A high resolution transect of dissolved barium in the Southern Ocean

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[1] The dissolved Barium (Ba_d) distribution in the whole water column was examined along the WOCE SR3 line in the Southern Ocean (Australian sector, late winter-spring 2001). The high sampling resolution offered an excellent opportunity to relate the Ba_d distribution to frontal structures and the water masses. Such a high resolution was not achieved in previous Southern Ocean studies and showed the tight overprinting of the frontal zones by Ba_d gradients. Hydrodynamic control on Ba_d is evident in the case of Antarctic Bottom Water formation, westward flow of Tasman Sea waters and return flow of an eddy of the SubAntarctic Front. However biogeochemical processes are also acting, as witnessed by enhanced Ba_d contents in deep waters of the SubAntarctic Front zone and by a local mesopelagic minimum in the Inter Polar Front Zone. These features are respectively ascribed to the dissolution of Ba-rich phases and Ba transfer from solution to particles. *INDEX TERMS:* 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4808 Oceanography: Biological and Chemical: Chemical tracers; 4825 Oceanography: Biological and Chemical: Geochemistry. **Citation:** Jacquet, S. H. M., F. Dehairs, and S. Rintoul (2004), A high resolution transect of dissolved barium in the Southern Ocean, *Geophys. Res. Lett.*, *31*, L14301, doi:10.1029/2004GL020016.

1. Introduction

[2] Studies of the global ocean have shown that dissolved Barium (Ba_d) behaves as a bio-intermediate element showing lowered concentrations in surface waters without, however, reaching depletion [*Chan et al.*, 1977; *Östlund et al.*, 1987; *Jeandel et al.*, 1996]. This distribution largely results from the formation of micro-crystalline barite ($BaSO_4$) in the upper water column and its dissolution at depth, but the exact mechanism of this process remains debated [*Dehairs et al.*, 1980; *Stroobants et al.*, 1991; *Bertram and Cowen*, 1997; *Ganeshram et al.*, 2003; *Bernstein and Byrne*, 2004]. Results support the idea that biogenic microenvironments provide the necessary thermodynamic conditions for barite precipitation via biogeochemical Ba subtraction in a World Ocean mostly undersaturated for $BaSO_4$ [*Monnin et al.*, 1999; *Rushdi et al.*, 2000]. Observed correlations between surface water productivities and barite fluxes in deep-sea and sediments has led to the recognition of Ba being a powerful proxy of past export production [*Paytan et al.*, 1996].

[3] Zonal coverage of Ba_d data in the Southern Ocean is still limited today, especially for the major frontal systems through which strong physico-chemical gradients occur and which are well known to sustain enhanced biological activity and trophic gradients [*Arrigo et al.*, 1998; *Moore et al.*, 1999]. This situation renders the Southern Ocean a suitable site to investigate the different processes controlling the Ba_d distribution. In other systems such as the Arctic basin, conservative mixing clearly appears to be the main control on Ba_d distribution [*Taylor et al.*, 2003]. The high sampling resolution along WOCE SR3 line in the Australian sector of the Southern Ocean, achieved during the CLIVAR-SR3 cruise, offered a unique opportunity to compare the Ba_d distribution in a late winter-spring situation with frontal structures and characteristics of the water masses present and to shed more light on the relative importance of physico-chemical versus biogeochemical controls.

2. Sampling and Analysis

[4] The whole water column was sampled at 53 stations separated by ~½ degree of latitude, along the 140–142°E meridian (43–68°S) in the Australian sector of the Southern Ocean (CLIVAR SR3 cruise, AU0103, Oct. 29–Dec. 11 2001, R/V *Aurora Australis*). The water column was sampled at 12 to 24 depths depending on bathymetry. On board, 15 ml of water was collected in polyethylene vials that were rinsed thrice with the seawater. Unfiltered samples were acidified with concentrated Suprapur HCl (20 μl) and stored at room temperature till analysis.

