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## Distribution of barium in the Weddell Gyre: Impact of circulation and biogeochemical processes

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## Abstract

1 The Southern Ocean data base of dissolved barium ( $Ba_d$ ) has been augmented significantly  
2 with two sections across the Weddell Gyre sampled by the icebreaker FS Polarstern during  
3 February and March 2005.  $Ba_d$  was found to be relatively high in the surface layer as  
4 compared to the adjacent waters north (Antarctic Circumpolar Current) and east (Antarctic  
5 Zone of the Indian sector). Compared to the inflowing water into the Weddell Gyre and also  
6 to the surface water, the deep water is characterized by a  $Ba_d$  enrichment. We identified sea-  
7 ice formation as a further process, besides well-known biogeochemical processes, that leads  
8 to the extraction of Ba from solution via barite ( $BaSO_4$ ) precipitation. The particles rain down  
9 the water column and redissolve in deeper water where undersaturation of barite is prevalent.  
10 In the bottom layer, an enhanced enrichment of  $Ba_d$  occurs, exhibited as a  $Ba_d$  maximum,  
11 which is caused by Ba efflux from the sediments. In recently formed Weddell Sea Bottom  
12 Water, though, a  $Ba_d$  minimum is observed, imposed by the shelf water component of bottom  
13 water, which has relatively low  $Ba_d$  concentration. Like in other Southern Ocean regions, all  
14 through the water column a strong correlation exists between  $Ba_d$  and dissolved silicate,  
15 although the relationship is different from that in the Antarctic regions to the east. The  
16 Weddell Gyre appears to be a source of  $Ba_d$  to the deep and abyssal world oceans via  
17 Antarctic Bottom Water export. The aforementioned mechanism of barite precipitation  
18 accompanying sea ice formation and subsequent redissolution in the deep Weddell is a main  
19 factor in this.

## Introduction

20 The distribution of barium (Ba) in the ocean is not only controlled by water mass mixing but  
21 also by biologically-mediated uptake followed by dissolution (Chan et al., 1977; Jeandel et al.  
22 1996). These conditions impose that Ba be categorized as a bio-intermediate element. This fits  
23 ~~in~~ the picture that higher biomass and productivity in the upper mixed layer usually coincide  
24 with higher Ba concentrations in suspended matter (e.g., Cardinal et al., 2005; Jacquet et al.,  
25 2007a). Most of this upper mixed layer particulate, non-lithogenic Ba is not yet in the form of  
26 the compound barite, but rather consists of Ba absorbed by or adsorbed on planktonic material  
27 (Cardinal et al., 2005; Jacquet et al. 2007b, 2008a). Apart from Fresnel et al. (1979), we are  
28 not aware of any other study reporting the presence of barite in living marine phytoplankton.  
29 However, freshwater and marine benthic microbial organisms have been reported to be  
30 associated with barite (e.g., Hopwood et al., 1997; Bertram and Cowen, 1997). For the water

1 column underneath the surface mixed layer it is well established that barite is the major carrier  
2 of Ba in suspended matter (Dehairs et al., 1980; Jacquet et al., 2007b; Stroobants et al., 1991).  
3 Barite formation has been demonstrated to be associated with degradation of phytoplankton  
4 material (Ganeshram et al., 2003). This process occurs essentially below the mixed layer in  
5 the mesopelagic zone (100-1000 m) within aggregates of decomposing organic detritus  
6 (Cardinal et al., 2005; Dehairs et al., 1980, 1990; Stroobants et al., 1991). These subsurface  
7 particulate Ba-barite stocks were observed to be correlated with oxygen consumption rates  
8 (Dehairs et al., 1997) and more recently evidence was found that mesopelagic excess Ba, or  
9 barite is correlated with subsurface bacterial activity (Dehairs et al., 2008; Jacquet et al.,  
10 2008a).

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20 The present study explores the distribution of dissolved Ba and silicate in the water column of  
21 the Weddell Gyre, an area for which there is a dearth of data on Ba, despite its importance in  
22 terms of formation of ventilated deep and bottom water, upwelling and sea-ice formation.  
23 Earlier data for the Weddell region were obtained during the GEOSECS project but they  
24 consist only of few full-depth profiles and some surface plus bottom water only data (Chan et  
25 al., 1977; Östlund et al., 1987). Expedition ANT-XXII/3 in 2005 offered the possibility to  
26 investigate Ba along the Prime Meridian and at a section across the Weddell basin (Fig. 1),  
27 thereby significantly expanding the Southern Ocean data set which thus far consists of  
28 sections along 30°E (WOCE I6; Dehairs et al., unpublished results) and 145°E (WOCE SR3;  
29 Jacquet et al., 2004).

## 30 31 32 33 34 35 36 37 38 39 40 **Material and methods**

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43 Data were collected (Fig. 1) during FS Polarstern cruise ANT-XXII/3 from Cape Town, South  
44 Africa to Punta Arenas, Chile, 22 January to 6 April 2005 (Fahrbach, 2006). Water was  
45 sampled with the rosette sampler coupled to the CTD instrument (conductivity temperature  
46 depth; SBE911plus) all through the water column, with a bias to the upper 1000 m.  
47 Temperature and salinity were measured with a precision of 0.001°C and 0.002, respectively  
48 (Fahrbach, 2006).

