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Trace element composition of suspended particulate matter along three meridional CLIVAR sections in the Indian and Southern Oceans: Impact of scavenging on Al distributions



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ABSTRACT

We present the trace element composition (Al, Si, P, Ca, Fe, and Zn) of suspended particulate matter (SPM) samples collected in the upper 1000 m along U.S. CLIVAR/CO2 Repeat Hydrography meridional section I09N/ I08S from the Southern Ocean to the Bay of Bengal at 95°E and in surface waters along meridional section I06S from the South African margin to the Antarctic shelf edge at 30°E. A band of elevated surface-ocean pCa $(0.5-0.3 \,\mu\text{M})$ over $30-60^{\circ}\text{S}$ is consistent with the global pattern of high coccolithophore production encircling the Southern Ocean suggested by remote sensing. Over 50-60°S, both sections exhibit a sharp transition from Carich to Si-rich particulate matter (up to $2.8-6.5\,\mu$ M), indicating a change from coccolithophore to diatom communities in waters with low residual nitrate. Along IO8S, diatom blooms display elevated pZn concentrations and Zn:P ratios $(14.9 + 5.7 \text{ mmol mol}^{-1})$, reflecting cellular Zn stoichiometry of Southern Ocean diatoms. Regions of high primary productivity in the Southern Ocean are coincident with unexpectedly high surfaceocean pAl concentrations (max 12.6-26.5 nM) compared to background concentrations (typically < 2 nM along 109N/108S and < 5 nM along I06S). We estimate that > 50% of surface-ocean pAl in these regions originates from adsorptive scavenging of dissolved Al onto biogenic particles. Along IO8S, dissolved Al reservoirs likely originate from transport of Al-enriched waters by the Agulhas Return Current, local dust deposition, and seasonal ice melt. Along I06S, pAl distributions suggest larger inputs of dust to the surface mixed layer than have previously been described. By contrast, pFe concentrations remain low in both surface (< 0.3 nM I09N/I08S, 0.1-0.8 nM I06S) and intermediate (< 0.4 nM I09N/I08S) waters away from coastal and shelf inputs. Inputs of lithogenic material from resuspended shelf sediments are apparent in the distributions of pFe and pAl close to the Antarctic margin (up to 10 nM pFe and 23.4 nM pAl) and the South African coast (up to 3.1 nM pFe and 8 nM pAl). At intermediate depths along I08S, elevated pFe concentrations (up to 1.0 nM) are observed downstream of the Kerguelen Plateau, reflecting lateral transport of resuspended plateau sediments or glacial runoff.

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1. Introduction

The distribution and bioavailability of trace metals in the ocean are strongly influenced by partitioning between the dissolved phase and suspended and sinking particles (e.g., Balistrieri et al., 1981). The size and composition of biotic and abiotic particles (e.g., CaCO₃, biogenic

silica, lithogenic minerals, organic carbon) can impact the affinity of individual trace metals for a specific particle type and determine the relative strength of scavenging pressures on particle-reactive trace metals (Chase et al., 2002).

The distribution of Al in the world oceans has been utilized to estimate the flux of mineral dust to the surface ocean (dissolved Al)

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(Measures and Vink, 2000) and as a tracer for the distribution of crustally-derived particles in the water column (particulate Al) (e.g., Lam et al., 2015). Particle-mediated scavenging of dissolved Al, especially by siliceous diatom frustules in the surface ocean, is thought to be the primary removal mechanism for dissolved Al (Orians and Bruland, 1986). Adsorptive scavenging has also been shown to impact surfaceocean particulate Al distributions in certain Al-rich, biologically productive regimes such as the North Atlantic (Moran and Moore, 1988; Barrett et al., 2012; Twining et al., 2015). However, particle scavenging pressures vary significantly across ocean regimes and uncertainties in this parameter limit current modelling approaches (Gehlen et al., 2003; van Hulten et al., 2012). A better understanding of particle-mediated removal processes is needed to interpret dissolved Al as a tracer of dust deposition and constrain the atmospheric input of Fe and other biologically important trace elements to the oceans (Anderson et al., 2016). Additionally, the impact of adsorptive scavenging on surface-ocean particulate Al distributions is largely unexplored, a source of uncertainty in estimates of lithogenic particle loadings.

Global trace element sampling programs (e.g., CLIVAR (Grand et al., 2014), GEOTRACES (Anderson et al., 2014)) have accelerated progress towards a global view of trace element distributions and a database from which to improve biogeochemical ocean models. However, the Indian Ocean is still relatively understudied with respect to particulate trace metals. With the exception of pFe data from the Crozet and Kerguelen regions (Sarthou et al., 1997; Planquette et al., 2009, 2011; Chever et al., 2010; Bowie et al., 2014; van der Merwe et al., 2015), there is a scarcity of particulate trace metal data, especially with respect to the high-resolution, basin-scale datasets that have been reported for the Atlantic (e.g., Barrett et al., 2015; Lam et al., 2015) and Pacific Oceans (e.g., Lee et al., 2018).

The focus of this manuscript is the trace element composition (Al, Si, P, Ca, Fe, and Zn) of suspended particulate matter (SPM) samples collected along the U.S. CLIVAR/CO₂ Repeat Hydrography sections $I09N/I08S (\sim 95^{\circ}E)$ and I06S section ($\sim 30^{\circ}E$) in the Indian sector of the



Southern Ocean (Fig. 1). These sections include ocean regions with significant variation in local and advective inputs of Al to the upper ocean and span the oligotrophic waters of the South Indian subtropical gyre to productive, particle-rich waters in the Southern Ocean. The distributions of dissolved Al (dAl) and Fe (dFe) along the entire IO8S/ I09N section and a subset of the I06S section have been previously reported in Grand et al. (2015a, 2015b, 2015c). Samples from the I09N/I08S section in the Bay of Bengal and subtropical stations will be discussed more extensively in a separate paper with additional data from a 2009 occupation of CLIVAR zonal section I05 across the subtropical gyre (Barrett et al., in preparation). In this work, we discuss the dominant sources of particulate Al (pAl) and Fe (pFe) and the processes that control their distributions in the upper water column. Using the biogenic particle distributions and expected lithogenic particle composition, we attempt to quantify the impact of scavenging on the pAl distribution and discuss implications for Al (and Fe) cycling in the Southern Ocean.

