^{234}Th deficit and excess in the Southern Ocean during spring 2001: Particle export and remineralization

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[1] ^{234}Th deficit and excess were examined in the upper 500 m of the Southern Ocean from Sub-Antarctic to Seasonal Ice Zones (Australian sector) during austral spring 2001. ^{234}Th fluxes at 100 m indicate that particle export was low in the North (46.9–51.0°S), minimal in the Polar and Inter-Polar Frontal Zones and high in the South (≥61°S). These results are in tight agreement with new production estimates from the same cruise. Our data indicate that Polar and Inter-Polar Frontal Zones were not zones of intense export in the Australian sector at this time of year, in contrast with other sectors of the Southern Ocean. Also, we highlight the usefulness of ^{234}Th excess below the mixed layer as a tool to study mesopelagic remineralization. *INDEX TERMS:* 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4806 Oceanography: Biological and Chemical: Carbon cycling; 4815 Oceanography: Biological and Chemical: Ecosystems, structure and dynamics. **Citation:** Savoye, N., K. O. Buesseler, D. Cardinal, and F. Dehairs (2004), ^{234}Th deficit and excess in the Southern Ocean during spring 2001: Particle export and remineralization, *Geophys. Res. Lett.*, *31*, L12301, doi:10.1029/2004GL019744.

1. Introduction

[2] The radioisotope ^{234}Th is produced in ocean water from ^{238}U decay. Because of ^{234}Th's short half-life (24.1d) and its strong adsorption on particles, its deficit with respect to ^{238}U has been used as a powerful tool to study biogenic particle export from surface ocean [*Coale and Bruland*, 1985]. In contrast, ^{234}Th excess with respect to ^{238}U has been only occasionally reported and explained as the result of remineralization process [e.g., *Usbeck et al.*, 2002].

[3] The Southern Ocean plays a key role in the global climate. Indeed, global modeling output indicates that it acts as a net sink for atmospheric CO_2, mainly due to phytoplankton uptake [*Takahashi et al.*, 2002]. Thus, studying biogenic particle export and remineralization in the upper few hundred meters of the Southern Ocean water column is important to improve our understanding of atmospheric CO_2 sequestration by the global ocean.

[4] Here we present a study of ^{234}Th:^{238}U disequilibria performed in the upper 500 m of the Southern Ocean during spring 2001 (WOCE SR3 transect, Australian sector). We report ^{234}Th fluxes along the transect, highlight ^{234}Th excess as a tool for studying particle remineralization in subsurface water, and discuss the particle export variability in the Southern Ocean.

2. Experimental and Methods

[5] ^{234}Th:^{238}U disequilibrium was studied during the CLIVAR SR3 cruise (aa0103 30 October–14 December 2001). Seven stations were sampled between 46.9°S and 64.9°S; stations at 63.9 and 60.9°S were re-visited after a delay of 11 and 17 days, respectively. The location of the stations as well as the major fronts and zones and their acronyms are indicated on Figure 1. The station at 63.9°S was located within sea ice (first and second visits), while the station at 64.9°S was ice-free.

[6] The upper 125 to 500 m were sampled for total (i.e., dissolved + particulate) ^{234}Th using Niskin bottles, typically from 12 depths. Total ^{234}Th was processed following *Pike et al.* [2004]. Briefly, ^{230}Th was added as a yield monitor to a 4L-seawater sample. After equilibration, Mn precipitate was formed by addition of $KMnO_4$ and $MnCl_2$ to scavenge Th and filtered on quartz fiber filter. Beta radioactivity was measured on board generally over a 12–24 hour counting period using low level beta counters (Risø, Denmark). Filters were re-counted after 6 months for beta background, after which ^{230}Th was analyzed by ICP-MS and Th yield calculated. Average Th recovery was 91%. The final relative uncertainty on total decay corrected ^{234}Th activity was 2%.