[5] The analytical protocol for Ba_d was as described in the work of S. H. M. Jacquet et al. (Barium distribution across the Southern Ocean Frontal System in the Crozet-Kerguelen Basin, submitted to *Marine Chemistry*, 2004, hereinafter referred to as Jacquet et al., submitted manuscript, 2004). Briefly, Ba_d was measured using an isotope dilution inductively coupled plasma quadrupole mass spectrometry method (ID-ICP-MS) as described by *Klinkhammer and Chan* [1990] and *Freydier et al.* [1995]. This method was adapted for application on a VG Plasma-Quad 2+ instrument by adding Neodymium as internal standard to correct for mass bias [*Navez et al.*, 1999]. Reproducibility of our method is ±1.2% (1sd).

3. Results and Discussion

[6] Definitions and positions of zones and fronts discussed here (Figures 1 and 2) are mainly based on potential temperature (θ) and salinity (S) characteristics, as discussed by *Sokolov and Rintoul* [2002] and *Rintoul and Bullister* [1999]. Nutrient conditions encountered during the

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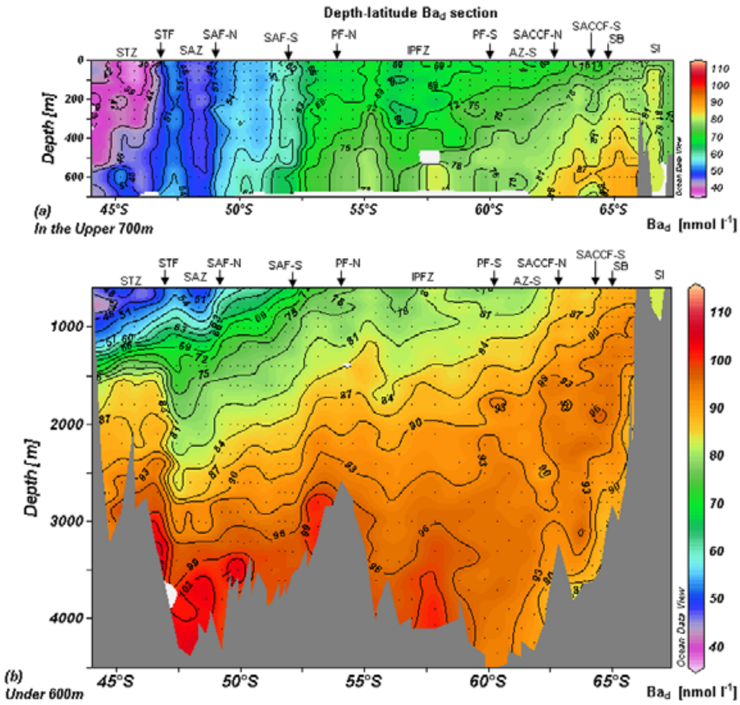

Figure 1. High resolution whole water column Ba_d distribution (nmol l^{-1}) along SR3 transect from Tasmania to Antarctica (October–November 2001); (a) in the upper 700 m and (b) between 600 m and seafloor. Position of fronts and zones are as given by *Sokolov and Rintoul* [2002]. STZ = the Subtropical Zone, STF = the Subtropical Front, SAZ = the SubAntarctic Zone, SAF-N and SAF-S = the SubAntarctic Front northern and southern branches, PFZ = the Polar Front Zone, PF-N and PF-S = the Polar Front northern and southern branches, IPFZ = InterPolar Front Zone, AZ-S = the southern Antarctic Zone, SACCF = the Southern Antarctic Circumpolar Current Front, SB = the Southern Boundary and SI = the zone under Sea Ice influence. Figure elaborated using Ocean data view: Schlitzer R., Ocean Data View, http://www.awi-Bremerhaven.de/GEO/ODV, 2003.

cruise were rather typical of the area and season [*Trull et al.*, 2001]. Sampled zones and fronts were from north to south: the Subtropical Zone (STZ), the Subtropical Front (STF), the SubAntarctic Zone (SAZ), the SubAntarctic Front (SAF, northern and southern branch), the Polar Front Zone (PFZ), the Polar Front (northern and southern branch, with the InterPolar Front Zone (IPFZ) between the two branches), the southern Antarctic Zone (AZ-S), the Southern Antarctic Circumpolar Current Front (SACCF, northern and southern branch), the Southern Boundary (SB) and the zone under Sea Ice influence (SI).