### 49 50 51 52 53 54 55 56 *Dissolved barium*

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58 Volumes of 15 ml of unfiltered seawater were sampled in polypropylene vials (Nalgene),  
59 which were rinsed three times with the sample seawater. Samples were acidified with 15 µl  
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HCl (Merck Suprapur) and stored at room temperature until analysis in the home laboratory. No filtration of the seawater was attempted based on the well documented knowledge that dissolved Ba represents in general a very large fraction (> 99%) of total Ba. In productive surface mixed layers this may be different but also here particulate Ba is usually <3% of total Ba (see e.g., Jacquet et al., 2007a; 2008). Dissolved Ba was measured using an isotope dilution method described below; in fact it constitutes dissolvable Ba, consisting of dissolved Ba plus a very small fraction (generally <1% of total Ba) that is generated from the particulate Ba pool as a result of the acidification. For the sake of simplicity we prefer to use the term dissolved Ba in this manuscript. Sample preparation is as follows: 1 g of seawater is spiked with 0.7 g of <sup>135</sup>Ba-spike solution yielding a <sup>138</sup>Ba/<sup>135</sup>Ba ratio between 0.7 and 1 to minimize error propagation (Webster, 1960; Klinkenberg et al., 1996). Subsequently the sample is diluted with Milli-Q grade water to a final weight of 30 g. Blanks consist of acidified (nitric acid) Milli-Q water. Quantities of sample, spike and dilution water were accurately assessed by weighing. Isotope ratios were measured with a SF-ICP-MS (Element 2 Thermo Finnigan). Reproducibility of our method is ± 1.5% (RSD) as tested on repeat preparations of reference solutions. Average Ba values obtained for reference waters SLRS-3 and an in-house standard (a Mediterranean Sea standard prepared by C. Jeandel) were 13.48 ± 0.21 µg l<sup>-1</sup> (1σ) with RSD of 1.55% and 10.49 ± 0.29 µg l<sup>-1</sup> (1σ) with RSD of 2.75%, respectively, which is in good agreement with certified values (SLRS-3: 13.4 ± 0.6 µg l<sup>-1</sup> and OMP: 10.4 ± 0.2 µg l<sup>-1</sup>). Overall precision (including sampling precision) based on 6 dissolved Ba profiles sampled in a hydrographically stable environment is ± 0.3 µg l<sup>-1</sup> (1σ) with an RSD of 5% (Dehairs et al., 2008; Jacquet, 2007); for further details we refer to the latter two studies. Ba<sub>d</sub> concentrations are expressed in nmol kg<sup>-1</sup>.

### *Silicate*

Nutrients were measured on board with a Technicon TRAACS 800 rapid flow autoanalyzer (see also Fahrbach, 2006) by the Royal Netherlands Institute for Sea Research (NIOZ, Texel). Accuracy was determined using stock standards diluted in low-nutrient sea water, as prepared in the home lab by weighing. The precision for silicate was estimated to be 0.66 µmol l<sup>-1</sup> at two calibration stations, where all 24 rosette bottles were fired at the same depth. Part of the surface layer nutrient data of this cruise have also been reported by Hoppema et al. (2007). Silicate (or silicic acid) concentrations are expressed in µmol kg<sup>-1</sup>.

### *BaSO<sub>4</sub> saturation index calculation*

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2 The barite saturation index (SI) is defined as the ratio of the ionic product of barium sulfate  
3 (Q) to the solubility product of barite ( $K_{sp}$ )  
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$$7 \quad SI = \frac{Q}{K_{sp}} = \frac{m_{Ba(aq)} \cdot m_{SO_4(aq)} \cdot \gamma_{BaSO_4(aq)}^2}{K_{sp}} \quad (1)$$

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14 in which m is the measured concentration (molality) and  $\gamma$  the activity coefficient of aqueous  
15 barium sulfate. Monnin (1999) has developed a model of the Na-K-Ca-Mg-Sr-Ba-Cl-SO<sub>4</sub>-  
16 H<sub>2</sub>O system that allows the calculation of the solubility and saturation indices of some  
17 minerals, including barite, as a function of the solution composition, temperature (up to  
18 200°C) and pressure (up to 1 kbar). It has been used to investigate the saturation state of the  
19 ocean with respect to pure barite (Monnin et al., 1999) and Sr-substituted barites (Monnin and  
20 Cividini, 2006). The criterion for equilibrium retained in these studies is a saturation index  
21 between 0.9 and 1.1, which has been inferred from an evaluation of the mean accuracy of the  
22 solubility calculations during model development (Monnin, 1999). The measured quantities  
23 used are dissolved barium molarity, salinity, pressure and potential temperature. The  
24 concentrations of Na, K, Ca, Mg, Ba, Cl, SO<sub>4</sub> and Cl are calculated from the measured  
25 salinity and the composition of standard seawater of salinity 35 using:  
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$$43 \quad c_i(S) = c_i(35) \times \frac{S}{35} \quad (2)$$

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50 with  $c_i(S)$  the concentration (molarity) of the  $i^{\text{th}}$  element for the sample with salinity S. The  
51 Na concentration is calculated from the electroneutrality condition. Molarities are converted  
52 to molalities using the VOLUMETRIC\_PROPERTIES (VOPO) code (Monnin 1994). The  
53 thermodynamic model then calculates the stoichiometric BaSO<sub>4</sub>(aq) activity coefficient, the  
54 barite solubility product and the barite saturation index at the given temperature and  
55 pressure.  
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## Hydrographic background

The region of investigation is situated in the Antarctic Zone, i.e. south of the Polar Front. The boundary between the Antarctic Circumpolar Current (ACC) and the Weddell Gyre can be identified at about 56°S on the Prime Meridian (Klatt et al., 2005). Thus the majority of data stem from the Weddell regime. North of 56°S the potential temperature maximum of the Upper Circumpolar Deep Water (UCDW) can be distinguished, centered at 500-600 m (Fig. 2). Circumpolar Deep Water (CDW) characterized by a maximum in the potential temperature ( $\theta$ ) is transferred into the Weddell Gyre near its eastern end. We observed the temperature maximum at 64-69°S in 150-400 m depth reaching 0.8-1°C (Fig. 2); this coincides essentially with the westward flowing southern limb of the Weddell Gyre – note that the  $\theta$  maximum layer is interrupted near 66°S by a lower  $\theta$  maximum around the undersea mountain Maud Rise. At the northern part (56-63.5°S) of the Prime Meridian section, constituting the northern limb of the gyre with generally eastward flow, a  $\theta$  maximum was observed as well, but it reaches only about 0.5°C (Fig. 2). This is CDW which has been modified by mixing with waters above and below during its course through the Weddell Gyre. The  $\theta$  maximum layer is separated from the base of the surface layer (identified by a temperature minimum) by a sharp pycnocline. In the upper part of the surface layer, temperatures were often >1.0 °C, but in the coastal region it was significantly colder. These are summer temperatures; in winter the entire surface layer is at or close to the freezing point of about -1.85°C. Note that the surface layer is deeper in the coastal zone than elsewhere in the basin. The Weddell Gyre is a divergent feature with upwelling of deep water, mainly more or less modified CDW; the surface layer is eventually generated from this upwelled water. In the deep Weddell basin,  $\theta$  decreases monotonically from the  $\theta$  max to a minimum at the sea floor. Weddell Sea Bottom Water (WSBW) is present along the section, being defined by  $\theta < -0.7^\circ\text{C}$ . Between the lower boundary of the CDW at 0°C and the WSBW, the most voluminous water mass of the Weddell Gyre is found, the Weddell Sea Deep Water (WSDW). It is replenished by upward mixing of WSBW with CDW, by local water mass formation processes (Orsi et al., 1993), but also by advective transport from the east (Meredith et al. 2000; Hoppema et al., 2001).