2. Methods

Trace element data reported are from the upper 1000 m along the CLIVAR I08S/I09N sections and from surface waters along the CLIVAR I06S section in the South Indian Ocean (Fig. 1). Suspended particulate matter samples were collected at 85 stations along meridional section I09N/I08S (15 February to 26 April 2007) from the Southern Ocean to the Bay of Bengal. Meridional section I06S (6 February to 6 March 2008) was sampled at 61 stations from the South African margin to the Antarctic shelf edge. Seawater was collected from 12 depths in the upper 1000 m using 12 L GO-FLO bottles on a trace metal-clean rosette and processed in a clean laboratory van equipped with a HEPA filtered air system (Measures et al., 2008). Spacing between stations was typically 1 degree of latitude, although inclement weather occasionally resulted in some stations not being occupied, particularly in the Southern Ocean. During occupation of I06S, the trace metal rosette was

Fig. 1. Location of trace metal sampling stations along CLIVAR meridional sections I09N/I08S (2007) and I06S (2008). Shown with approximate locations of Southern Ocean currents and frontal zones along the I09N/I08S and I06S transects: Subtropical Front (STF), Subantarctic Front (SAF), Polar Front (PF), South ACC Front (SACCF), Subantarctic Zone (SAZ), Polar Frontal Zone (PFZ), Antarctic Zone (AZ), Southern Zone (SZ). Large-scale circulation patterns based on Stramma and Lutjeharms (1997).



lost mid-cruise due to rough seas. At remaining stations south of 48° S, samples were collected in the mixed layer (typically at ~40 m) using GOFLO bottles on a Kevlar line that were tripped with a Teflon-coated messenger.

Suspended particulate matter samples were collected by pressurefiltering seawater (using < 55 kPa, filtered compressed air) through acid-washed, 0.4 μ m track-etched, polycarbonate filters (Nuclepore) with backing filters of mixed cellulose ester to facilitate even sample loading in polypropylene filter holders. The average filtration volume was 8.8 <u>+</u> 2.2 L. Filters were rinsed with deionized water that was adjusted to pH 8 with ammonium hydroxide with a low vacuum applied to remove residual sea-salt while avoiding loss or redistribution of particles.

Sample filters were analyzed using energy-dispersive x-ray fluorescence (ED-XRF) at NOAA PMEL on a Thermo Fisher Quant'X equipped with a Rhodium Target X-Ray tube and an electronically cooled, lithium-drifted solid state detector using thin-film principles under a vacuum atmosphere as previously described in Barrett et al. (2012). Calibration was performed using commercial thin film standards (MicroMatter) and standards prepared using a modification of the method reported by Holynska and Bisiniek [1976] that employs diethyldithiocarbamate to quantitatively precipitate trace metals from a solution of known concentration. Method-blank values were determined from analysis of acid-cleaned filter blanks and subtracted from measured sample values. Detection limits (DL) were determined from a standard of known concentration and are defined as:

$$DL = (3\cdots\sqrt{I_b})/(I_p/c)$$
⁽¹⁾

where I_b is the background intensity, I_p is the peak intensity, and c is the concentration of the standard. Method-blank values and minimum detection limits for trace elements of interest are reported in Table 1. Analytical accuracy of the ED-XRF analysis is confirmed by analysis of certified reference material NIST SRM 2783 (Table 1); no corrections based on SRM yield were applied to measured concentrations (Table 1).

Shipboard analysis of dFe and dAl in filtered seawater samples was performed using the flow injection methods of Measures et al. (1995) and Resing and Measures (1994), respectively; these dissolved trace metal data have been previously reported for the I09N/I08S section (Grand et al., 2015a, 2015b) and for stations north of 48°S along the I06S section (Grand et al., 2015c). The dFe and dAl datasets from I09N (Expocode 33RR20070322), I08S (33RR20070204), and I06S (33RR20080204) are publicly available on the CCHDO website (http:// cchdo.ucsd.edu). All particulate trace metal datasets reported in this manuscript are provided in supplemental files and will also be shortly

Table 1

Detection limits and method blank values for trace elements of interest as given in filter sample concentrations (ng cm⁻²) and equivalent seawater concentration (nM) for the average filtration volume (8.8 L) with results of analysis of NIST 2783 (air particulate on filter media) compared to certified values. Where no method blank is given, the signal peak was indistinguishable from the background.

	Detection limit		Method blank		NIST 2783	
	(ng cm ⁻²)	nM	(ng cm ⁻²)	nM	Certified value $(ng \text{ cm}^{-2})$	Measured $(ng cm^{-2})$
Al	9.4	0.49	14.5	0.76	2330 <u>+</u> 53	2133 + 77 (n = 30)
Fe	0.95	0.02	4.32	0.11	2660 <u>+</u> 160	2937 + 74 (n = 30)
Р	2.01	0.09	41.9	1.9	N/A	N/A
Ca	3.99	0.14	9.25	0.33	1325 <u>+</u> 110	1307 + 45 (n = 30)
Si	4.61	0.23	BDL	-	5884 <u>+</u> 160	5804 + 196 (n = 30)
Zn	1.28	0.03	BDL	-	180 <u>+</u> 13	153 + 4 (n = 30)

made available on CCHDO.

For all sections, hydrographic measurements (salinity, dissolved oxygen, nitrate, silicate) were taken from the main 36-bottle rosette with CTD profiles (pressure, temperature, and fluorescence) from a Sea-Bird Electronics SBE9*plus* CTD with dual pumps, dual temperature (SBE3*plus*), and fluorometer (Wetlabs CDOM) deployed at stations with 0.5-degree spacing. Bottle samples were analyzed for salinity using a Guildline Autosal 8400A salinometer, for dissolved oxygen using a modified Winkler titration, and for nutrients using a modified Technico Autoanalyzer II. Nutrient and salinity samples taken from trace metal rosette GO-FLO bottles were compared to values from the main CLIVAR rosette to confirm correct trip depth. Further methodological information, details for sensor calibrations, and all ancillary data presented in supporting information are publicly available on the CCHDO website under the same Expocodes noted above.

3. Results

3.1. Surface circulation

A full discussion of general circulation patterns and hydrography has previously been presented for the upper 1000 m along both I09N/ I08S (Grand et al., 2015a, 2015b) and I06S (Grand et al., 2015c). Here, we briefly describe the circulation patterns relevant to the particulate trace element distributions discussed below. A simplified schematic of surface circulation patterns is shown in Fig. 1. Distributions of salinity, temperature, dissolved oxygen, nitrate, silicate, and fluorescence in the upper 1000 m are presented in Fig. S1 for section I09N/I08S and in Fig. S2 for section I06S, which have been presented and discussed more fully by Grand et al. (2015a, 2015b, 2015c).

The South Equatorial Current (SEC) at ~15°S represents the northern boundary of the South Indian subtropical gyre. From the westwardflowing SEC, the anti-cyclonic subtropical gyre circulation cell in the South Indian Ocean continues with the Agulhas Current, the western boundary current flowing south along the South African shelf. The I06S section sampled the Agulhas Current at stations closest to the African shelf north of 34°S. At the southern tip of the African continent, the majority of the current flow turns back into the central Indian basin and becomes the Agulhas Return Current (Lutjeharms and Ansorge, 2001), which intersects the I06S transect at ~40°S. Much of the water carried by the eastward-flowing Agulhas Return Current is recirculated within the western gyre (Stramma and Lutjeharms, 1997) while the remaining flow becomes the South Indian Ocean Current, which intersects the I09N/I08S transect (~95°E) at ~40–45°S in the eastern basin.

