

Particle transformations and export flux during an *in situ* iron-stimulated algal bloom in the Southern Ocean

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Abstract. During the first Southern Ocean Iron Release Experiment (SOIREE), a suite of biogeochemical measurements (water column ^{234}Th and $\delta^{13}\text{C}_{\text{org}}$ inventories, particle fluxes from sediment traps, phytoplankton sinking rates) were undertaken to test the hypothesis that the vertical export of particulate organic carbon (POC) is enhanced due to iron-induced increases in phytoplankton production. During the 13-days that the SOIREE bloom was monitored, export fluxes within the iron-fertilised patch were not substantially different to those in waters outside the bloom. On days 11-13, iron enrichment may have caused particle transformations that could lead to elevated future export via particle aggregation and/or diatom chain formation. The unknown time-lag between increased production and export, the longevity of the SOIREE bloom, and the absence of nutrient limitation over days 1-13, however, prohibit prediction of any iron-induced export. This conclusion highlights the difficulties of fully testing the "Iron Hypothesis" and for evaluating the implications for global climate change.

1. Introduction

The two principal components of the "Iron Hypothesis" [Martin, 1990; Morel *et al.*, 1991] are that: (1) phytoplankton growth is limited by iron in High Nitrate-Low Chlorophyll (HNLC) regions, and (2) iron-stimulated shifts to large, fast-sinking diatoms and elevated productivity lowers atmospheric

CO_2 levels and results in greater carbon sequestration due to POC sinking to the deep ocean. The first tenet has been suggested in shipboard incubations [Martin *et al.*, 1991; Buma *et al.*, 1991], field surveys [de Baar *et al.*, 1995, 1999] and demonstrated in meso-scale iron enrichment experiments [Martin *et al.*, 1994; Coale *et al.*, 1996; Boyd *et al.*, 2000]. The second tenet is supported by some Southern Ocean paleoceanographic studies [Kumar *et al.*, 1995; Broecker and Henderson, 1998], and partially by models [Lefèvre and Watson, 1999; Watson *et al.*, 2000], but has not been tested adequately in the present-day [Longhurst, 1996]. Such an understanding is crucial in the Southern Ocean where carbon sequestration to the deep ocean may be more significant than in other HNLC regions [Cooper *et al.*, 1996].

2. Materials and Methods

During the 13-day SOIREE experiment (61°S, 140°E), we undertook a comprehensive time-series of biogeochemical measurements designed to test whether iron-stimulated phytoplankton growth results in significant increases in downward POC flux. Thorium-234 [Charette and Buesseler, 2000] and $\delta^{13}\text{C}_{\text{org}}$ [Trull and Armand, 2001] water column samples were collected using high-volume pumps, while free-drifting sediment traps were used to determine particle fluxes (total mass, POC, BSi, Nodder and Waite, 2001). This approach allowed us to evaluate the temporal evolution of iron-mediated particle changes in relation to direct estimates of export flux (^{234}Th , traps) and to other pelagic time-series measurements [Boyd *et al.*, 2000]. Since particle export is expedited via two principal routes (sinking faecal pellets and algal cells or aggregates), we also used mesozooplankton

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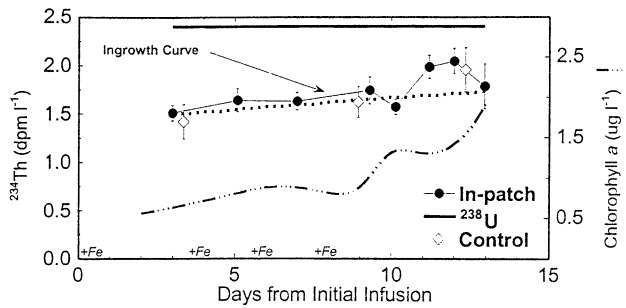


Figure 1. Time-series of vertically integrated ^{234}Th (0–100 m) in patch center (solid dots) and outside the patch (open diamonds) relative to parent ^{238}U (solid dark line) and surface chlorophyll-*a* concentrations (dashed green line) during the SOIREE bloom. The rate of increase in ^{234}Th due to radioactive ingrowth alone is also shown (dashed gray line, $2.9\% \text{ d}^{-1}$). +Fe refers to the timing of iron infusions during SOIREE.

grazing [Zeldis, 2001] and shipboard phytoplankton sinking rate experiments [Waite and Nodder, 2001] as biological indices for potential export production.