## Results

The most conspicuous feature in the  $Ba_d$  distribution is the difference between the upper 500-1000 m and the deep basin (Fig. 3), which is similar to the  $\theta$  distribution (Fig. 2).

1 Concentrations below about 500-1000 m are mainly ranging between 90 and 105 nmol kg<sup>-1</sup>,  
2 which appears to be the background level of Ba<sub>d</sub> of the deep Weddell-Enderby basin. At the  
3 Prime Meridian, Ba<sub>d</sub> concentrations in the deep basin (>1000 m) appear to be highest in the  
4 central part (Fig. 3A), reaching up to 107 nmol kg<sup>-1</sup> between 2000 and 3000 m at 61.5°S.  
5 Over the seamount Maud Rise (65-66°S) and over the northernmost part of the Weddell Gyre  
6 (56-58°S) deep and bottom water Ba<sub>d</sub> concentrations are the lowest. Further south, between  
7 Maud Rise and the Antarctic margin (67-68°S), Ba<sub>d</sub> in the bottom layer is again slightly  
8 higher (up to 100 nmol kg<sup>-1</sup>). In the deep Weddell Sea (Fig. 3B; below 1000 m) the Ba<sub>d</sub>  
9 concentration range is 84-104 nmol kg<sup>-1</sup>, with lowest values in the western part (in the vicinity  
10 of the peninsula margin) and highest in the eastern part of the Weddell transect.  
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20 The deep waters (i.e. below 200 m in the central part of the section and below 600 m toward  
21 the western and the eastern margins of the basin) are separated from an upper layer which has  
22 concentrations < 90 nmol kg<sup>-1</sup>, largely coinciding with the surface mixed layer. Since surface  
23 waters of the Weddell Gyre are eventually formed from upwelled deep water, the lower Ba<sub>d</sub>  
24 contents in surface waters must be the result of non-conservative processes which cause a  
25 partial depletion of Ba<sub>d</sub>. Between 58° and 65°S at the Prime Meridian, the Ba<sub>d</sub> isolines in the  
26 upper 500-1000 m exhibit an upward hump, typical of the divergent Weddell Gyre with  
27 westward flow in the south and eastward flow in the north, and which is also seen in the  
28 distributions of other parameters like  $\theta$  (Fig. 2) and silicate (see below). As a consequence of  
29 this, the vertical extent of the Ba<sub>d</sub> depleted upper layer is zonally variable, being larger near  
30 the northern and southern boundaries of the section. North of 56°S, i.e. outside the Weddell  
31 Gyre, the Ba<sub>d</sub> depletion zone appears to overlap with the  $\theta$  maximum core of the UCDW (Fig.  
32 2). As UCDW waters were reported to contain less Ba<sub>d</sub> than the deep waters of the Antarctic  
33 Zone (Jacquet et al., 2004; Jeandel et al., 1996), this hints that the low Ba<sub>d</sub> in the upper water  
34 column of the Weddell Gyre could at least partly result from advection of CDW into the  
35 Weddell Basin via the westward flowing southern limb of the gyre. It should be appreciated  
36 that the front between the ACC and the Weddell Gyre at 56°S also constitutes a divide  
37 between the near-surface water with lower Ba<sub>d</sub> to the north and waters with higher Ba<sub>d</sub> to the  
38 south. In the coastal current at the southern end of the Prime Meridian the mixed layer is deep  
39 because of convection, mixing and downwelling (see also  $\theta$  distribution; Fig. 2) which leads  
40 also to a deeper penetration of low Ba<sub>d</sub> waters. In addition, the Ba<sub>d</sub> concentration in the upper  
41 few hundred m in the coastal current appears to be lower (about 77 nmol kg<sup>-1</sup>) than north of it  
42 along the section, where it reaches about 85 nmol kg<sup>-1</sup>. In the area between 64°S and 66.5°S  
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1 the  $Ba_d$  depletion reaches greater depths than north and south of it. Here Maud Rise exerts  
2 influence on the entire water column: As circulation-topography interaction induces a Taylor  
3 column over the rise, the mixed layer extends deeper over the crest of Maud Rise than over its  
4 flanks.  
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9 Along the Weddell Sea section the near-surface layer exhibits similar  $Ba_d$  concentrations (Fig.  
10 3B) as observed at the Prime Meridian. At both ends of the section, the low- $Ba_d$  layer also  
11 extends deeper than in the central part. At the continental shelf break of the Antarctic  
12 Peninsula, the low- $Ba_d$  surface layer is linked to a plume of  $Ba_d$  depleted water hugging the  
13 continental slope until about 4000 m depth. This plume consists of Weddell Sea Bottom  
14 Water, which has very recently been formed at the southern and western shelves of the  
15 Weddell Sea and which has not yet reached the bottom of the central basin (Fahrbach et al.,  
16 2001; Gordon et al., 1993). Since WSBW is a mixing product of CDW and shelf water, it  
17 carries the low- $Ba_d$  properties of the latter water mass. In the WSBW at the continental slope  
18 the shelf water component is particularly large; on its further way through the Weddell Sea,  
19 mixing with adjacent deep waters will reduce the overall contribution of the shelf water  
20 component to the WSBW, thus also increasing the  $Ba_d$  concentration.  
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## 32 Discussion

