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Does iron fertilization lead to rapid carbon export in the Southern Ocean?

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[1] **Abstract:** The Southern Ocean has the potential to influence climate due to its large inventory of excess macronutrients such as nitrate and phosphate. It has been hypothesized that if the supply of the micronutrient iron increased, it would lead to enhanced uptake of atmospheric CO_2 and hence the sequestration of carbon via sinking particles [*Martin*, 1990]. While much has been learned about iron limitation and low phytoplankton biomass in high-nutrient, low-chlorophyll regions [*Martin*, 1991; *Coale et al.*, 1996], less is known about the effect of Fe on particle export. Here we present results from the first detailed study of particle export during a mesoscale iron fertilization experiment (the Southern Ocean Iron Release Experiment (SOIREE)). Measurements of the natural tracer thorium-234 indicate negligible particle export within 14 days after the initial infusion of iron. We attribute this lack of response to colder water temperatures that promote slower cell metabolism in phytoplankton and hence slower secondary responses of herbivores and particle aggregation.

Keywords: Iron hypothesis; Southern Ocean; particle export; thorium-234, HNLC.

Index terms: Arctic and Antarctic oceanography; biogeochemical cycles; carbon cycling.

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1. Introduction

[2] During February 1999 a 50 km^2 patch of ocean in the Tasman sector of the Southern Ocean (61°S, 140°W) was seeded with iron sulfate (10,275 kg over four infusions) dissolved in acidified seawater (Southern Ocean Iron Release Experiment (SOIREE)). In order to track the location of the patch over the course of the experiment, sulfur hexafluoride was simultaneously released along with the iron and continually monitored via the ship's underway system. All "in-patch" samples for this work were collected in the center of the iron-fertilized patch as determined from mapped SF_6 concentrations. By the end of the 13-day experiment, the patch had expanded in size to over 200 km^2.

[3] Though nearly 5 days elapsed before any observable biogeochemical change, the ensuing biological response resulted in a 400% increase in chlorophyll concentrations at the center of the patch (0.49 to 1.94 $\mu g\ L^{-1}$) [*Boyd et al.*, 2000]. This increase in chlorophyll corresponded to a 50% increase in the particulate

organic carbon (>1.2 μm) standing stock over the upper 100 m. This ecosystem response led to a 10% drawdown in surface water pCO_2 (365 to 330 μatm) by the end of 2 weeks [*Watson et al.*, 2000].

2. Utility of Thorium-234 as Tracer of Upper Ocean Particle Export During SOIREE

[4] In an attempt to quantify the removal of particulate organic carbon during SOIREE, we employed the natural radiotracer thorium-234 (^{234}Th). With a half-life of 24.1 days and a strong affinity for particles, ^{234}Th has proven to be a useful tracer of particle export on the timescale of days to weeks, typical of upper ocean processes. The particle-reactive nature of ^{234}Th often results in a disequilibrium relative to its parent nuclide ^{238}U ($t_{1/2}$ = 4.47 x 10^9 years), which is chemically inert and remains dissolved in seawater (Figure 1). The activity balance for ^{234}Th over time can be expressed mathematically as

$$\frac{d^{234}Th}{dt} = \lambda(^{238}U - {}^{234}Th) - P_{Th} \pm V, \qquad (1)$$

where P_{Th} is the loss of ^{234}Th on particles from the upper ocean, V is the contribution or removal of ^{234}Th via advective or diffusive processes, λ is the decay constant for ^{234}Th (0.0288 d^{-1}), and ^{234}Th and ^{238}U are the activities of the nuclides in units of disintegrations per minute per liter (dpm L^{-1}) of seawater.

[5] Large-volume (400 L) samples of ^{234}Th in two particulate fractions (>70 and 1–70 μm) and the dissolved form (<1 μm) were obtained using an in situ battery-operated pump deployed on the conductivity-temperature-depth (CTD)/Rosette frame [*Buesseler et al.*, 1992a]. To obtain a single, integrated measure of ^{234}Th activity over the upper 0–100 m, the pump was lowered slowly and programmed to collect 20 L at 5-m intervals over this depth range. Integrated samples were taken a total of eight times inside the fertilized patch and three times at control stations outside the patch. Samples were analyzed according to the procedures outlined by *Charette and Moran* [1999] and modified from *Buesseler et al.* [1992a].