The I09N/I08S and I06S sections extend into the Indian sector of the Southern Ocean where the eastward-flowing Antarctic Circumpolar Current (ACC) dominates circulation patterns. Using the property criteria of Orsi et al. (1995), the location of the major fronts constituting the ACC transport were identified along both sections (Grand et al., 2015c). Along I09N/I08S, the ACC is bounded to the north by the Subtropical Front (STF) at 38–40°S with the SubAntarctic Front (SAF) at 49°S, the Polar Front (PF) at 54–57°S, and the South ACC Front (SACCF) at 63°S. Along I06S, the STF was located near ~42.5°S, the SAF at ~46.5°S, the PF at 51°S, and the SACCF over 57–59°S. Approximate locations of the Southern Ocean fronts along each transect are indicated in Fig. 1.

3.2. I09N/I08S trace element concentrations

The distributions of particulate P, Ca, Si, Al, and Fe, the particulate Fe:Al molar ratio, and the distribution of dAl measured along the I09N/I08S section are shown in Fig. 2. The plot of particulate P is restricted to the upper 500 m as concentrations at greater depths were typically below the ED-XRF detection limit (0.1 nM); all other plots extend to the full 1000 m sampling limit.



Fig. 2. Distribution of particulate P, Ca, Si, Zn, Al, Fe, particulate Fe:Al ratio, and dissolved Al in the upper 1000 m along the CLIVAR I09N/I08S section. Black points indicate individual samples; note the reduced depth scale (500 m) in the plot of particulate P. Dissolved Al data previously reported by Grand et al. (2015b). The location of fronts from Fig. 1 are indicated by black squares and the locations of the South Equatorial Current (SEC) and the South Indian Ocean Current (SIOC) are indicated by black diamonds.

3.2.1. Particulate P, Ca, Si, and Zn along IO9N/IO8S

Elevated concentrations of particulate P (pP) are observed in the euphotic zone along I09N/I08S and generally covary with fluorescence in the upper 200 m (p < 0.05, $R^2 = 0.64$, n = 579), consistent with a biogenic source. pP concentrations decline rapidly with depth and are relatively homogenous below 200 m throughout the entire section, averaging 0.9 \pm 0.8 nM (mean \pm 1 SD). Particulate Ca (pCa) and particulate Si (pSi) concentrations are also elevated in the surface ocean; in absence of direct observations of phytoplankton community structure, pCa and pSi are assumed to largely reflect biogenic CaCO₃ and coccolithophore abundance, and biogenic silica and diatom abundance, respectively.

South of ~30°S, surface-ocean pP concentrations increase (averaging 20 ± 10 nM) compared to concentrations observed in the subtropical gyre and are highest (up to 75 nM) at stations closest to the Antarctic shelf. Concentrations of pCa and pSi are also elevated in surface waters in the Southern Ocean, linked to the spatial separation between coccolithophore and diatom populations. North of the PF between approximately 30°S and 55°S, surface-ocean pCa concentrations

average 140 ± 60 nM in the upper 50 m, then drop sharply to 16 ± 5 nM south of the PF. Surface-ocean pSi concentrations are relatively low (< 0.2 µM) in the northern part of the section, and high pSi concentrations up to 6.5μ M (averaging $3.1 \pm 1.7 \mu$ M) are observed in surface waters south of the PF to the Antarctic shelf. Relatively elevated pZn concentrations (0.1–0.8 nM) are found in the upper 100–200 m of the water column within this region of high diatom productivity.

3.2.2. Particulate Al and Fe along I09N/I08S

Concentrations of pAl are relatively low throughout the upper water column (< 200 m) in the subtropical gyre (0.4–2.0 nM). However, from the southern edge of the subtropical gyre into circumpolar waters, a local maximum in surface-ocean pAl concentrations (up to 12.6 nM) spans the STF over 28–44°S. In this region, concentrations of pAl in the upper 50 m average 4.4 \pm 3.5 nM and are correlated with surface-ocean pCa concentrations (p < 0.05, R² = 0.36, n = 34) (Fig. S3). At five stations south of this feature, pAl concentrations in surface waters decline to levels comparable to those observed in the subtropical gyre (1.2 \pm 0.7 nM), then increase sharply near the PF and remain elevated

south to the Antarctic shelf. Surface-ocean pAl concentrations south of the PF average 12.0 ± 6.8 nM (4.3-26.5 nM) and are correlated with surface-ocean pSi (p < 0.05, R² = 0.67, n = 28) (Fig. S3). By contrast, with the exception of the three southernmost stations closest to the Antarctic margin where pFe concentrations are slightly elevated (0.18-0.96 nM), pFe concentrations in Southern Ocean surface waters are uniformly low, averaging 0.14 ± 0.07 nM (0.05-0.29 nM). These values are comparable to pFe concentrations reported in Southern Ocean waters at 62° E by Sarthou et al. (1997) (0.03-0.20 nM). They are somewhat lower than those reported by Chever et al. (2010) (0.34-0.84 nM) at stations in open-ocean waters over 77-78°E and the average mixed layer pFe at 66° E (0.57 nM) reported by Bowie et al. (2014).

Concentrations of pAl in intermediate and deep waters (> 200 m) in the Southern Ocean are generally < 2.0 nM and subsurface pFe values typically range over 0.09–0.38 nM. However, two regions of elevated subsurface pAl and pFe are apparent in the Southern Ocean along I09N/ I08S. At the 3 stations sampled closest to the Antarctic shelf (south of 64°S), vertical profiles show maximum pAl and pFe concentrations of 23.4 nM and 10.7 nM, respectively, at depths of 150–300 m. Farther north at stations between ~40 and 60°S, pFe concentrations up to 1.0 nM are observed at depths greater than 400 m.

3.3. I06S trace element concentrations

The distributions of particulate P, Ca, Si, Al, and Fe, and the Fe:Al molar ratio of particulate matter samples collected in surface waters (typically 20–40 m) along the I06S section are shown in Fig. 3.

3.3.1. Particulate P, Ca, Si, and Zn in surface waters along I06S

Surface-ocean pP concentrations are lowest at stations within 350 miles of the South African coast $(4.1 \pm 2.2 \text{ nM})$. Concentrations increase sharply at 40°S to ~40 nM and then range from 5 to 30 nM in surface waters in the Southern Ocean, with highest concentrations observed at stations within 200 km of Antarctica.

Similar to patterns observed along the I09N/I08S section, there is strong spatial separation between regions of elevated surface-ocean pCa and pSi in the Southern Ocean along I06S. Maximum pCa concentrations up to 470 nM are observed approximately between the STF and the PF (38°S–51°S). Surface-ocean pCa concentrations remain slightly elevated in the Polar Frontal Zone (77 \pm 24 nM), but drop to very low average concentrations (9 \pm 11 nM) throughout the rest of the Southern Ocean to Antarctica. In contrast, pSi concentrations are lowest in surface waters north of the PF (< 0.1 to 0.5 μ M). A region of high surface-ocean pSi (0.6–2.8 μ M) extends from the PF to ~61°S and pSi concentrations also increase slightly at stations closest to the Antarctic coast. South of the PF, pZn concentrations are also elevated (0.2–1.0 nM). However, unlike the distribution of surface-ocean pSi, pZn remains relatively high south of the SACCF.