[7] The observed vertical and latitudinal Ba_d variations are consistent with those observed elsewhere in the Southern Ocean [*Chan et al.*, 1977; *Östlund et al.*, 1987; *Jeandel et al.*, 1996; Jacquet et al., submitted manuscript, 2004]. Figure 1 shows the Ba_d distribution along the CLIVAR-SR3 transect. The general picture for the upper 1000 m shows a Ba_d increase from north to south, similar to what is commonly observed for nutrients. This general latitudinal pattern is overprinted by sharp gradients of Ba_d, coinciding with the different frontal structures. From north to south the following features are observed (Figures 1a and 2): (1) The STZ surface waters at 45°S present low Ba contents (<45 nmol l^{-1}), with a minimum of 35 nmol l^{-1}. Water properties and altimeter maps (not shown) indicate the section crossed an eddy of subtropical Tasman Sea water between 45°S and 47°S. The STF (corresponding to a

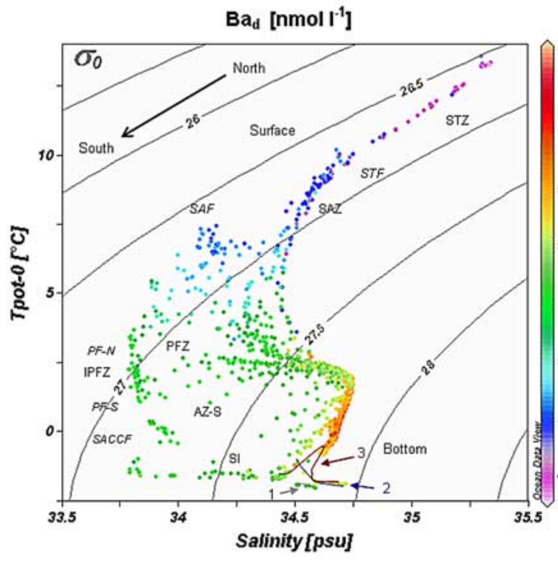

Figure 2. θ-S diagram superposed with Ba_d concentration ranges (nmol l^{-1}). STZ, STF, SAZ, SAF, PFZ (PF-N, -S), IPFZ, AZ-S, SACCF, SI: as in Figure 1. Arrows 1, 2 and 3 represent stations on the Antarctic shelf discussed in paragraph [9]. Figure elaborated using Ocean data view: Schlitzer R., Ocean Data View, http://www.awi-Bremerhaven.de/GEO/ODV, 2003.