[6] Surprisingly, the time series measurements for ^{234}Th display a trend of increasing activity during the course of the experiment (Figure 2). In addition, total ^{234}Th activities (sum of dissolved plus particulate fractions) did not vary between the control stations and those located at the center of the patch. The initially low ^{234}Th is an indication that a substantial particle export had taken place prior to our arrival.

[7] If we assume steady state, a single water column ^{234}Th measurement can provide an estimate of particle export averaged over its mean lifetime (~35 days). We can therefore apply our first ^{234}Th observations (day 3) to equation (1) and, with $d^{234}Th/dt = 0$ (and no advection/diffusion), estimate particulate ^{234}Th export prior to SOIREE. The resulting P_{Th} of 2600 dpm m^{-2} d^{-1} is comparable to a post-bloom value of 3200 dpm m^{-2} d^{-1} observed subsequent to the spring phytoplankton bloom at these latitudes in the South Atlantic sector of the Southern Ocean [*Rutgers van der Loeff et al.*, 1997]. This is likely a lower-limit estimate since we cannot know exactly when the export event took place. Also, Sea-Viewing Wide Field-of-View Sensor (Sea-WiFS) ocean color images of this region for the previous 2 months provided little evidence for a bloom of this magnitude. This suggests that there was either a significant delay in export or because of the limited optical depth of the satellite that the event was a subsurface phenomenon.

[8] Regardless of pre-SOIREE events, the increasing ^{234}Th activities with time can only be explained by two processes: (1) negligible particle export coupled with radioactive ingrowth