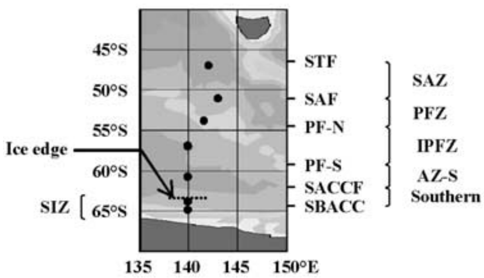

Figure 1. Location of the stations in the study area. STF: Sud-Tropical Front; SAF: Sub-Antarctic Front; PF-N and PF-S: northern and southern branches of the Polar Front, respectively; SACCF: Southern Antarctic Circumpolar Current Front; SBACC; Southern Boundary of the Antarctic Circumpolar Current; SAZ: Sub-Antarctic Zone; PFZ: Polar Front Zone; IPFZ: Inter-Polar Front Zone; AZ-S: southern Antarctic Zone; SIZ: Seasonal Ice Zone. See *Trull et al.* [2001] and references therein for definition of fronts and zones. See color version of this figure in the HTML.

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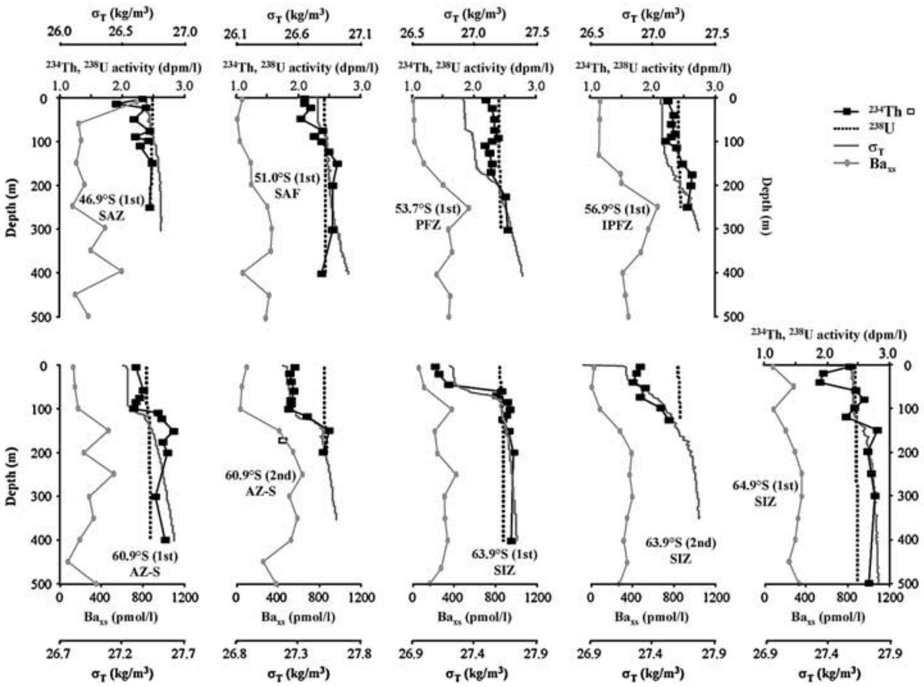

Figure 2. ^{234}Th and ^{238}U activity, biogenic particulate barium (Ba_{xs}) and density (σ_T) profiles for the first (1st) and second (2nd) visits of stations. SAZ, SAF, PFZ, IPFZ, AZ-S, SIZ: see Figure 1. Ba_{xs} is from Cardinal et al. (submitted manuscript, 2003).

^{238}U activity was calculated from salinity following *Chen et al.* [1986]. Total accuracy of the method was evaluated by comparison to deep water samples where ^{234}Th = ^{238}U.