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36 The concentrations of  $Ba_d$  are generally higher in Weddell Gyre surface waters compared to  
37 the Antarctic Zone in the Indian sector of the Southern Ocean (see Jacquet et al., 2005;  
38 Jeandel et al., 1996). Such zonal variation is mainly caused by varying upwelling activity of  
39 Ba-enriched deep waters southward in the ACC, although zonal differences in phytoplankton  
40 activity probably contribute as well. The latter usually is highest in the Subantarctic zone and  
41 Polar Frontal Zone to the north and decreases southwards into the Antarctic Zone to increase  
42 again in the vicinity of the ice edge (Jochem et al., 1995; Moore et al., 1999; Savoye et al.,  
43 2004). Our Weddell data were collected during summer, at the height of the growth season,  
44 and thus we expect the impact of biological uptake on  $Ba_d$  to have been at its climax. The  
45 smaller  $Ba_d$  depletions in Weddell surface waters could thus reflect lower production in the  
46 Weddell region compared to elsewhere in the ACC. However, it is likely that this smaller  
47 apparent  $Ba_d$  depletion is in part due to the intensity of upwelling in the divergent Weddell  
48 Gyre transferring Ba-enriched waters into the surface layers. Additionally, deep water which  
49 is being upwelled into the surface layer appears to have a higher  $Ba_d$  concentration in the  
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1 Weddell Gyre than in the Antarctic Zone of the Indian sector (~~compare~~ Jacquet et al., 2004;  
2 Jeandel et al., 1996).  
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### 5 *Correlation between barium and silicate*

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7 The distribution of  $Ba_d$ , both lateral and vertical, is known to show similarities with that of  
8 silicate in several ocean provinces (e.g., Chan et al., 1977; Jacquet et al., 2007a; Jeandel et al.,  
9 1996). We explore the occurrence of such a similarity for the Weddell Gyre with the  
10 corresponding silicate sections along the Prime Meridian and across the Weddell Sea (Fig. 4).  
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16 The vertical profile of silicate in the Weddell Gyre is typical for that of the major nutrients,  
17 i.e., relatively low concentrations in the surface layer, a maximum at intermediate depth and a  
18 decrease towards the sea floor. Frequently a silicate maximum is observed in the bottom layer  
19 (Edmond et al., 1979; Hoppema et al., 1998). Our data demonstrate a high agreement between  
20 the distributions of silicate and  $Ba_d$  in the Weddell Gyre (Figs. 3 and 4). Even the lateral  
21 variation of the extent of the surface layer appears to be congruent. This condition is largely  
22 due to hydrographic processes such as upwelling and convective overturning of the surface  
23 layer.  
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32 Newly formed WSBW at the continental slope off Joinville Island can be recognized by its  
33 low silicate and  $Ba_d$  concentrations (see NW end of the Weddell section; Figs. 3b and 4b). It  
34 is intriguing that even the wide, but not very pronounced, silicate minimum at 3000-3500 m  
35 emerging from the lower continental slope off Kapp Norvegia (see SE end of the Weddell  
36 section; Figs. 3b and 4b) appears to correspond to a  $Ba_d$  minimum. This core of ventilated  
37 water, characterized by a CFC maximum (Hoppema et al., 2001; Meredith et al., 2000) and  
38 thus a large surface water component, originates east of the Weddell Gyre. Obviously, just  
39 like WSBW from the Weddell Sea, it is characterized by relatively low concentrations of  
40 silicate and  $Ba_d$ , although the signal has been attenuated ~~on its long way~~ from the region of  
41 origin.  
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52 The deep silicate maximum (Fig. 4), which is slightly visible in plots of silicate versus salinity  
53 (Fig. 5) is caused by dissolution of biogenic silica at depth (Rutgers van der Loeff and Van  
54 Bennekom, 1989). There is no clear ~~coinciding~~  $Ba_d$  maximum - the variability of  $Ba_d$  in the  
55 deep Weddell Gyre appears too large - although the  $Ba_d$  data from the Weddell section seem  
56 to point to a weak feature (Fig. 5). Differences between the deep distributions of silicate and  
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1 Ba<sub>d</sub> should not be surprising, because the saturation state of ocean waters with respect to  
2 silica/opal and BaSO<sub>4</sub> is different, as well as the dissolution kinetics of these minerals. The  
3 water column in the Weddell Gyre is oversaturated with respect to barite in the upper 1500 m  
4 with barely any regional variability (Fig. 6). This indicates that no dissolution of BaSO<sub>4</sub>  
5 should occur in the upper 1500 m of the water column. Based on the saturation state, no large  
6 Ba<sub>d</sub> depth gradients are expected. Silicate shows a much larger surface to depth gradient since  
7 the entire oceanic water column is undersaturated for opal (Brzezinski et al., 2003; Hurd,  
8 1972).

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16 Regression of Ba<sub>d</sub> against silicate shows a high correlation for the combined Prime Meridian  
17 and Weddell sections ( $r^2 = 0.81$ ; Fig 7). The Ba<sub>d</sub>-silicate regression for the Weddell region is  
18 slightly different from that for a meridional section south of the Polar Front along 30°E (1993  
19 CIVA-1 cruise; WOCE I6 line, F. Dehairs & C. Jeandel, also in Fig. 7). For a given silicate  
20 concentration the Ba<sub>d</sub> concentrations in the Weddell system exceed those at 30°E by about 5  
21 nmol kg<sup>-1</sup> - note that the 30°E section is quite near the far eastern rim of the Weddell Gyre.  
22 Also, the slope of the Ba<sub>d</sub> versus silicate regression is larger and Ba<sub>d</sub> intercept at zero silicate  
23 smaller at 30°E (differences are significant;  $p < 0.005$ ). In the Weddell region the higher Ba<sub>d</sub>  
24 level highlights the decoupling between barium and silicate and points to a mechanism  
25 retaining Ba<sub>d</sub> within the Gyre system relative to silicate. A likely mechanism is Ba  
26 translocation to particles in surface waters and the Ba efflux from the sediments as discussed  
27 below. However, a smaller biological Ba over Si uptake ratio in the upper waters of the  
28 Weddell Sea, as compared to the ACC could also lead to the peculiar Ba vs. silicate  
29 regression in the Weddell Gyre.