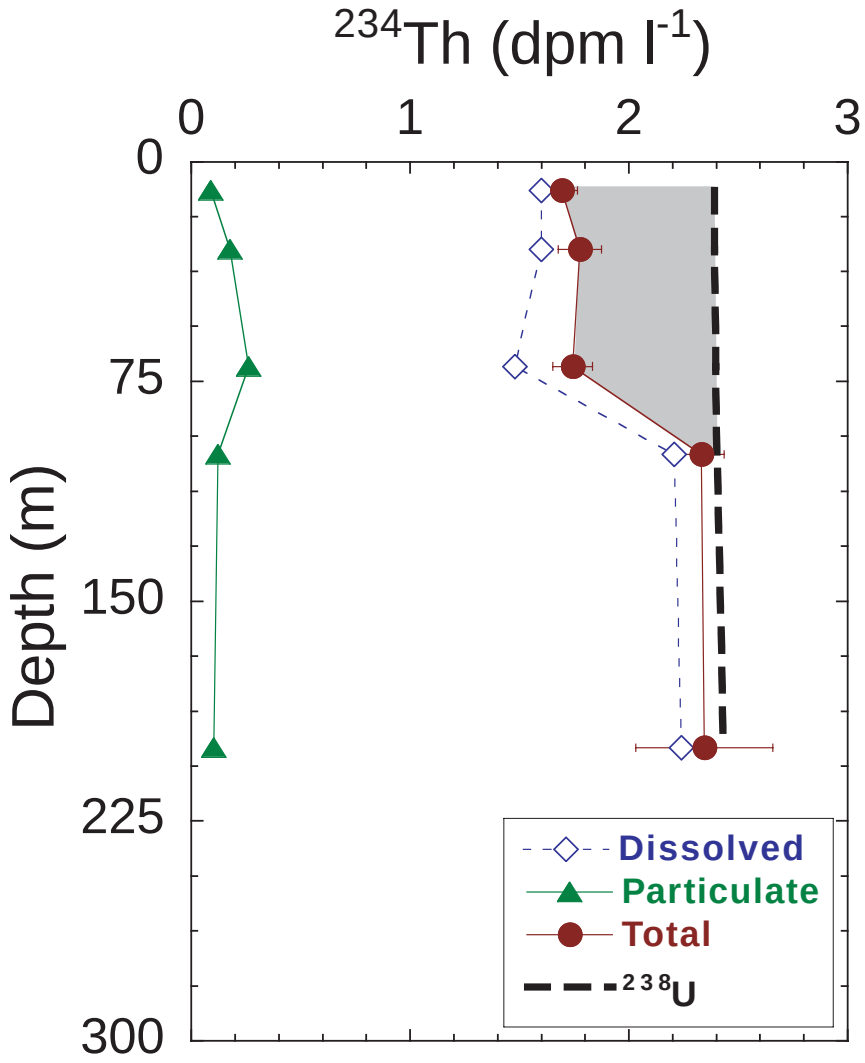

Figure 1. Vertical profiles of dissolved, particulate, total (dissolved plus particulate) ^{234}Th, and its parent nuclide ^{238}U collected on day 9 of the experiment inside the iron-fertilized patch. Uranium 238 is chemically nonreactive in seawater and can be determined from salinity (^{238}U (dpm L^{-1}) = 0.07081 x salinity (‰) [*Chen et al.*, 1986]). The disequilibrium between the parent and daughter nuclides (shaded area) is due to scavenging and vertical export of ^{234}Th on rapidly sinking particles. Since the biological pump is often the major source of these particles in open ocean waters, ^{234}Th:^{238}U disequilibria is mainly confined to the euphotic zone (upper ~100 m). Error bars are propagated from counting statistics (1σ) and measurement uncertainties.

of ^{234}Th from its parent isotope ^{238}U and/or (2) entrainment of ^{234}Th:^{238}U equilibrated deep water into the upper 100 m. Also, and perhaps most convincingly, the agreement in ^{234}Th between the fertilized patch and control stations suggests no change in particle export.

[9] A decrease in the ^{234}Th inventory in the water column is often associated with periods of increased biological activity such as a phytoplankton bloom and subsequent particle export [*Buesseler et al.*, 1992b; *Rutgers van der Loeff et al.*, 1997]. Conditions following this

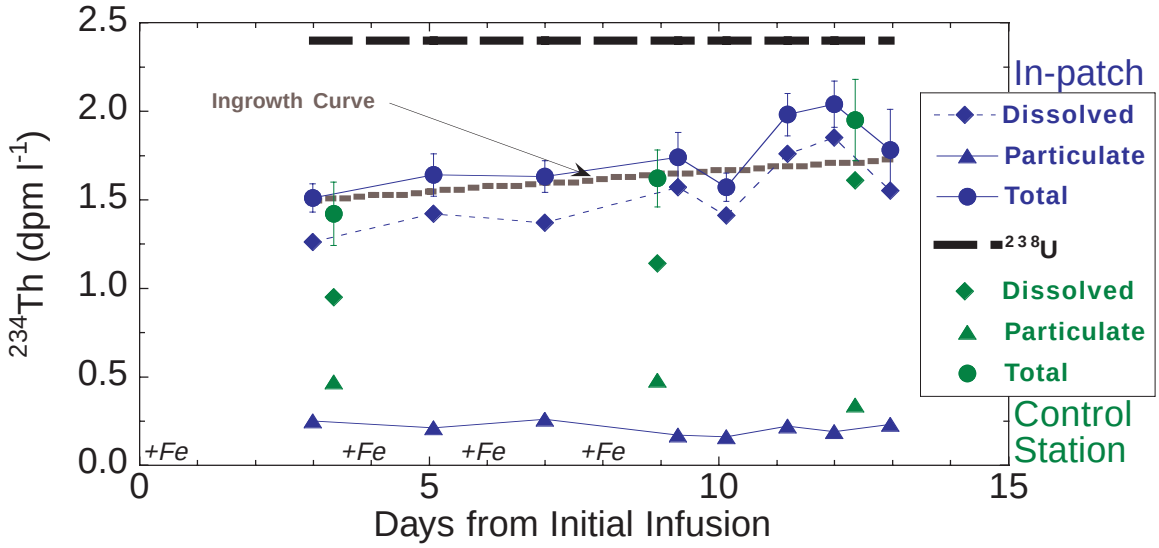

Figure 2. Time series measurements of vertically integrated ^{234}Th (0–100 m) during SOIREE at stations located in the center of the iron-fertilized patch (solid, blue symbols) and at control stations outside the patch (open, green symbols). Uranium 238 (solid dashed line) was determined from the average salinity over the 0–100 m. Also shown is the rate of increase in ^{234}Th that would be expected from radioactive ingrowth alone (~2.9%/d). The +Fe symbols along the *x* axis indicate the approximate timing of the four iron enrichments.