drop in temperature from 11 to 9.5°C and salinity >35.0 to <34.8 from north to south in the upper 300 m) is located at 47°S at the southern edge of the eddy. The STF coincides with a Ba_d gradient from ~48 to 54 nmol l^{-1} in the upper 400 m; (2) At 47°S, just south of the STF, Ba_d values are locally quite high (reaching up to 54 nmol l^{-1} in the upper 600 m), similar to values found further south, between the northern and southern branch of the SAF. Water properties and altimetry (not shown) suggest that this water mass coincides with a cold-core eddy pinched off from the SAF. The juxtaposition of these two eddies results in a very strong Ba_d front between the subtropical waters to the north and the SAF waters to the south. South of the cold-core eddy and north of the SAF, a relatively homogeneous water mass, the Subantarctic Mode Water (SAMW), is found between the surface and 700 m depth. Ba_d content in the SAMW is between 45 and 49 nmol l^{-1}, higher than the subtropical waters but lower than values found in the SAF and the eddy spawned from the SAF, resulting in a local minimum between 48 and 49°S. Between 49 and 49.3°S a surface water Ba_d gradient from ~47 to 53 nmol l^{-1} coincides with the position of the northern branch of the SAF (SAF-N). Here, steep Ba_d isolines extend beyond 600 m in the water column and this is observed also for the other water mass properties. The southern branch of the SAF (SAF-S) is located between ~51.5 and 52°S and coincides with a slightly weaker Ba_d gradient from 60 to 63 nmol l^{-1}; (3) The Polar Front, which marks the northern limit of the Antarctic Zone, is also composed of two branches, the PF-North and the PF-South. Taking the northern most extent of the 2°C water in the temperature minimum as the subsurface expression of the northern branch of the Polar Front, positions the latter at ~54°S. The southern-most extent of the temperature maximum waters warmer than 2.2°C sets the PF-S at ~60°S. Besides small Ba_d gradients through the PF-N (~68 to 69 nmol l^{-1}) and the PF-S (71 to 72 nmol l^{-1}), no peculiar feature in the Ba_d distribution coincides with the position of the PF. Interestingly, the upper 300 to 400 m in the IPFZ (~54 to 60°S) between the PF-N and PF-S, is relatively homogenous in Ba_d (69 to 70 nmol l^{-1}) as it also is for salinity, except for four stations between 55.9 and 57.8°S where slightly lower Ba_d concentrations are observed in the upper 300 m (between ~65 and 67 nmol l^{-1}). The fact that the same Ba_d section plotted versus neutral density instead of depth (not shown) also presents the anomaly indicates that the feature is not associated with differences in water column stratification. It is possible we witness the effect of enhanced translocations of Ba from the dissolved to the particulate phase. This fits also with the observation of higher particulate Ba concentrations in the mesopelagic waters at ~57°S [*Savoye et al.*, 2004; D. Cardinal et al., Variations of carbon remineralisation in the Southern Ocean illustrated by the Ba_{xs} proxy, submitted to *Deep Sea Research*, *Part I*, 2004]; (4) The AZ-S is delineated to the south by the SACCF, also characterized by a northern and southern branch, the positions of which are set by the southernmost extension of θ maximum water warmer than 2°C (~62.4°S) and 1.8°C (at 64.2°S), respectively. Surface concentrations in the AZ-S range between 70 and 72 nmol l^{-1}. In surface waters the northern branch is not associated with peculiar Ba_d features whereas the southern branch shows slightly lower Ba_d concentrations in the upper 1000 m, reflecting the transition between the two branches of the SACCF and the SB (Southern Boundary). Surface waters at the SB of the ACC (set by the southernmost extension of the O_2 minimum waters) and in the Seasonal Ice Zone (SI) south of the SB, have Ba_d contents >75 nmol l^{-1}, reaching a maximum of 78 nmol l^{-1}. The situation over the Antarctic shelf is discussed later.