3. Results and Discussion

Results from ^{234}Th : ^{238}U disequilibria modelling indicated that, within uncertainties, particle export rates were low and invariant over the first 13-days following iron fertilisation (Fig. 1, Table 1) [Charette and Buesseler, 2000], despite chlorophyll *a* biomass increasing 6-fold [Boyd et al., 2000] (Fig. 1). Average integrated POC: ^{234}Th ratios increased substantially inside the patch (Table 1), consistent with the greater volume-to-surface ratio of large diatoms, which increased in abundance as a result of iron addition [Boyd et al., 2000]. Particles collected by sediment traps within and outside the patch had $\delta^{13}\text{C}_{\text{Org}}$ ratios of -26 to -27‰ over the entire experiment (Fig. 2), while bloom-forming diatoms (20–70 μm size-fraction in water column, high-volume pump samples) had ratios of -20 to -24‰ [Trull and Armand, 2001]. The lack of change in ^{234}Th and $\delta^{13}\text{C}_{\text{Org}}$ suggests that export remained low and that these bloom diatoms did not reach the traps in significant numbers during the log phase growth of the SOIREE bloom.

Similarly, downward biogenic particle fluxes measured by traps exhibited no clear indication of iron-elevated export [Nodder and Waite, 2001]. Although up to two-fold increases in flux were observed (Fig. 2), variations of 50% were also found in waters outside the patch, therefore confounding the ability to quantify significant increases in export flux within the patch. Trap arrays of similar design have been shown to overtrap or undertrap [Buesseler et al., 1994; Murray et al., 1996] with traps generally overcollecting during low flux periods [Buesseler et al., 1994]. Thorium trap fluxes during SOIREE were invariant and low ($990\text{--}1015 \text{ dpm m}^{-2} \text{ d}^{-1}$), while Charette and Buesseler (2000) estimated the SOIREE ^{234}Th flux (at 100 m) to be negligible, suggesting the traps overcollected thorium-bearing particles. Thus, given variability of trap measurements, the SOIREE particle flux data support the low levels of export as suggested by water column ^{234}Th and $\delta^{13}\text{C}_{\text{Org}}$.

This interpretation is supported by indications that almost 70% of the fixed algal carbon accumulated in the mixed-layer as chlorophyll *a* [Boyd et al., 2000]. Grazing and sedimentation can be significant loss terms, but both were low during the SOIREE bloom [Nodder and Waite, 2001; Zeldis,

Table 1. Time-series of inside and outside patch comparisons of water column ^{234}Th : ^{238}U activities and POC:Th ratios in the upper 100 m and Th flux in sediment traps during SOIREE. * ratios were calculated using OUT stations from the last trap deployment on days 11–13.

	Water column		Sediment traps	
	IN/OUT	IN/OUT	IN/OUT	IN/OUT
	Th:U	POC:Th	Th flux	POC:Th
	Activity Ratio	Error	Ratio	
Days 0–2	1.06	0.14	1.7	-
Days 7–9	1.04	0.12	2.2	0.99* 1.7*
Days 11–13	0.99	0.14	3.2	0.97 1.9