event may result in little or no export, and ^{234}Th activities will increase as they approach secular equilibrium with ^{238}U. The trend of ^{234}Th activity during SOIREE indicates an increase that is consistent with ingrowth for the majority of the time series (Figure 2). However, the evidence of total ^{234}Th activities above the ingrowth curve might in part be explained by the entrainment of deep water into our 100-m box.

[10] Since horizontal processes can be ignored owing to the Lagrangian nature of our study, we are left with the possibility that vertical mixing processes increased the supply of ^{234}Th-rich deep water to our 100-m box. To quantify this exchange process, we examined the evolution of the depth of the mixed layer during SOIREE. The base of the mixed layer had progressively deepened as much as 15 m during the 2-week experiment, equivalent to an upper-limit vertical mixing rate of ~1 m d^{-1}.

[11] Given these observations, we set out to calculate the rate at which ^{234}Th was exported on particles (P_{Th}) from our 100-m box during SOIREE. Solving equation (1) for P_{Th}, three variables remain which we must determine based on our data set: (1) production and decay of ^{234}Th, (2) the change in ^{234}Th activity with time, and (3) vertical supply of deep-water ^{234}Th.

3. Discussion

[12] Average activities of ^{234}Th and ^{238}U are used to estimate the production and decay terms. Given the average activities of 2.40 dpm L^{-1} for ^{238}U and 1.72 dpm L^{-1} for ^{234}Th, there is a net production of ^{234}Th of 19.3 ± 1.4 dpm m^{-3} d^{-1} within the upper 100 m. The slope in the total ^{234}Th data from Figure 2 gives the change in ^{234}Th with time: 39.3 ± 5.6 dpm m^{-3} d^{-1}. Finally, using the vertical resupply rate based on mixed-layer depth changes (1 m d^{-1}) and the depth gradient in

^{234}Th from a profile obtained on day 9 (Figure 1; 19.6 dpm m^{-4}), we obtain a supply rate for ^{234}Th to the 100-m box of 19.6 dpm m^{-3} d^{-1} (assuming 25% error). The balance results in a P_{Th} of -0.40 dpm m^{-3} d^{-1} or, when integrated over the 100-m box, -40 dpm m^{-2} d^{-1} ($\pm$760 dpm m^{-2} d^{-1}). Therefore, within our ability to measure fluxes using ^{234}Th the SOIREE value becomes indistinguishable from zero, a result that suggests that particle export did not occur during the 2 weeks that the patch was occupied.

[13] This conclusion is supported by several other parameters measured during SOIREE. The F_v/F_m ratio is a measure of the photosynthetic competency of the phytoplankton [*Falkowski and Kolber*, 1995]. Whereas this parameter increased exponentially in the first 24 hours after Fe infusion in the equatorial Pacific during IronEx II [*Behrenfeld et al.*, 1996], several days elapsed before an increase was observed during SOIREE. In the equatorial Pacific Ocean, there was no increase in ^{234}Th-derived particle export while F_v/F_m remained high; conversely, the IronEx II particle flux increase coincided with reduced F_v/F_m levels [*Behrenfeld et al.*, 1996; *Bidigare et al.*, 1999]. *Boyd et al.* [2000] did not observe a decline in F_v/F_m during SOIREE, consistent with a lack of particle export. Also, *Hutchins and Bruland* [1998] demonstrated that iron-stressed diatoms would enter a stage of heavy silicification thereby decreasing their buoyancy. Since dissolved iron levels remained high after the final infusion, we can only surmise that this led to a further delay in export from the SOIREE-induced diatom bloom.