[7] ^{234}Th fluxes were calculated using steady state (Equation 1) and/or non-steady state (Equation 2) models [*Buesseler et al.*, 1992].

$$P = \sum_{i=1}^{i=n} \lambda z_i \left[{}^{238}U_i - {}^{234}Th_i\right] \quad (1)$$

$$P = \sum_{i=1}^{i=n} \lambda z_i \left[{}^{238}U_i - \frac{{}^{234}Th_{i,1} + {}^{234}Th_{i,2}}{2}\right] - \left[\frac{{}^{234}Th_{i,2} - {}^{234}Th_{i,1}}{t_2 - t_1}\right] \quad (2)$$

P: net loss of ^{234}Th on sinking particles (i.e., vertical ^{234}Th flux); i: layer of water column; n: number of layers of interest; λ: decay constant for ^{234}Th (λ = 0.0288d^{-1}); z: layer thickness; ^{238}U: activity of ^{238}U; ^{234}Th: activity of total ^{234}Th; t_1, t_2: time of the first and second visit of a station, respectively. Uncertainties on fluxes at 100 m and 300 m were 50 and 120 dpm/m^2/d, respectively. We assume in these models that supply and loss of ^{234}Th via horizontal and vertical mixing are small, relative to the rates of ^{234}Th production from ^{238}U, its decay, and loss on sinking particles. Physical processes have only been found to impact ^{234}Th activity balances significantly in sites of intense upwelling or coastal regions where tidal pumping and activity gradients are a larger component of the ^{234}Th activity balance [*Buesseler*, 1998]. Using the ratio of particulate C to ^{234}Th, one can also derive POC flux from the ^{234}Th flux but we leave this discussion to a forthcoming article where this approach will be more fully evaluated and compared to other estimates of C export.

3. ^{234}Th Activity

[8] The lowest and highest ^{234}Th activities were measured in surface and subsurface water of southern stations, respectively (Figure 2). With respect to ^{238}U, there was a deficit of ^{234}Th in the upper water column; it increased and deepened between the first and second visits at 60.9 and 63.9°S. As the ^{234}Th deficit is due to exported particles which remove adsorbed ^{234}Th [*Coale and Bruland*, 1985], it defines an "export layer" where ^{234}Th < ^{238}U activity. The export layer depth varied from 75 m at 63.9°S (SIZ)—where sea ice was melting—to 200 m in the PFZ.

[9] Below the export layer a zone of ^{234}Th excess, i.e., ^{234}Th > ^{238}U, was often observed. In some cases (e.g., AZ-S and SIZ, first visits), ^{234}Th excess was observed at depths as deep as 400–500 m. ^{234}Th excess at similar depths has been reported in previous studies but only few authors have interpreted these data since (1) particle export from the surface layer is usually of primary interest and (2) previous methods did not allow for high vertical resolution needed to resolve excess ^{234}Th. *Rutgers van der Loeff et al.* [2002] reported a large ^{234}Th excess in surface water near the retreating ice edge and under the ice. These authors argued that this was related to ^{234}Th accumulation in the ice (adsorption on phytoplankton and/or ice) and release during melting. *Usbeck et al.* [2002] reported ^{234}Th excess between 100 and 400 m within the Weddell Gyre and interpreted it as being induced by remineralization of particles exported from the surface layer. *Buesseler et al.* [2004] report a persistent ^{234}Th excess at 80–120 m in Fe-depleted water during SOFeX. These authors attribute this to release of

^{234}Th to the dissolved phase from sinking particles or disaggregation of sinking into suspended material.

[10] During the CLIVAR SR3 cruise, the transition from the surface export layer to deeper waters is defined by the gradient in ^{234}Th activity from deficit to excess (Figure 2). This gradient was either small and stretched over a quite broad depth interval (e.g., at 56.9°S) or sharp and stretched over a narrow depth interval (e.g., at 63.9°S). ^{234}Th gradients superimposed nicely onto density gradients (Figure 2) and were usually very pronounced in the south and smoother in the north. The ^{234}Th increase below the export layer indicates that this density gradient defines the depth at which net particle export on sinking particles exceeds its supply.