### 30 ***Barium depletion in the surface layer***

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45 ~~Depletions of nutrients or TCO<sub>2</sub> in the surface layer have been used frequently to determine~~  
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47 the net community production from the onset of the growth season until the time of  
48 measurement (e.g., Hoppema et al., 2007). We are using an approximate depletion here to  
49 obtain the seasonal changes of the Ba<sub>d</sub> concentration between the winter and the time of  
50 sampling. Usually, depletions are computed from the vertical integration of the substrate  
51 concentration above the remnant Winter Water, which is identified by its temperature  
52 minimum, and is assumed to reflect the initial pre-bloom conditions. Since sampling  
53 resolution in the upper layers was insufficient to warrant a reliable integration over the surface  
54 layer, we simply consider the difference in Ba<sub>d</sub> between the temperature minimum layer and  
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1 the shallowest sample (at about 20 m). This difference in Ba<sub>d</sub> concentrations is proportional to  
2 ~~the depletion and is an approximate measure of it.~~  
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5 At the Prime Meridian, the Ba<sub>d</sub> difference between the temperature minimum and surface  
6 waters is generally in the range 0-6 nmol kg<sup>-1</sup>, ~~on average~~ 3.6 ± 3.9 nmol kg<sup>-1</sup> (Fig. 8A). A  
7 slight trend of higher values towards the ~~centre~~ of the transect may be discerned. At the  
8 Weddell section, the Ba<sub>d</sub> difference exhibits a range of -2 to 6 nmol kg<sup>-1</sup>, with few deviations  
9 to higher and lower values (Fig. 8B). We further show that the Ba difference is independent  
10 ~~on the~~ temperature ~~in~~ the temperature minimum (Figs. 8C and 8D). At the Weddell section the  
11 temperature minimum remains close to ~~the freezing point of seawater~~ of -1.85°C and  
12 ~~therefore it~~ appears that the observed Ba<sub>d</sub> depletions are real and not affected by erosion of the  
13 temperature minimum layer.  
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23 As a bio-intermediate element, Ba becomes depleted in the surface layer with respect to the  
24 deep water underneath it (e.g., Chan et al., 1977; Jacquet et al. 2007a). Our data show that  
25 surface water Ba depletions reaching up to 8 and 12 nmol kg<sup>-1</sup> (for the Prime Meridian and  
26 Weddell section, respectively; Fig. 8) are generated within a few months ~~since~~ the end of  
27 winter. There are several possible processes that may be responsible for this: ~~First,~~ active or  
28 passive biologically-mediated uptake of Ba; and second, abiotic precipitation of Ba as the  
29 mineral barite (BaSO<sub>4</sub>). As to the first cause, there are only very few phytoplankton species  
30 known to actively take up Ba (e.g., Gayral and Fresnel, 1979), which classifies active uptake  
31 ~~rather as an~~ unlikely contributor to Ba depletion. However, high particulate Ba concentrations  
32 have been reported in Southern Ocean surface waters (Cardinal et al., 2005; Jacquet et al.,  
33 2007a) usually associated with elevated biomass contents. This Ba is generally not present as  
34 barite (Dehairs et al., 1980; Stroobants et al., 1991), but is likely adsorbed onto organic matter  
35 (diatom tests; see Sternberg et al., 2005) or is incorporated into the skeletal matrix, e.g., in  
36 Acantharia (Bernstein et al., 1998; Jacquet et al., 2007b). As to the second cause, our results  
37 for Weddell Gyre surface waters point to a slight barite supersaturation in the upper water  
38 column with a maximum saturation index of 1.4 (Fig. 6). Monnin et al. (1999) and Monnin  
39 and Cividini (2006) identified the Weddell Sea as the only system in the world's ocean where  
40 BaSO<sub>4</sub> supersaturation prevails. Note that when barite saturation is reached, equilibrium  
41 should be the rule, as expected for salts whose kinetics of dissolution/precipitation are  
42 generally believed to be fast. Nevertheless, large BaSO<sub>4</sub> supersaturations have also been  
43 documented for the sedimentary environment (e.g., Aloisi et al., 2004).  
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1 In the seasonally ice-covered Weddell Gyre, a third cause of depletion should be considered,  
2 namely, barite precipitation during sea-ice formation. During ice formation in an already  
3 oversaturated surface ocean, the salinity and solutes concentrations in brine channels may  
4 reach very high values (e.g., Anderson and Jones, 1985), eventually leading to extreme  
5 supersaturation of barite. This will result in inorganic precipitation of barite. The large  
6 biomass of sea-ice algae visible as green or brown ice at the base of ice floes may further  
7 enhance Ba depletion as a result of Ba adsorption on algal cells (thereby depleting also the  
8 surface water underneath the ice) and may also result in barite formation due to organic matter  
9 degradation within the sea-ice (Carson, 2008). Very high particulate Ba concentrations were  
10 measured in brown ice (up to 8 nM Ba correlating with high POC contents (EPOS-2 cruise; F.  
11 Dehairs unpublished results). Also, Carson (2008) reports dissolved Ba concentrations in sea-  
12 ice brine ranging widely from surface water values to as low as 6 nM. These observations  
13 suggest that significant Ba translocation from the dissolved to the particulate phase does occur  
14 in sea-ice brines. It is worthwhile contemplating that barite precipitation during sea-ice  
15 formation occurs in autumn and winter and therefore this process as such cannot explain the  
16 observed  $Ba_d$  depletion of the seasonal summer mixed-layer. However, barite formed within  
17 the sea ice will eventually be released in the surface waters, either during draining and  
18 flushing of brine waters or ultimately when the ice is melted at the end of the winter. The  
19 released barite cannot dissolve in the supersaturated surface waters but when associated with  
20 aggregates of ice algae, it may sink out to the undersaturated deep ocean where it may  
21 eventually dissolve. Overall, such a process would subtract  $Ba_d$  from surface waters and  
22 redistribute it in the deep ocean. As to the seasonal depletion, the melting of sea ice at the end  
23 of the winter will dilute the upper part of the winter mixed layer more than the lower part,  
24 which also has impact on the  $Ba_d$  concentrations. It also is manifest that the mechanism  
25 described above would lead to variability of the  $Ba_d$  depletion. Due to ice motion (which is  
26 different from the movement of the underlying water) and spatially variable rates of ice  
27 formation, the variation of  $Ba_d$  depletion is further enhanced and even enrichment (i.e.,  
28 negative depletion; see Fig. 8B) of  $Ba_d$  is possible. We speculate that barite dissolution may  
29 even occur within the melting ice matrix in micro-environments with very low salinity, since  
30 the solubility of barite is higher at low salinity.