3.3.2. Particulate Al and Fe in surface waters along I06S

Stations north of 34°S along I06S are located within the Agulhas Current and elevated pAl (5–8 nM) and pFe (0.9–3.1 nM) concentrations are observed here in surface waters within 100 km of the South African coast. The Agulhas Current transports significant amounts of fine, resuspended sediment along the African margin (Flemming, 1981) that results in high pAl, pFe, and dFe concentrations (Grand et al., 2015c) in the upper water column that decrease with increasing distance from the shelf source.

Surface-ocean pFe concentrations range from 0.22 to 0.84 nM in subtropical waters, then decline to uniformly low concentrations (0.26 + 0.12 nM) throughout the Southern Ocean. Surface-ocean pAl concentrations are also relatively low throughout the subtropical gyre and north of the PF (2.5 <u>+</u> 1.4 nM). However south of the PF to the SACCF (~51°S–61°S), surface-ocean pAl concentrations increase, averaging $8.2 \pm 4.1 \text{ nM}$ (3.0–15.9 nM), and are highly correlated with

surface-ocean pSi (p < 0.05, R² = 0.90, n = 14) (Fig. S4). South of this feature, average pAl in surface waters declines to 2.4 \pm 0.6 nM, similar to concentrations observed north of the PF. South of 68°S, somewhat higher pAl (4.0 \pm 1.2 nM) and pFe concentrations (0.47 \pm 0.27 nM) are observed at stations closest to Antarctica.

4. Discussion

In the following sections, we will discuss the pCa and pSi distributions as they compare to previous observations of phytoplankton biogeography in the Southern Ocean. We will then discuss how these biogenic particle loads impact the distribution of pAl in Southern Ocean surface waters via scavenging pressures and the processes that supply Al to these waters. Finally, we consider the subsurface pAl and pFe distributions that are influenced by lateral transport of shelf sediments.

4.1. Southern Ocean phytoplankton assemblages

High surface-ocean pCa concentrations are observed in surface waters between 30°S and the PF (~55°S) along I09N/I08S and between 40°S and the PF (~51°S) along I06S. Measurement of pCa to determine CaCO₃ has been shown to be comparable to other direct measurements of particulate inorganic carbon (PIC) (Lam et al., 2015). The latitudinal distribution of pCa across frontal systems along our sections is similar to trends in surface-ocean PIC reported previously (Holligan et al., 2010; Balch et al., 2011), with elevated PIC found throughout the sub-Antarctic and Polar Frontal zones, then declining sharply south of the PF (Table 2). Maximum concentrations found along I09N/I08S and I06S are somewhat lower than those observed previously in the Atlantic, consistent with remote sensing showing most intense reflectivity from surface-ocean PIC in the Atlantic sector and decreasing to the east in the Pacific and Indian Oceans (Balch et al., 2011). Hence, our observations are consistent with a global pattern of high coccolithophore production in a band around the Southern Ocean between approximately 30 and 60°S (the "Great Calcite Belt") as suggested by previous in situ studies and remote sensing PIC algorithms (Balch et al., 2005, 2011; Sadeghi et al., 2012).

The distinct separation in the geographic ranges of Ca-rich and Sirich particles along both I09N/I08S and I06S suggest strong oceanographic controls on phytoplankton ecology and interspecies competition in the Indian sector of the Southern Ocean. Distinct geographic separation between coccolithophore and diatom populations in the Southern Ocean has also been observed in previous studies (Townsend et al., 2010; Brzezinski et al., 2011; Balch et al., 2014). It has been hypothesized that favorable conditions for diatom growth in the Southern Ocean occur when residual nitrate ([NO₃]-[Si(OH)₄]) is negative; positive residual concentrations likely represent a competitive advantage for phytoplankton not requiring silicate for growth, such as coccolithophores (Townsend et al., 2010; Balch et al., 2014). Observations of residual nitrate in this area are generally consistent with this conceptual model. Along I09N/I08S, residual nitrate in Southern Ocean surface waters is positive north of 57.5°S where pSi concentrations are relatively low ($< 1 \mu$ M), while residual nitrate is negative to the south of the PF, where pSi increases sharply up to $5\,\mu\text{M}$ (Fig. S5). Along I06S, residual nitrate is positive in surface waters between the subtropical front and the PF (51°S) where pSi concentrations are low $(< 0.5 \,\mu\text{M})$ but high pCa concentrations indicate presence of a coccolithophore bloom. To the south, where pSi concentrations increase at 51°S, residual nitrate becomes negative and generally decreases with increasing latitude, although several stations between 51 and 56°S do have positive values for residual nitrate (Fig. S6).

Elevated surface-water concentrations of pZn along I09N/I08S (0.11–0.75 nM) and I06S (0.12–0.68 nM) coincide with high pSi concentrations. Diatom Zn uptake is thought to be a critical control on Zn biogeochemistry in the global ocean (Vance et al., 2017). Previous studies have found that Southern Ocean diatom populations have

uniquely high cellular Zn:P ratios compared to other Southern Ocean phytoplankton communities and to diatom species in other open-ocean regions (Twining and Baines, 2013 and references therein). The Zn:P ratios in particulate matter samples collected in the mixed layer at stations within the diatom bloom along I09N/I08S average $14.9 \pm 5.7 \text{ mmol mol}^{-1}$ (n = 37), comparable to the cellular Zn stoichiometry of Southern Ocean diatom populations (11–15 mmol mol⁻¹) observed in previous studies (Table 3). By contrast, average Zn:P ratios in regions of high pSi concentrations (~50–60°S) along I06S are much lower ($3.0 \pm 0.9 \text{ mmol mol}^{-1}$, n = 12) than along I08S and not significantly different than Zn:P ratios in surface-ocean samples elsewhere along the section ($3.8 \pm 5.1 \text{ mmol mol}^{-1}$, n = 34; two-tailed *t*-test, p > 0.1). It is possible that the phytoplankton assemblage south of the PF along I06S is more diverse than that along I08S. The more variable

and sometime positive residual nitrate concentrations south of the PF along I06S (Fig. S6) support the idea that the nutrient balance favors a diatom-dominated community less strongly than along I08S (Fig. S5). Alternatively, it is possible that diatoms communities along these sections experience differing levels of Fe stress as dFe supply within the ACC is likely attenuated with distance from source regions near the Antarctic peninsula and Patagonian shelf (Measures et al., 2013), resulting in increased cellular Zn:P ratios from I06S to I09N/I08S (Twining and Baines, 2013 and references therein).

4.2. Scavenging of Al in Southern Ocean surface waters

The close association of surface-ocean pAl with pSi and pCa in highproductivity regimes in the Southern Ocean (Fig. 4) and the low surface



Fig. 3. Distribution of particulate P, Ca, Si, Zn, Al, and Fe (nM), and Fe:Al ratio of suspended particulate matter samples in surface samples (< 50 m) along CLIVAR section I06S; black dots represent individual samples. The location of fronts from Fig. 1 are indicated by dashed lines with the approximate location of the Agulhas Current (AC) and the Agulhas Return Current (ARC) shown by solid arrows.



