *et al.*, 2006; Twining *et al.*, 2014],  $C_{\text{effx}}$  might be further depressed as the ratio between new and recycled Fe supply (termed the “fe-ratio” [Boyd *et al.*, 2005]) decreases, as might be expected in chronically low Fe systems or the latter stages of the seasonal cycle [Tagliabue *et al.*, 2014].

Overall, on the basis of available data (Figure 3), it thus appears that  $C_{\text{eff}}$  exhibits systematic variability which is not a simple function of the magnitude of new Fe inputs (Figure 3a) but is instead related to the mode of new Fe supply and the duration of the bloom/export phase (Figures 3b, 3c, and 3d), potentially moderated further by the intensity of subsequent recycling. Consequently, differences in the natural modes of new Fe supply likely result in spatio-temporal gradients in  $C_{\text{effx}}$  within both the modern and paleo-oceans. For example, relatively low but continuous benthic Fe inputs to coastal upwelling regions would be expected to result in high  $C_{\text{effx}}$ ; however, this efficiency would be expected to decrease as inputs increase, particularly if it exceeds biological demand or the complexing capacity of natural organic Fe binding ligands [Elrod *et al.*, 2004]. In contrast, aerosols inputs to Fe-limited regions, representing localized and seasonally variable sources of Fe deposited over timescales of weeks to months [Jickells *et al.*, 2005; Mahowald *et al.*, 2009], might be expected to be associated with mid range values of  $C_{\text{effx}}$  which could vary as a function of deposition intensity, alongside other factors which may alter overall biological demand, such as the availability of macronutrients. A more complete mechanistic understanding of linkages between atmospheric  $\text{CO}_2$  and past [Martinez-Garcia *et al.*, 2014; Ridgwell and Watson, 2002] or future [Jickells *et al.*, 2005] natural Fe fertilization from dust deposition may thus need to consider such processes. More broadly, any attempts to quantitatively link the oceanic Fe and C cycles will need to consider the potential for delivery mode to control the amount of carbon sequestered per unit Fe added.

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