31  $Ba_d$  concentrations in the surface waters are generally lower in the coastal current at the Prime  
32 Meridian (Fig. 3A), off Kapp Norvegia and off Joinville Island (Fig. 3B), than elsewhere in

1 the Weddell Gyre. There are two possible explanations for this, and one is related to sea-ice  
2 formation. Close to the coast, ice is formed which is blown off the coast by strong, cold  
3 winds; new ice is readily formed in the near coastal area and therefore these regions are  
4 sometimes denoted as sea-ice factories (e.g., Barber and Massom, 2007). Hence, if ice plays a  
5 major role in the depletion of  $Ba_d$  in the surface water, one would expect the lowest  $Ba_d$   
6 concentrations near the coast indeed. Another factor could be differences in upwelling rates,  
7 combined with biologically-mediated draw-down of  $Ba_d$  in the surface layer: The region with  
8 higher upwelling rates (bringing much  $Ba_d$  into the surface layer) would have the higher  $Ba_d$   
9 concentration. Since upwelling in the divergent Weddell Gyre tends to occur towards its  
10 centre, the coastal region would have lower  $Ba_d$  concentrations. This trend is reinforced by the  
11 higher biological activity at the shelves (Arrigo et al., 1998; Hoppema et al., 2007).

21 It is interesting to note that the larger surface Ba depletion around 62°S on the Prime Meridian  
22 (Fig. 8A) appears to coincide with elevated  $Ba_d$  concentrations in the deep basin between  
23 2000 m and the bottom (Fig. 3A). This strongly hints at a mechanism whereby barite is being  
24 formed in the surface layer and is subsequently transferred to the deep ocean. At greater  
25 depths where undersaturation prevails (Fig. 6), dissolution of barite causes elevated  
26 concentrations of  $Ba_d$ . It should be added that this mechanism is not only active in the central  
27 Weddell Gyre; it is merely most salient there. Also in other parts of the basin the  $Ba_d$   
28 concentration is to some degree determined by dissolution of barite – if the surface depletion  
29 of  $Ba_d$  is less, also less barite can be dissolved at depth. Also note that the vertical  
30 correspondence between Ba depletion in the surface and Ba enrichment at depth is not perfect  
31 because water currents (strength and direction) are depth-dependent. That there is a good  
32 correspondence in the central gyre makes sense because the currents are weakest there  
33 (Fahrbach et al., 1994).

### 47 ***Bottom layer enrichment***

48 A remarkable observation is that both silicate and  $Ba_d$  are enriched in the bottom layer of the  
49 Weddell Sea; actually, the highest absolute concentrations of both species were observed  
50 there (Figs. 3B and 4B). For silicate this has been reported early by Edmond et al. (1979).  
51 Note, in contrast, that newly formed WSBW (which is the source of all bottom water in the  
52 Weddell Gyre) along the slope of the Antarctic Peninsula (Figs. 3B and 4B) is characterized  
53 by minima of silicate and  $Ba_d$ . This highlights that subsequent enrichment of bottom water  
54 occurs locally in the Weddell-Enderby basin. Even the spatial distributions of bottom layer

1 enrichment of silicate and dissolved Ba largely conform; Strong enrichments were found  
2 along most of the Weddell section (Figs. 3B and 4B), and at the Prime Meridian especially in  
3 the southern part (66.5-68.5°S; Fig. 3A and 4A). Note, though, that in the north  
4 of the Prime Meridian section at 55.5-56.5°S a silicate maximum was observed at the bottom, but this  
5 appears to be spatially associated with deep waters; no Ba<sub>d</sub> analogue was found at that  
6 location. Hoppema et al. (1998) have demonstrated that especially in the region off Kapp  
7 ~~Norvegia~~ strong enrichment of the bottom water with silicate occurs, supported by a local  
8 bottom water recirculation cell. This could also explain higher Ba<sub>d</sub> enrichment in that region.  
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16 Enrichment of Ba<sub>d</sub> in the bottom layer may have two causes. First, particulate barite could  
17 ~~massively~~ dissolve at these depths because of the pressure dependence of the solubility  
18 product of barite (Monnin et al., 1999; Monnin and Cividini, 2006). Note that the saturation  
19 index  $\Omega$  for BaSO<sub>4</sub> close to the seafloor at depths >4000m drops to values as low as < 0.6  
20 (Fig. 6) and enhanced dissolution of barite may only start at  $\Omega$  well below 1 due to kinetic  
21 effects. However, this explanation is unlikely since we found evidence for Ba<sub>d</sub> enrichment in  
22 the deep water column (see above) which hints at dissolution at depths well above the bottom  
23 layer. Second, there may be input of Ba<sub>d</sub> from the sediments to the overlying water. Biogenic  
24 barium is abundantly present in sediment cores from the Weddell Sea and environs (e.g., Ó  
25 Cofaigh and Dowdeswell, 2001). The occurrence of enhanced vertical gradients of Ba<sub>d</sub> in the  
26 deepest samples combined with the fact that significant epibenthic flux of dissolved Ba to the  
27 water column has been reported for other oceanic areas as well (e.g., McManus et al., 1994,  
28 1998), suggest that efflux of Ba from the sediments contributes to the elevated bottom water  
29 Ba concentrations. It is worthwhile adding that the spatial coincidence of Ba<sub>d</sub> and silicate  
30 enrichment lends high credibility to the case for Ba<sub>d</sub> input from the sediments because opal  
31 dissolution occurs all through the water column, and silicate effluxes from the sediments have  
32 been reported in the Weddell basin indeed (Edmond et al., 1979; Holby and Anderson, 1996;  
33 Rutgers van der Loeff and Van Bennekom, 1989).  
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51 A very rough estimation of the Ba flux from the sediments is presented. We take the Ba<sub>d</sub>  
52 enrichment in the bottom layer to be 5 nmol kg<sup>-1</sup>, whereas the vertical extent of that layer is  
53 about 500 m (see Fig. 3B). This results in an enrichment of 2500  $\mu\text{mol m}^{-2}$ . It has been  
54 generated at the time scale of the residence time of the WSBW in the bottom layer. The  
55 residence time is tentatively computed as 6 years, using the horizontal extent of the Weddell  
56 Gyre where WSBW occurs (assumed about  $1 \cdot 10^{12} \text{ m}^2$ ), combined with the vertical extent (500  
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1 m) and the ventilation rate of WSBW ( $2.6 \text{ Sv} = 2.6 \cdot 10^6 \text{ m}^3 \text{ s}^{-1}$ ; Fahrbach et al., 1994). This  
2 yields an efflux of  $\text{Ba}_d$  amounting to about  $400 \text{ } \mu\text{mol m}^{-2} \text{ yr}^{-1}$ . This value falls well within the  
3 range reported in the literature for other open ocean environments, e.g., in the Equatorial  
4 Pacific:  $160\text{-}1060 \text{ } \mu\text{mol m}^{-2} \text{ yr}^{-1}$  (McManus et al., 1999; Paytan and Kastner, 1996). Integrated  
5 over the Weddell Basin surface area of  $1 \cdot 10^{12} \text{ m}^2$  this adds up to  $0.4 \cdot 10^9 \text{ mol yr}^{-1}$ .  
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### 10 *Enrichment of dissolved barium in deep water*