Fe:Al ratios of particulate matter in these regions suggests that the pAl distribution may be strongly controlled by scavenging of dAl by high biogenic particle loads. Particle scavenging is a primary mechanism by which dAl is removed from surface waters, with especially efficient adsorptive scavenging by the siliceous frustules of diatoms (Hydes, 1979; Orians and Bruland, 1986; Moran and Moore, 1992; Dymond et al., 1997).

The high surface-ocean pAl concentrations are unlikely to be due to incorporation of lithogenic particles into biological aggregates. Inclusion of mineral grains in biological aggregates, facilitated by the production of extracellular organic material, has been demonstrated experimentally in cultures and with detrital organic material (Hamm, 2002; Passow and De La Rocha, 2006). However, pFe and particulate Fe:Al molar ratios in these highly-productive regions of the Southern Ocean along I09N/I08S and I06S are very low and unlikely to result from the presence of crustally-derived particles. Along I09N/I08S,

particulate Fe:Al ratios average 0.04 + 0.03 in Southern Ocean surface waters. By contrast, average Fe:Al in surface-ocean particulate matter throughout the sub-tropical gyre and Bay of Bengal is 0.32 + 0.13, which is close to the composition of the bulk continental crust (0.26 Fe:Al) [Wedepohl, 1995] and consistent with a largely lithogenic particle source that may be slightly enriched in Fe by active biological uptake or scavenging of Fe in the euphotic zone. Along IO6S, the average particulate Fe:Al in the Southern Ocean diatom bloom (0.04 ± 0.02) is also significantly lower than Fe:Al ratios observed in surface waters elsewhere along the transect (0.18 \pm 0.14; two-tailed ttest, p < 0.01). We do consider the possibility that atmospheric processing of aerosol dust during long-range transport could lead to deposition of mineral particles with extremely low Fe:Al ratios that are then incorporated into organic aggregates, leading to the observed correlation between pAl and biogenic particles in surface waters. However, to our knowledge there have been no prior observations of

Table 2

Comparison of pCa concentrations with prior observations of PIC (μ M) measured in Southern Ocean surface waters within the Sub-Antarctic zone (SAZ), Polar Frontal Zone (PFZ), Antarctic Zone (AZ), and Southern Zone (SZ). Range of concentrations with average values given in parentheses. Location of Southern Ocean fronts observed during this study are discussed in Section 3.1 and noted in Fig. 1.

Reference	Sector	SAZ	PFZ	AZ	SPZ
PIC, Holligan et al. (2010)	Atlantic, ~55°W	0.1–1.3 (0.4)	0.04–0.2 (0.1)	< 0.01–0.1	< 0.01-0.1
PIC, Balch et al. (2011)	Atlantic	0.5–1.0	-	-	-
pCa, this study pCa, this study	Indian, ~30°E Indian, ~90°E	0.1–0.3 (0.2) 0.1–0.3 (0.2)	0.01-0.2 (0.1) 0.1-0.2 (0.1)	0.01-0.1 (0.03)	< 0.01-0.02 (0.02) < 0.01-0.1 (0.01)

Table 3

Ratio of Zn:P in suspended particulate matter (SPM) samples from mixed layer depths along CLIVAR I08S (53–66°S) and I06S (52–61°S) shown with prior estimates of Zn:P cellular stoichiometries.

Reference	Sample	Location	Zn:P (mmol:mol)
This study	Bulk SPM	I08S, Southern Ocean	14.9
This study	Bulk SPM	I06S, Southern Ocean	3.0
COLLIER and Edmonds (1984)	Bulk SPM	Southern Ocean	13.3
Cullen et al. (2003)	Diatom	Southern Ocean	11.1
Twining et al. (2013)	Diatom	Southern Ocean	15.0
Twining et al. (2014)	Diatom	subtropical Pacific	6.7

marine aerosols with such trace metal composition. Rather, aerosols are often enriched in Fe due to mixing with anthropogenic sources (Witt et al., 2010; Srinivas and Sarin, 2013) or depleted in Al from specific continental source regions [e.g., Shelley et al., 2015 and references therein]. Additionally, pAl in the upper 1000 m along these Southern Ocean transects show markedly different depth profiles than those in regions heavily impacted by lithogenic particles, such as under the Saharan dust plume in the eastern tropical North Atlantic (Barrett et al., 2012). In the North Atlantic of high lithogenic particle loads, pAl profiles typically display a mid-depth minimum coincident with the fluorescence max where aggregation and export processes dominate to transport pAl out of the surface layer (Ohnemus and Lam, 2015). By contrast, pAl profiles in bloom regions in this study generally show a maximum at the depth of the fluorescence max, consistent with accumulation from scavenging of dAl by high biogenic particle loads.

We attempt to assess the relative importance of adsorptive scavenging processes in contributing to measured pAl concentrations. First, we estimate the biogenic pFe pool using the observed pP distribution and an intracellular Fe:P ratio for Southern Ocean phytoplankton populations ($0.54 \text{ mmol mol}^{-1}$) (Twining et al., 2004), then assume the remaining pFe represents a lithogenic pFe fraction (Planquette et al., 2013). We then determine the expected lithogenic Al distribution by using a crustal Fe:Al ratio (0.26 mol:mol) (Wedepohl, 1995) and attribute the remaining pAl to scavenging of dAl onto particles. The percentage of the observed pAl concentration resulting from particle scavenging processes (pAl_{scav}) is calculated as follows:

$$pAl_{scav}(\%) = \left[pAl_{obs} - \frac{(pFe_{obs} - pP_{obs} * Fe: P_{phyto})}{Fe: Al_{crustal}} \right] \div pAl_{obs} * 100$$
(2)

Eq. (2) is dependent on the choice of values for Fe:P in phytoplankton communities and Fe:Al expected in lithogenic particles. For example, modifying Eq. (2) using a range of intracellular Fe:P ratios observed in cultured and natural phytoplankton populations (0.54 to 9.1 mmol mol⁻¹) (Twining et al., 2004 and references therein) changes the percentage of pFe associated with the biogenic pool from < 1% to > 100% in surface waters along I06S. However, average %pAl_{scav} is relatively insensitive to this parameter and varies by < 10 percentage points. By using the lowest intracellular Fe:P ratio that has been observed in Fe-limited phytoplankton populations and neglecting any contribution from authigenic pFe, Eq. (2) should represent a conservative estimate of pAl_{scav}. The percentage of pAl_{scav} is more sensitive to the choice of crustal Fe:Al ratio; varying Fe:Al from 0.21 to 0.41 mol:mol (Taylor and McLennan, 1995) changes average %pAl_{scav} in surface waters along I06S by 13–17 percentage points.