2001], thereby facilitating biomass accumulation in the mixed-layer. Zooplankton faecal pellets were only a minor component of trapped material, which was dominated instead by diatom-rich aggregates, even before iron fertilisation. Furthermore, neither silicate nor iron concentrations appeared to be limiting before Day 13 [Boyd et al., 2000], and accordingly, bloom-forming phytoplankton were largely physiologically healthy, as suggested by their reduced sinking rates within the patch (Fig. 3) [Waite and Nodder, 2001] and heightened photosynthetic competency [Boyd et al., 2000]. Actively growing, nutrient-replete diatoms have lower sinking rates and higher ascent rates than physiologically stressed cells [Waite et al., 1992; Muggli et al., 1996; Villereal et al.,

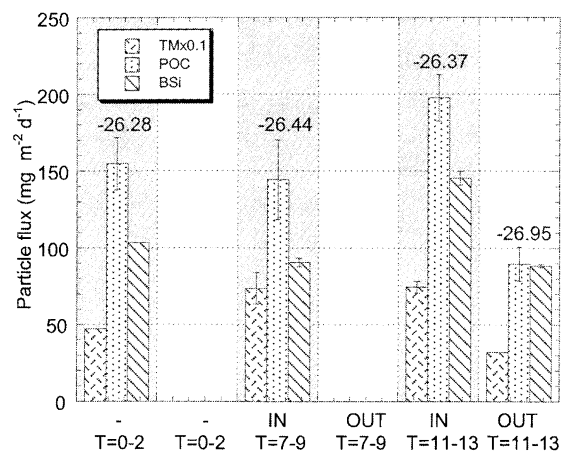


Figure 2. Particle fluxes at 110 m during SOIREE determined from sediment traps. From left to right at each time-step, histogram bars relate to mean (± 1 standard deviation) or single flux measurements of total dry mass (TM $\times 0.1$), particulate organic carbon (POC) and biogenic silica (BSi). Values of $\delta^{13}\text{C}_{\text{Org}}$ in trapped material are shown above each set of bars. Duplicate arrays of baffled, cylindrical MULTI-traps, with a 1-trap diameter thick, 50% excess NaCl basal brine, were deployed inside the patch for 48 hrs each on days 7 and 11 after iron fertilisation. Single “control” trap deployments were undertaken at day 0 and outside the patch at day 11. Swimmer contamination in all trap samples was minimal ($<5\%$ total mass).

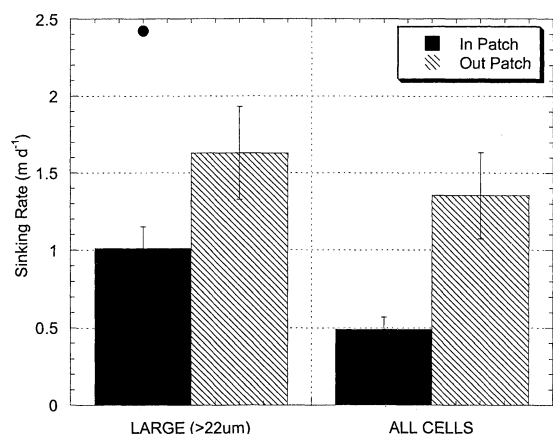


Figure 3. Mean chlorophyll sinking rates of all phytoplankton (ALL) and >22 µm fraction (LARGE), within (IN) and outside (OUT) the patch, from shipboard SETCOL settling columns. Measurements are averaged over the entire time-series and error bars are ± 1 standard error. The last point of the LARGE IN time-series on Day 12 was significantly higher (p<0.05) than the other points, suggesting the early onset of iron stress near the end of the time-series, and is indicated separately.

1999], providing a potential link to export processes [Jackson, 1992].