11 Since water mass transformation and mixing take place in the Weddell-Enderby basin, the  
12 bottom water  $\text{Ba}_d$  enrichment is also transferred to other water masses, in particular the  
13 voluminous deep water. We can make a rough estimation of the enrichment of  $\text{Ba}_d$  in the deep  
14 Weddell basin in the following way, using specific characteristics of the hydrography of the  
15 region. The main source of deep water of the Weddell Gyre is the inflowing CDW of the  
16 ACC near the eastern boundary. Other water masses are eventually derived from that source.  
17 At the Prime Meridian the source water mass can be distinguished at depths of about 200-  
18 1500 m at  $64\text{-}69^\circ\text{S}$  (see Fig. 2, and Hoppema et al., 1997). Its upper boundary is the  $\theta$   
19 maximum, while the lower boundary is distinguishable as a weak maximum both of  $\text{TCO}_2$   
20 and nutrients occurring at  $\theta$  of about  $0\text{-}0.2^\circ\text{C}$  (Hoppema et al., 1997). We compare the  $\text{Ba}_d$   
21 concentration of the CDW source water (marked as “inflow”) with that of the remaining deep  
22 water masses at the Prime Meridian in a diagram of  $\text{Ba}_d$  against  $\theta$  (Fig. 9). The  $\text{Ba}_d$   
23 concentration in the inflow CDW tends to be lower than that in the rest of the basin - recall  
24 that lower  $\text{Ba}_d$  concentrations were observed in the CDW of the Antarctic Circumpolar  
25 Current indeed; see Results section and Fig. 3A. However, there is a large overlap of  $\text{Ba}_d$   
26 values for the two sub-regions. At the highest  $\theta$  values, representing the core of the  $\theta$   
27 maximum which is associated with inflowing CDW,  $\text{Ba}_d$  is the lowest ( $85\text{-}94 \text{ nmol kg}^{-1}$ ).  
28 Beneath the  $\theta$  maximum of the inflow water,  $\text{Ba}_d$  is higher and similar to  $\text{Ba}_d$  in the low  $\theta$   
29 maximum of the remaining basin. In the deep Weddell basin with a  $\theta$  range of roughly  $0.2$  to -  
30  $0.7^\circ\text{C}$  the  $\text{Ba}_d$  concentration is constant within about  $93\text{-}101 \text{ nmol kg}^{-1}$ . Some higher values of  
31  $\text{Ba}_d$  appear to show enrichment in the bottom layer possibly resulting from epibenthic outflow  
32 of Ba (see above).  
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54 Since  $\text{Ba}_d$  in the water of about  $0.5^\circ\text{C}$  in the central and northern Weddell along the Prime  
55 meridian coincides with that of  $0.5^\circ\text{C}$  in the inflow area ( $64\text{-}69^\circ\text{S}$ ), it appears that the upper  
56 portion of the inflow water with the high  $\theta$  maximum ( $>0.5^\circ\text{C}$ ) is upwelled into the surface  
57 layer during its further course through the gyre. Of note is that at the Prime Meridian we do  
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1 not catch the ~~whole~~ extent of upwelling of low- $Ba_d$  subsurface water in the inflow. Actually,  
2 much upwelling has already taken place in the eastern Weddell Gyre between the eastern  
3 boundary and  $0^\circ E$ , changing water properties considerably (Bakker et al., 2008; Gouretski  
4 and Danilov, 1993). In the deep Weddell basin ( $\theta$  about  $0.2$  to  $-0.7^\circ C$ ) the  $Ba_d$  concentration is  
5 higher than in the  $\theta$  maximum layer, but it is largely independent of  $\theta$  (with a range of about 5  
6  $nmol\ kg^{-1}$ ; Fig. 9). Further  $Ba_d$  enrichment occurs in the bottom layer (see above). This  
7 suggests that the  $Ba_d$  level of the deep water is fed by input from above (surface water) and  
8 below (water with  $\theta < -0.7^\circ C$ ): Within the deep basin mixing and ~~uplifting of the~~ deep water  
9 takes place, which ~~relocates dissolved Ba~~. Another source of  $Ba_d$  for the deep Weddell Gyre is  
10 ~~the~~ dissolution of barite raining down from the upper layers, as the deep water below about  
11 1500 m is undersaturated with respect to barite (Fig. 6).  
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### 22 *Mass balance of Ba in the deep Weddell Gyre*