Plots of %pAlscav along the I09N/I08S and I06S sections are shown in Fig. 5. Along I09N/I08S, pAlscav is close to 0% of measured pAl concentrations in parts of the subtropical gyre, at depths > 400 m over 45-55°S where sediment resuspension and lateral transport from the Kerguelen Plateau is thought to supply pFe (see discussion in Section 4.3), and below the mixed layer at stations closest to Antarctica where shelf sediments are likely a source of pFe. In the Bay of Bengal, estimates for pAl_{scav} are largely negative, likely due to some combination of uncertainties introduced into Eq. (2) from underestimation of phytoplankton intracellular Fe:P under Fe-replete growth conditions and excess pFe in suspended particulate matter from scavenging of the high dFe concentrations found in the oxygen minimum zone (Grand et al., 2015b). However, scavenging appears be the dominant source of pAl in highly productive surface waters in the Southern Ocean, where 50-98% of measured pAl concentrations in the upper 50 m is estimated to originate from scavenging processes. Similarly, estimated pAlscav along section I06S is highest (70-95% of measured pAl) in surface waters between \sim 50 and 60°S where high diatom productivity is evident from elevated surface-ocean pSi concentrations.

Scavenging of dAl from surface waters and resulting elevated surface-ocean pAl concentrations have been observed previously following seasonal bloom conditions (Moran and Moore, 1992; Barrett et al., 2015; Li et al., 2013). However, these prior studies have examined regions such as the North Atlantic or East China Sea where a relatively large supply of dAl is expected from dust deposition or fluvial inputs. The few observations of Southern Ocean dAl report relatively low concentrations in surface waters, typically ranging from < 1 to 3 nM (Sanudo-Wilhelmy et al., 2002; Middag et al., 2011; Grand et al., 2015a). Below, we discuss possible sources that could supply Al to open-ocean surface waters in key regions along I09N/I08S and I06S.

4.2.1. North of the Polar Front along IO9N/IO8S

The local maximum in surface-ocean pAl $(4.4 \pm 2.4 \text{ nM})$ along I09N/I08S over ~30–45°S in the southern extent of the South Indian subtropical gyre and the northern edge of circumpolar waters is associated with high pCa concentrations (Fig. 4). Profiles of dAl concentrations in this region show minimum concentrations in the surface mixed layer, typically < 1 nM [Grand et al., 2015a], and a sharp increase in dAl concentrations at 100–200 m (Fig. 2), consistent with strong removal of dAl in the surface ocean from scavenging by the high loading of biogenic particles.

Likely sources of dAl to this region include deposition of atmospheric dust and advection of dAl originating in the Agulhas Current region. Modelled dust deposition of 200–750 mg m⁻² yr⁻¹ (Moore et al., 2002; Mahowald et al., 2005) from a mixture of South American, South African, and Australian sources (Li et al., 2008) could deliver an estimated 0.4–1.6 nM dAl yr⁻¹ to a surface mixed layer of 50 m (assuming Al content of mineral dust of 8.1% (Heimburger et al., 2012) and aerosol Al solubility of 3.6% (Grand et al., 2015a). In addition to local dust sources, the Agulhas Current system carries dAl-rich waters along the South African shelf and then eastward across the southern edge of the subtropical gyre as the Agulhas Return Current and the South Indian Ocean Current (Fig. 1) (van Beusekom et al., 1997; Grand



Fig. 4. Average surface-ocean (< 50 m) particulate Si (black symbols), particulate Ca (grey symbols) and particulate Al (open symbols) in the South Indian subtropical gyre and Indian sector of the Southern Ocean along CLIVAR sections I09N/I08S (top) and I06S (bottom). Note the differences in scale between plots. Approximate location of fronts from Fig. 1 shown by dashed lines.

et al., 2015b, 2015c). A comparison of dAl concentrations in this latitudinal band across the basin reveals that the dAl signal decreases as waters are transported to the east (Table 4). To the west of the I09N/ I08S section, dAl concentrations of 2.5 nM have been observed in surface waters at $\sim 60^{\circ}$ E by van Beusekom et al. (1997), representing the potential dAl reservoir that could be delivered via lateral advection to waters along I09N/I08S prior to seasonal bloom conditions. Although high pCa concentrations extend southward along I09N/I08S until the PF at ~58°S, surface-ocean pAl concentrations drop abruptly to concentrations < 2 nM at 44°S (Fig. 4). This transition is coincident with sharp gradients in dAl observed throughout the water column separating Al-rich subtropical waters to the north from Al-depleted waters to the south (van Beusekom et al., 1997; Grand et al., 2015b). The decoupling of pCa and pAl concentrations in circumpolar waters suggests that the spatial extent of the high pAl concentrations is primarily controlled by supply of dAl and the meridional extent of the advection of Al-rich subtropical waters by the Agulhas Return Current.

4.2.2. South of the Polar Front along I09N/I08S

South of the PF, scavenging by diatoms leads to another region of elevated surface-ocean pAl along I09N/I08S with average pAl concentrations of 12 nM. Previous researchers have also observed high

surface-ocean pAl concentrations in the Southern Ocean near the I09N/I08S transect. Copin-Montegut and Copin-Montegut (1978) found pAl concentrations of 1–28 nM south of the PF between 50 and 80°E in waters with high pSi concentrations (0.1–3.4 μ M). Similarly, Tréguer et al. (1988) reported pAl concentrations of 6.7–48.4 nM in surface waters with high diatom production (0.2–3.5 μ M pSi) south of the PF between 60 and 85°E. In the absence of other trace metal data, these authors attributed correlation of pAl, pSi, and POC to co-aggregation of organic and mineral particles; however, we suggest that elevated surface-ocean pAl in this region is more likely to result largely from scavenging of the dAl pool by biogenic particles.

Release of dAl from seasonal ice melt and localized circulation patterns are most likely responsible for supplying dAl to surface waters between the Antarctic shelf and the PF. Previous studies of dAl distributions in the Southern Ocean have found that surface-ocean concentrations are often negatively correlated with salinity, indicating that ice melt is an important source of dAl to Antarctic surface waters (Middag et al., 2011, 2013). Concentrations of dAl in free-drifting pack ice (1.3–7.2 nM; Lannuzel et al., 2011) are elevated compared to the Southern Ocean dAl concentrations observed along I09N/I08S (Grand et al., 2015b). However, it is unclear if seasonal melt of an ice cover with a maximum thickness of several meters would be a sufficient



Fig. 5. Percentage of observed pAl concentrations estimated to result from scavenging of the dissolved pool (pAl_{scav}) by biogenic particles in the upper 1000 m along section I09N/I08S and in surface waters along section I06S as calculated using Eq. (2). Approximate location of fronts and surface currents indicated as in Fig. 2 and Fig. 3 for I09N/I08S and I06S, respectively.

Table 4

Surface-ocean dissolved Al concentrations in the Indian Ocean impacted by advection of dissolved Al from the Agulhas current system in the western basin.

Cruise	CLIVAR I06S ^a	CLIVAR I06S ^a	ANTARES I ^b	CLIVAR I08S ^a
Location	Agulhas current 28°E	Agulhas return current 30°E	Agulhas return current ~60°E	South Indian Ocean current 95°E
Dissolved Al	16–22 nM	5–8 nM	2.5 nM	< 1 nM

^a Grand et al. (2015c).