Between days 11-13, we documented particle transformations likely to eventually lead to heightened export production. The 5-fold increase in primary productivity is expected to lead to elevated export flux [Bishop, 1989; Berger and Wefer, 1990], as is the concomitant shift in the SOIREE phytoplankton community from pico-eukaryotes to large diatoms [Boyd and Newton, 1999]. Large, bloom-forming diatoms play an important role in oceanic carbon export in the Southern Ocean [Rutgers van der Loeff et al., 1997] and elsewhere [Smetacek, 1985; Boyd and Newton, 1999]. SOIREE particle time-series data indicates that diatoms, *Fragilariopsis kerguelensis* (40-50% of cell numbers in trap aggregates) and *Nitzschia cf. sicula* (~50%), were the dominant phytoplankton captured by traps over days 11-13, mainly as aggregates and/or chains [Waite and Nodder, 2001]. Chain formation has been shown to lead to dramatic increases in export flux during diatom blooms [Riebesell and Wolf-Gladrow, 1992] and during SOIREE, chain lengths of water column *F. kerguelensis* increased 2-fold inside the patch, compared to outside (F. H. Chang, pers. comm.). Novel

particle-sizing techniques [Waite et al., 2000] reveal that marine snow particles collected by traps inside the patch were 2-times larger on days 11-13, compared to outside (Table 2). Furthermore, elevated POC:²³⁴Th ratios over the course of SOIREE (Table 1) also support increased particle size within the patch, probably due to aggregation and/or chain formation.

These observations imply that iron-elevated export fluxes would be expected to occur some time in the future, but only if and when extensive nutrient-limitation occurred, thereby increasing particle sinking rates (assuming insignificant degradation and grazing). By the time, we left the SOIREE bloom, cells exhibited an F_v/F_m close to the theoretical maximum [~0.6, Boyd et al., 2000], suggesting that there was little evidence of nutrient limitation. Since the sinking rate of phytoplankton cells generally increases under nutrient stress [Waite et al., 1992; Muggli et al., 1996; Villereal et al., 1999; Waite and Nodder, 2001], it is likely that at an unspecified time in the future nutrient limitation would become a factor, and only then would cells within the bloom population exhibit elevated sinking rates.

The problems of assessing the relationship between bloom peaks and eventual export [Buesseler, 1998] is therefore related to our ability to predict biological iron availability, which did not decline significantly during the 13-day SOIREE experiment [Boyd et al., 2000]. Within the limitation of our understanding of iron dynamics, the time-lag between the SOIREE bloom peak and export is likely to be on the order of weeks rather than days, since satellite imagery indicates that an iron-stimulated phytoplankton bloom persisted for 30-45 days after the completion of SOIREE [Abraham et al., 2000]. In contrast, a 7-fold increase in export occurred just 7 days after iron fertilisation in the equatorial Pacific [Bidigare et al., 1999].

This time-series study is the first to follow particle transformations and document the export flux of an iron-stimulated bloom in the Southern Ocean. Although there are tantalising indications of iron-mediated changes in key determinants of particle export, we did not measure a significant increase in POC export during the 13-days that we monitored the bloom. Furthermore, the unexpected longevity of the SOIREE bloom has been described by Boyd et al. [2000] as an experimental artefact, akin to a chemostat, with horizontal dispersion and stirring of the phytoplankton patch controlling the availability of vital macro- and micronutrients, such as silicate and iron, and resulting in cell wash-out [Abraham et al., 2000]. These factors further highlight the logistical difficulties of testing an essential tenet of Martin's original "Iron Hypothesis" [Martin, 1990; Martin et al., 1994; Coale et al., 1996]. Therefore, although results from SOIREE have unequivocally shown that iron does limit phytoplankton growth resulting in CO₂ drawdown in the Southern Ocean [Boyd et al., 2000], the fate of this carbon remains unknown, implying serious uncertainties in linking Southern Ocean productivity to global climate change [Kumar et al., 1995; François et al., 1996; Broecker and Henderson, 1998].

Table 2. Size characteristics of trapped particles (>10 µm diameter) inside and outside the patch at the end of SOIREE.

Parameter		Days 11-13	
		IN	OUT
AREA (x10 ⁴ µm ²)	Average	2.68	1.21
	Standard error	0.08	0.85
LENGTH (x10 ² µm)	Average	2.44	1.86
	Standard error	0.03	0.22
Sample size (n)		6774	5050

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