[8] Concerning the deeper (>1000 m) water column (Figures 1b and 2), major features are: (1) North of 45.5°S, deep waters between the Tasmanian shelf and the South Tasman Rise show significant build-up of Ba resulting in quite strong surface to deep Ba_d gradients. The space between Tasmania and the SAZ is occupied by a westward flowing poorly ventilated (low CFC), warm, salty and O_2 poor water coming from the Tasman Sea [*Rintoul and Bullister*, 1999]. The long residence time of these deep waters from the Tasman Sea could give rise to a build-up of Ba_d from the dissolution of barite and other Ba-rich particles in these undersaturated waters [*Monnin et al.*, 1999; *Rushdi et al.*, 2000]; (2) At ~45.5°S near the top of the South Tasman Rise, lower Ba_d values probably reflect the Tasman Sea origin of the subtropical eddy; (3) The upper ocean Ba_d gradients coinciding with the positions of STF, SAF-N and SAF-S reach very deep and clearly extend over most of the water column; between STF and SAF-N (~49°S) a wedge of relatively low Ba_d extends between ~1000 and 3000 m, a feature that is also observed for other physico-chemical characteristics and remains visible in a Ba_d vs. neutral density transect plot; (4) Between 47.5 and 53°S bottom waters reach the highest Ba_d values observed along the whole transect (between 100 and 115 nmol l^{-1}). This could reflect dissolution of Ba-rich phases such as barite in the under-saturated deep Southern Ocean waters [*Monnin et al.*, 1999; *Rushdi et al.*, 2000]. However, since deep waters (>2000 m) over the whole latitudinal extent of the Southern Ocean basin are reported to be under-saturated for barite [*Monnin et al.*, 1999], the high bottom water concentrations at 47.5–50°S probably also reflect higher export of Ba-rich particles to the seafloor at these latitudes. This is corroborated by sediment trap flux data showing higher Ba fluxes in the deep water column at 47–51°S (traps between 1000 and 3300 m) compared to 54°S (traps between 800 and 1500 m), generally following a north – south decrease in this latitudinal depth ranges [*Cardinal et al.*, 2001; *Savoye et al.*, 2004]. It is also possible that the high Ba concentrations are due to epibenthic fluxes of Ba, in which case as well they would reflect a larger flux or rain rate of Ba-rich particles to the sea floor in the SAZ region; (5) The presence of the ridge between 52.5 and 55°S clearly affects the deep Ba_d distribution showing a sharp Ba_d gradient on its northern side, coinciding with the position of the SAF-S; (6) Bottom waters in the vicinity of the Antarctic margin, south of 63°S, show decreased Ba_d concentrations. These bottom waters have lower temperatures, increased O_2 and CFC contents (M. Warner, personal communication, 2003) and reflect the sinking of dense waters over the Antarctic shelf and along the margin, forming Antarctic Bottom Water (AABW). When comparing these bottom waters with waters at 100 m having similar CFC contents (i.e., comparing water masses of same origin and age), we observe for Ba_d a slight enrichment in bottom water. Again, this may indicate release

of Ba from settling Ba-enriched particles such as barite, as discussed above.

[9] We now focus on the Antarctic shelf. Most waters here spread along the freezing line (−1.8°C; see Figure 2). The southernmost station (67.15°S; see 1 on Figure 2) is homogenous in Ba_d content with concentrations not exceeding 76 nmol l^{-1}. The profile at 66.59°S in the central part of the shelf (see 2 on Figure 2) contrasts sharply, showing much higher Ba_d values (>83 nmol l^{-1}) with deep and bottom waters on the freezing line. The origin of the waters at this shelf station is likely Circumpolar Deep Water upwelling at the Antarctic Divergence (SB) and (occasionally) spilling over on the shelf, a process recognized as essential to the formation of Antarctic Bottom Water [e.g., *Orsi et al.*, 1999]. This explanation is supported by the physico-chemical characteristics (θ; Salinity; O_2; CFC's; nutrients and Ba_d) of the CDW waters at station at 66°S (see 3 in Figure 2) which are similar to the characteristics both at 66.59 and 67.15°S on the shelf.

[10] The present paper brings information on the Ba_d distribution in the Australian sector of the Southern Ocean along the WOCE SR3 line (140–142°E) during spring 2001. Our results reveal a situation where the Ba_d distribution appears mainly driven by hydrodynamics, while regionally enhanced Ba_d contents in the deep ocean north of the mid-ocean ridge, could reflect the combined effect of a higher particulate Ba flux towards undersaturated deep waters and poorer ventilation of some of these deep basins. Future work will focus on the sensitivity of Ba_d to the onset of the phytoplankton growth season along this same WOCE SR3 line (S. H. Jacquet et al., Dynamics of barium in the Southern Ocean, manuscript in preparation, 2004) with the aim to deconvolve conservative and non-conservative behavior of Ba. It is expected that this will contribute to a better understanding of the dynamics of dissolved and particulate Ba and so to better constrain this proxy.

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