[11] Biogenic particulate barium (Ba_{xs}) in mesopelagic waters is used as a proxy of remineralization in mesopelagic waters [*Dehairs et al.*, 1997]. Ba_{xs} was studied during the CLIVAR SR3 cruise (D. Cardinal et al., Particulate Ba distributions and fluxes suggest latitudinal variations of carbon remineralization in the Southern Ocean, submitted to *Deep-Sea Res. I*, 2003, hereinafter referred to as Cardinal et al., submitted manuscript, 2003) (Figure 2). At most of the stations, Ba_{xs} increased from 50–100 m to a maximum at 200–300 m. Ba_{xs} and ^{234}Th gradients superpose (e.g., at 60.9°S, second visit). This feature was not observed in the SAZ, however ^{234}Th was sampled only in the first upper 250 m, i.e., above the Ba_{xs} increase. In addition, O_2 concentration decrease coincides with Ba_{xs} and ^{234}Th increase in and south of PFZ (not shown), i.e., where mesopelagic remineralization seems to be higher.

[12] From the above it appears that (1) ^{234}Th excess starts within or just below the density gradient at the bottom of the upper mixed layer, (2) relative to particle export, particle break-up and remineralization were intense within the first 300–500 m along the transect, especially from IPFZ to SIZ, and (3) ^{234}Th excess is a powerful indicator of remineralization processes in the mesopelagic zone. Estimates of remineralization flux give values ranging between 60 ± 90 dpm/m^2/d at 46.9°S and 3800 ± 200 dpm/m^2/d at 60.9°S with highest values in the AZ-S and SIZ. However, except for the two northern stations, these values may be underestimates since the deepest samples of the profiles were not always at equilibrium, indicating that remineralization process may still occur at deeper depths. Thus, for future studies, we recommend sampling the upper 500–600 m with a high vertical resolution in order to test the use of ^{234}Th excess as a proxy of mesopelagic particle break-up and remineralization.

4. ^{234}Th Fluxes

4.1. Steady Versus Non-Steady State Models

[13] The steady state model (Equation 1) indicates that the lowest ^{234}Th fluxes at 100 m were observed in the central part of the study area (PFZ and IPFZ) and during the first visit of the AZ-S (Figure 3). The highest values correspond to the second visit of the AZ-S and to the station at 63.9°S. After *ca* two weeks the 100 m-flux increased slightly at 63.9°S, and increased by a factor of *ca* 4 at 60.9°S. Except at 46.6 and 53.7°S, fluxes at 300 m (Figure 3) are much smaller than at 100 m and even negative, due to particle break-up and remineralization.

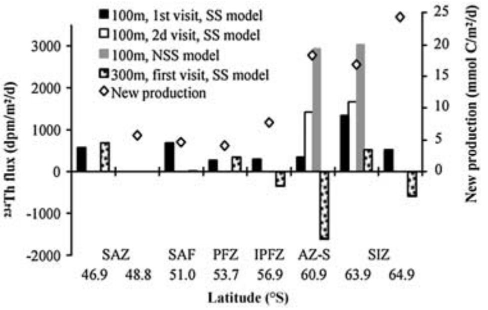

Figure 3. ^{234}Th fluxes (bars) at 100 and 300 meter depth calculated using steady state (SS) or non-steady state (NSS) model, and new production (diamonds; from *Savoye et al.* [2004]). SAZ, SAF, PFZ, IPFZ, AZ-S, SIZ: see Figure 1.

[14] The main assumption of the steady state model (Equation 1) is that there is no change over time in ^{234}Th activity (and consequently on ^{234}Th fluxes) at least at the time scale of ^{234}Th ($t_{1/2}$ = 24d). This is clearly not the case at 60.9°S and to a lesser extent at 63.9°S which show considerable change in the ^{234}Th flux over *ca* two weeks. Furthermore, under steady state conditions mesopelagic remineralization should at most be as large as surface export, i.e., export fluxes at depth should be nil or positive. The 300 m-flux is highly negative at 60.9°S and 64.9°S, indicating that surface export is greater than remineralization, which suggests that the steady state model is not valid for predicting export fluxes at these stations. In contrast, for the northern stations, the steady state approach seems valid since export and remineralization are in balance. This situation is consistent with our earlier findings [*Savoye et al.*, 2004] suggesting that the southern part of this transect acts as a pulsed production system contrasting with a more stable system in the north.