[14] Measurements of the stable carbon isotopic signature of particulate organic carbon (>1 μm) also support this conclusion. Suspended organic particles became enriched in ^{13}C during the experiment, a shift mainly due to the growth of the iron-limited >20-μm diatoms [*Trull et al.*, 1999]. Such enrichment was not observed in particles collected on filters or in sediment traps below 100 m, suggesting that these newly spawned large diatoms were not exported.

[15] A typical lower limit for the ^{234}Th method was published by *Charette et al.* [1999] for the subarctic northeast Pacific Ocean, where a measured ^{234}Th flux of 200–600 dpm m^{-2} d^{-1} in late winter translated to a particulate organic carbon flux of ~2–3 mmol m^{-2} d^{-1}. Owing to propagation in measurement uncertainties ($\pm$760 dpm m^{-2} d^{-1}), there exists the possibility that the calculated ^{234}Th flux of -40 dpm m^{-2} d^{-1} for SOIREE was as high as 720 dpm m^{-2} d^{-1}. We can empirically translate this particulate ^{234}Th flux (P_{Th}) to particulate organic carbon (POC) export (from 100 m) via the POC/^{234}Th ratio of sinking particles [*Buesseler et al.*, 1992b]. Using a measured POC/^{234}Th ratio of 10 μmol dpm^{-1} (average at 100 m), the upper-limit POC export for SOIREE would be ~7.2 mmol C m^{-2} d^{-1}. The relative magnitude of this flux is still minor when compared to a potential pre-SOIREE POC flux of 26 mmol C m^{-2} d^{-1} (calculated from the ^{234}Th flux of 2600 dpm m^{-2} d^{-1} and a POC/^{234}Th ratio of 10 μmol dpm^{-1}) and of other observations in the Southern Ocean at these latitudes [e.g., *Rutgers van der Loeff et al.*, 1997; K. O. Buesseler et al., Upper ocean export of particulate organic carbon and biogenic silica in the Southern Ocean along 170°W, submitted to *Deep Sea Research, Part II*, 2000]. Regardless of potential measurement error, the strength of our conclusion of negligible particle export is that the trend in our particle tracer ^{234}Th did not vary from the control stations located outside the iron-fertilized patch.

[16] In general, biological communities dominated by food webs with larger phytoplankton species have considerable potential for high export via sinking particles [*Michaels and Silver*, 1988; *Boyd and Newton*, 1995].

Although a significant biological response was observed within 1 day, *Bidigare et al.* [1999] reported a minimum delay of 1 week for surface water ^{234}Th-derived particle export during IronEx II. It is therefore conceivable that given the significant delay in the initial biological response during SOIREE, an export response of the larger-celled diatoms was delayed even longer in this colder water setting. In addition, since a typical bloom required around 15 days to reach its biomass peak in the Antarctic Polar Frontal Zone [*Abbot et al.*, 1999], the minimum 2-week delay observed during SOIREE may not be entirely anomalous.

[17] Our ability to speculate about potential particle export after SOIREE is further confounded by the apparent longevity of the iron-induced phytoplankton bloom. On the basis of ocean color satellite images recorded after completion of the experiment, the patch appears to have expanded in size and persisted for at least 30–45 days [*Abraham and Law*, 2000]. What factors allowed the SOIREE bloom to persist for such a period of time? One possibility is that the heterotrophic community eventually adapted to the shift from smaller to larger autotrophs, leading to a greater recycling efficiency for Fe. However, because the zooplankton community never responded to the larger phytoplankton, particle export, if it did in fact occur, would likely have been dominated by aggregation and sinking rather than zooplankton grazing [*Boyd et al.*, 2000].

4. Conclusion

[18] The magnitude of export following SOIREE remains unconstrained; yet it is key to our understanding of the ocean's role in carbon cycling over the last glacial-interglacial cycle. Most importantly, our results indicate that short pulses of iron do not necessarily lead to a net export of carbon from the surface ocean. Similarly, an iron-induced response in chlorophyll (increasing) or pCO_2 (decreasing) does not necessarily lead to a proportional response from the biological pump [*Abraham and Law*, 2000]. These results raise fundamental questions about the fate of organic carbon in iron-induced phytoplankton blooms in the Southern Ocean.

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