^b van Beusekom et al. (1997).

supply of dAl to support a significant portion (> 75%, Fig. 5) of the average 12 nM pAl observed in the upper 50 m of the water column in this region. However, because of the local circulation patterns in the vicinity of our study area, land-fast ice that forms along and remains attached the coastline is likely to supply additional dAl to waters relatively far from Antarctica.

Recent work examining dAl in land-fast ice in East Antarctica found

dAl concentrations in fast ice ~100 km from the southernmost station along I09N/I08S to range from 25 to 368 nM (Lannuzel et al., 2014), one to four orders of magnitude higher than typical dAl concentrations measured in Antarctic surface waters (Sanudo-Wilhelmy et al., 2002; Middag et al., 2011; Grand et al., 2015a). Similar to pack ice, fast ice may become a reservoir for dAl through incorporation of seawater dAl during ice formation and via deposition of aerosol dust particles. Fast ice may also incorporate lithogenic particles from sediment resuspension or glacial erosion (de Jong et al., 2013; Lannuzel et al., 2014). Physical breakdown and leaching of particles is thought to lead to subsequent enrichment in dAl concentrations (Lannuzel et al., 2010). Although previous studies in other sectors of the Southern Ocean have concluded that melting of land-fast ice is likely not an important source of dAl far from the ice edge (Middag et al., 2011; Middag et al., 2013), regional circulation patterns in our study area in East Antarctica favor unusually strong northward advection of surface waters and ice away from the continent. Topographic constraints placed on ACC flow by the southern Kerguelen Plateau leads to northwards-flowing currents and strong offshore transport from Antarctica between ~80 and 90°E; model output suggests that this offshore flow has a meridional extent up to 10° north of the ice shelf edge (Rintoul et al., 2008). This local circulation pattern is thought to be responsible for elevated dFe concentrations and anomalously high chlorophyll concentrations in nearsurface waters south of the PF along I09N/I08S compared to the Southern Ocean average (Grand et al., 2015b). The high concentrations of scavenged pAl observed south of the PF most likely originates from local seasonal ice melt and robust advective inputs of dissolved metals from land-fast ice meltwaters or glacial run-off from the Antarctic margin.

Other potential mechanisms of dAl supply such as upwelling or atmospheric deposition of mineral dust are unlikely to be important sources of dAl to surface waters in this region. Concentrations of dAl are extremely low (< 1 nM) throughout the entire upper 1000 m of the water column along IO9N/IO8S south of the PF (Fig. 2) (Grand et al., 2015b), hence, upwelling cannot deliver significant amounts of dAl. Likewise, input of dAl from deposition and partial dissolution of mineral aerosols is unlikely to supply sufficient dAl to the surface ocean to explain the magnitude of the particle-scavenged Al signal observed in this study. Dust deposition estimates for the Indian sector of the Southern Ocean based on atmospheric models, shipboard aerosol collection, and land-based measurements range from ~10 to 240 mg dust m^{-2} yr⁻¹ (Mahowald et al., 2005; Planquette et al., 2007; Wagener et al., 2008; Heimburger et al., 2012; Grand et al., 2015a), which would supply a maximum of only $0.5 \text{ nM} \text{ dAl yr}^{-1}$ to the surface mixed layer using the assumptions outlined in the previous section.

4.2.3. I06S

Along I06S, the region of high surface-ocean pAl (averaging 8.2 M) found between ~50 and 60°S, coincident with high pSi concentrations, is estimated to largely originate from scavenging of dAl (>70%) (Fig. 5). These waters are far from the Antarctic margin (>1000 km) and north of the winter sea ice extent (Parkinson and Cavalieri, 2012). Hence, sedimentary inputs and ice melt are unlikely to be important sources of dAl to surface waters. As in many remote open-ocean waters, dAl is most likely supplied by the deposition and partial dissolution of atmospheric dust.

Concentrations of dAl along IO6S are high in coastal waters and within the Agulhas Return Current, then decrease as the section crosses the subtropical front (Grand et al., 2015c). The southern-most station (48°S) where a full-depth vertical profile was collected, several hundred kilometers to the north of the region of high pAl and pSi, shows a modest surface dAl maximum (2.3 nM) and dAl concentrations of 1.3-1.9 nM in subsurface waters (Fig. S7), suggesting atmospheric input is the dominant source of dAl to the mixed layer in circumpolar waters (Grand et al., 2015c). The lowest dAl values measured along the entire 106S transect are found in the Southern Ocean south of the PF over where 52–58°S surface-ocean dAl concentrations average 0.76 ± 0.16 nM, coincident with the region of high diatom productivity and elevated pAl concentrations (Fig. 6). However, at the northern and southern extent of the high pAl and pSi feature, dAl concentrations up to 5.9 nM were found at several stations over 50-52°S and 59-61°S.

Several important points can be inferred from the surface-ocean dAl distribution along I06S. First, in surface waters just beyond the extent of the diatom bloom where scavenging pressures would be greatly reduced, pAl concentrations are low and dAl concentrations are relatively high, lending support to our conceptual model that the elevated pAl between 50 and 60°S arises primarily from particle scavenging processes. Second, dAl concentrations observed at stations adjacent to the bloom (~6 nM) are on the same order of magnitude as the estimated scavenged portion of pAl concentrations (~5 nM). Transfer of dAl to the particulate phase following seasonal bloom onset would imply that the residence time of this dAl pool is short compared to the multi-year residence time of dAl in surface waters over much of the world ocean (Measures and Vink, 2000). However, this may be a reasonable assumption based on the intense biogenic particle loading that occurs in seasonally productive Southern Ocean surface waters and the high



Fig. 6. Dissolved and particulate Al in surface waters along the CLIVAR I06S section between 45 and 65°S; dissolved Al data from stations north of 48°S have been reported previously in Grand et al. (2015c). Approximate location of fronts from Fig. 1 shown by dashed lines.

scavenging efficiency of diatom frustules. Model representation of Al cycling in the global ocean have proposed residence times as short as < 1 year for dAl in Southern Ocean surface waters centered at ~50°S (Gehlen et al., 2003; van Hulten et al., 2013).