[15] The repeat visits at 60.9 and 63.9°S after a delay of 11 and 17 days, respectively, allow calculation of the ^{234}Th flux using a non-steady state model (Equation 2). The 100 m-fluxes were *ca* 3000 dpm m^{-2} d^{-1}, greatly exceeding those obtained with the steady state model. In the following discussion and in Table 1, we use the steady state flux values from SAF to IPFZ and the non-steady state flux values in AZ-S and SIZ.

4.2. Comparison With Other Studies

[16] During spring 2001 ^{234}Th fluxes were low in the north (*ca* 630 dpm/m^2/d), minimal in the Polar and Inter Polar Frontal Zones (*ca* 300 dpm/m^2/d) and high in the south (*ca* 3000 dpm/m^2/d). The latter were similar to fluxes reported by *Buesseler et al.* [2001] at 170°W but much higher than fluxes reported by *Rutgers van der Loeff et al.* [1997] in the Atlantic sector for early spring conditions (Table 1). In contrast, from the SAZ to the IPFZ, ^{234}Th fluxes were much smaller in our study than generally reported in the literature, being similar only with early spring values [*Rutgers van der Loeff et al.*, 1997]. Our ^{234}Th fluxes indicate low particle export in the SAZ and SAF, very low particle export in the PFZ and IPFZ and high export in the AZ-S and SIZ during spring 2001. Interestingly, the phytoplankton assemblage was dominated by small cells (picoplankton and flagellates) from SAZ to IPFZ

Table 1. ^{234}Th Flux (dpm/m^2/d) at 100 m (#: 200 m) in the Southern Ocean From Steady-State and *Non Steady-State* Models

Period	STZ	SAZ, SAF	PFZ, IPFZ, PF	AZ-S, Southern	Ross Sea	Weddell Gyre	Ref
Nov–Dec		575/682	263/300	*2942/3034*			1
11–31 Oct			172/588	−114/476			2
10–22 Nov			1128/1697	1/1027			2
24 Oct–28 Jan		3573	1796/3170	2440/3480			3
16 Feb–15 Mar		2445	2755/3746	2467/3788	3134		3
30 Oct–20 Jan			*1680/3602*	*2360/3950*			3
20 Jan–01 Mar				*2122/4032*			3
Dec–Jan			865				4
Mar–Apr			250/2600#	400/1700#		−400/1000#	5
02 Oct–08 Nov					−300/500		6
13 Jan–11 Feb					750/2600		6
31 Mar–14 Apr					800/2500		6
Jan–Feb				*350/775*			7
Jan–Feb	122/1252 *1579*		735/1831 *−6009*				8

SAZ, SAF, PFZ, IPFZ, AZ-S: see Figure 1; STZ: Sub-Tropical Zone; PF: Polar Front. '/' indicates a range of values.

1: this study, 2: *Rutgers van der Loeff et al.* [1997], 3: *Buesseler et al.* [2001], 4: *Rutgers van der Loeff et al.* [2002], 5: *Usbeck et al.* [2002], 6: *Cochran et al.* [2000], 7: *Buesseler et al.* [2004], 8: L. Coppola et al. (Low particulate organic carbon export in the frontal zone of the Southern Ocean (Indian sector) revealed by ^{234}Th, submitted to *Deep-Sea Res. I*, 2003).

and by large cells (diatoms and dinoflagellates) in AZ-S and SIZ [*Savoye et al.*, 2004], suggesting that large phytoplankton contributed more efficiently to particle export.

[17] Latitudinal variations of ^{234}Th fluxes were in tight agreement with variations in new production (Figure 3)—estimated for the same cruise from *f*-ratio and primary production—which is considered as 'exportable' production. ^{234}Th data and new production values both indicate that PFZ and IPFZ were the regions of lowest export, contrasting with the widely accepted idea that the Polar Front favours export [e.g., *Usbeck et al.*, 2002]. This could be specific to the Australian sector because of hydrodynamic conditions: in the Australian sector (140°E), Polar Front divides into two branches 4–5° apart from each other [*Trull et al.*, 2001]. Elsewhere, the Polar Front branches are located closer to each other [*Pollard et al.*, 2002].

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