Dust deposition to Southern Ocean surface waters at ~30°E is thought to be primarily from the transport of dust south from South Africa and across the South Atlantic from source regions in South America (Li et al., 2008; Johnson et al., 2011). Model estimates of maximum dust deposition rates are $200-500 \text{ mg m}^{-2} \text{ yr}^{-2}$ for the region over 50-60°S along I06S (Moore et al., 2002; Mahowald et al., 2005; Li et al., 2008). Assuming an Al content of mineral dust of 8.1% (Heimburger et al., 2012) and an aerosol Al solubility of 3.6% (Grand et al., 2015a), this dust flux would deliver 0.4-1.1 nM dAl annually to a surface mixed layer of 50 m. This annual atmospheric input is likely several times smaller than the annual dAl reservoir that would be required to supply observed pAl concentrations primarily through adsorptive scavenging. There are significant uncertainties in some of the above assumptions relating dust flux estimates to resulting surfaceocean dAl concentrations. Studies of aerosol Al solubility have reported a wide range of values (< 1 to 50%) with significant regional variation (Buck et al., 2010, 2013; Witt et al., 2010; Han et al., 2012). In order for model estimates of dust deposition to deliver sufficient dAl to surface waters at 30°E to support the scavenged pAl signal, aerosol Al solubility would need to be on high end of current estimates (25-70%). Although shipboard daily-integrated aerosol samples collected along I06S appear to have low Al solubility (typically < 1%) (P. Morton, personal communication), other researchers have reported up to 92% solubility for Al delivered via wet deposition (i.e., rain events) in the Southern Ocean (Heimburger et al., 2013). Significant underestimation of either the fractional solubility of Al or the relative importance of aerosol delivery via wet deposition is possible. Alternatively, the pAl distributions observed along I06S in this study may indicate that transport and deposition of dust to this region of the Southern Ocean may be greater than currently represented by models.

In contrast to I09N/I08S, there is not a large change in the pAl distribution in surface waters between the STF and the PF where pCa concentrations are elevated (Fig. 4). However, our estimates of scavenged pAl (Fig. 5) suggest that scavenging by biogenic particles contributes to surface-ocean pAl concentrations; scavenged pAl jumps from < 0% to > 50% at the STF. The comparatively small change in pAl concentrations is a function of the very small pool of total Al in this region (Fig. 6).

4.3. Lateral transport of pAl and pFe from sediment sources along IO9N/ I08S

Subsurface concentrations of pFe and pAl in the Southern Ocean along I09N/I08S are primarily controlled by resuspension of lithogenic material over the Antarctic shelf and by lateral transport of Fe-rich particles likely sourced from the Kerguelen archipelago. Stations south of 64°S, closest to the Antarctic margin, show maximum pAl and pFe of 23.4 nM and 10.7 nM, respectively, at depths of 150–300 m (Fig. 2). The average Fe:Al of samples at depths > 100 m near the shelf is 0.38 ± 0.07 (n = 24), similar to the composition of moraine and shelf sediments in the Indian sector (0.28–0.35) (Lannuzel et al., 2014 and references therein), indicating the likely lithogenic origin of this particle signal. Concentrations of shelf-derived pAl and pFe decrease with increasing distance from the continent and appear to be restricted to within ~200 km of the shelf in the top 1000 m.

Below 400 m at stations between ~45 and 55°S, and in deepest samples (> 900 m) more broadly between 40 and 60°S, elevated pFe concentrations up to 1.0 nM are observed, with average concentrations of 0.53 + 0.20 nM compared to average background subsurface pFe concentrations of 0.23 + 0.12 nM. To the west of the I09N/I08S transect, the ACC interacts with the topography of the Kerguelen archipelago, resulting in ACC flow around the islands and over shallow plateau features (Park et al., 2008). Persistently elevated primary productivity downstream of the Kerguelen Plateau has been attributed to natural iron fertilization from ACC waters enriched in Fe from contact with Kerguelen and Heard Islands and shallow plateau sediments (Blain et al., 2008). The supply of Fe from the Kerguelen archipelago to downstream waters is dominated by particulate phases, attributed to lateral transport of pFe from resuspension of shelf sediments (Chever et al., 2010) and from glacial and fluvial inputs (van der Merwe et al., 2015). In particular, the pFe supplied by glacial outflow is thought to be a highly labile and potentially important source of bioavailable Fe in polar oceans (Poulton and Raiswell, 2005; Hawkings et al., 2014). The small size of Fe-rich particles in glacial meltwater is thought to result in sufficiently long particle residence times in the upper water column for pFe to be transported the ~1500 km eastward from Kerguelen to the I09N/I08S section (van der Merwe et al., 2015). The Fe:Al ratio of suspended particulate matter samples in the region of subsurface pFe enrichment is 0.26 ± 0.08 (n = 26, depths > 400 m 45–55°S), which is lower than Fe:Al ratios that have been reported for particulate matter waters over the plateau and at stations within 300 km of the Kerguelen Islands at ~72°E (0.53–0.86 Fe:Al) (van der Merwe et al., 2015). Highly reactive authigenic Fe oxyhydroxide nanoparticles formed during weathering processes are the likely source of this Fe enrichment (Raiswell, 2011), resulting in a supply of labile Fe, but not Al, over time. Hence, dissolution of Fe from particles during long-range transport eastward in the ACC could be responsible for gradual depletion of Fe in particulate matter with increasing distance from Kerguelen sources, a process thought to be important in supplying new Fe to sustain elevated primary productivity in the vicinity of Kerguelen (Bowie et al., 2014). Leaching of labile Fe would contribute to the elevated dFe concentrations also observed along I09N/I08S downstream of Kerguelen (Grand et al., 2015b).

5. Conclusions

The particulate trace element distributions along I09N/I08S and I06S illustrate the potential sensitivity of Al to particle scavenging pressures. Particle scavenging plays an important role in interpreting dAl inventories in steady-state models of dust deposition that deliver major and micro-nutrients to the open ocean. Where high biogenic particle loads appear to exert strong scavenging pressures, residence times for dAl in the surface ocean are likely much lower than the global average. Currently, model attempts to capture the spatial variability in scavenging rates parameterize particle pressures using distributions of

biogenic silica (Gehlen et al., 2003; van Hulten et al., 2012) due to our understanding of the high affinity of diatom frustules for dAl adsorption. However, as regions along I06S, and especially I09N/I08S, within the "Great Calcite Belt" demonstrate, biogenic CaCO₃ appears to also be an important substrate for scavenging of dAl in the surface ocean, which may alter our understanding of ocean regions where this process is important to evaluate. Low dAl inventories in regions where scavenging rates are high can lead to underestimation of dust fluxes when using surface ocean measurements to ground-truth atmospheric transport models, such as suspected for remote open-ocean waters along I06S.

This work also demonstrates that the potential fraction of scavenged pAl can be important to consider when estimating lithogenic particle distributions. Scavenged Al will introduce uncertainty into the use of these distributions in calculations to remove the lithogenic component and isolate an authigenic or biogenic fraction of other elements of interest (e.g., Planquette et al., 2013; Ellwood et al., 2014), or to estimate scavenging of other geochemical tracers onto lithogenic particles (e.g., Hayes et al., 2015; Lamborg et al., 2016). While in many ocean regimes, pAl distributions are clearly shown to be controlled by lithogenic particle inputs (e.g., Barrett et al., 2012; Ohnemus and Lam, 2015), the pAl distributions along IO9N/IO8S and IO6S underscore the dramatic impact that scavenging can have in producing unexpectedly high surface-ocean pAl concentrations in regions far from lithogenic particle sources; emphasizing the need to better constrain this process and its relevance to the interpretation of other trace element distributions.

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Appendix A. Supplementary data

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