23 We construct a tentative mass balance of  $Ba_d$  in the deep Weddell Gyre that must be  
24 consistent with the apparent enrichment of  $Ba_d$  within the Gyre compared to the source waters  
25 from the ACC. Orsi et al. (1999) estimated the total Antarctic Bottom Water export of the  
26 Atlantic sector of the Southern Ocean to be about  $11\ Sv$ . This is too high for the Weddell Gyre  
27 because Orsi et al.'s definition of the Atlantic sector includes large regions east of the gyre. A  
28 value of 8-9 Sv may be more representative for the subsurface Weddell Gyre as reported by  
29 Klatt et al. (2005), although ~~also~~ this should be considered as upper boundary. This outflow  
30 must be balanced by an inflow of CDW and surface water from the ACC. The Ba  
31 concentration difference between the inflowing CDW with low Ba and outflowing deep water  
32 with high Ba amounts to about  $5\ nmol\ kg^{-1}$  (see Fig. 9). Thus the net Ba loss of the Weddell  
33 Gyre to the ACC is about  $40-45\ mol\ s^{-1}$ , or  $1.3-1.4 \cdot 10^9\ mol\ yr^{-1}$ . The deep Weddell Gyre also  
34 loses water and  $Ba_d$  to the surface layer through upwelling and diffusion. Different estimates  
35 are being reported for the rate of vertical advection in the Weddell Sea: Hoppema et al. (2001)  
36 give a lower end range between 0.5 and 1.3 Sv, while Weppernig et al. (1996), Mensch et al.  
37 (1996) and Haine et al. (1998) estimate vertical advection to range between 1.5 and 1.7 Sv.  
38 Taking a mean deep ocean to Winter Water concentration difference of  $Ba_d$  of  $15\ nmol\ kg^{-1}$ ,  
39 vertical advection would convey between  $0.6 - 0.8 \cdot 10^9\ mol\ Ba_d\ yr^{-1}$  from the deep water to the  
40 surface. The total loss from the deep Weddell Gyre thus amounts to  $1.9-2.2 \cdot 10^9\ mol\ Ba_d\ yr^{-1}$ .  
41 Assuming steady state, this number must be identical to the supply of  $Ba_d$  to the deep water.  
42 The efflux of Ba from the Weddell Sea sediments contributes  $0.4 \cdot 10^9\ mol\ yr^{-1}$  to the deep  
43 water (see above). We assume that the remaining  $1.5-1.8 \cdot 10^9\ mol\ Ba_d\ yr^{-1}$  is ~~then by~~  
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1 difference contributed by supply from the surface layer, where  $Ba_d$  is subtracted and  
2 precipitated and brought to the deep Weddell as particulate matter, where it dissolves in the  
3 undersaturated ocean (see Fig. 6).  
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7 We calculated a net loss of  $Ba_d$  of the Weddell Gyre, but it should be stressed that this is only  
8 a loss from the *deep* gyre. This excess  $Ba_d$  originates predominantly from the surface layer.  
9 The surface layer of the Weddell Gyre is eventually generated through upwelling of CDW. It  
10 is manifest that the  $Ba_d$  concentration in the surface layer is much lower than that of the  
11 CDW, evidencing that  $Ba_d$  is lost from the surface layer. This loss is affected by biologically-  
12 mediated processes of  $Ba$  subtraction and barite formation within the sea ice (see above). The  
13  $Ba$  depleted surface water is transferred equatorwards from the Weddell Gyre through Ekman  
14 transport.  
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23 Considering a Weddell surface area of  $1 \cdot 10^{12} \text{ m}^2$ , the  $Ba_d$  supply needed for making up the  
24 balance for the deep Weddell Gyre equals  $4\text{-}5 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ . This is similar but generally  
25 somewhat larger than the  $Ba$  fluxes recorded by deep water sediment traps elsewhere. A trap  
26 at 4023 m from site M2 (French KERFIX/ANTARES program 1994-1995) located in the  
27 ACC beyond the eastern rim of the Weddell Gyre in the Indian sector ( $52^\circ\text{S} - 61^\circ 32'\text{E}$ )  
28 recorded  $Ba$  fluxes between  $0.2$  and  $2.8 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$  (average flux =  $0.94 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ ;  
29 Jeandel et al., unpublished results). At the M3 site ( $63^\circ\text{S}$ - $71^\circ\text{E}$ ; KERFIX/ANTARES  
30 program) in the SIZ further south,  $Ba$  fluxes at 1334 m and 3444 m were smaller (range:  $0.06$   
31 to  $0.34 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ ; average =  $0.14 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$  and range  $0.09$  to  $0.38 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ ;  
32 average =  $0.22 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ , respectively; Jeandel et al., unpublished results). Sediment traps  
33 moored in the Polar Frontal Zone, along  $145^\circ\text{E}$ , had average  $Ba$  fluxes of  $0.74$  and  $0.68 \text{ } \mu\text{mol}$   
34  $\text{m}^{-2} \text{ d}^{-1}$  at 800 and 1580 m, respectively (Jacquet et al., 2007a). The particulate  $Ba$  subtraction  
35 estimated here also is similar to the seasonal input of particulate  $Ba$  in the mesopelagic waters  
36 (as a result of barite precipitation in decomposing sinking aggregates) of the Polar Front along  
37  $6^\circ\text{W}$  ( $1.4 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ ; Dehairs et al., 1997) which represents at least part of the vertical flux  
38 of  $Ba$  in the water column. The derived apparent fluxes in the deep Weddell Gyre are likely to  
39 be on the high side. On the other hand, the total enrichment of  $Ba_d$  must by nature be larger  
40 than the particulate  $Ba$  fluxes captured by traps because the material caught in the traps is  
41 only part of the total, the rest having been dissolved on the way. Finally, subtraction of  $Ba$  in  
42 the surface layer from solution via barite precipitation associated with sea-ice formation and  
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1 biological activity may be more efficient in the Weddell Gyre than in other regions because of  
2 the large sea ice formation in the latter region.  
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### 5 **Concluding remarks**

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7 Two full-depth sections have provided insight into the factors determining the  $Ba_d$   
8 distribution. The Weddell Gyre is supplied with deep water from the ACC which is relatively  
9 low in  $Ba_d$ . The low  $Ba_d$  concentration could still be observed at the Prime Meridian (which is  
10 some distance away from the actual ACC source). In the gyre this low  $Ba_d$  subsurface water is  
11 upwelled into the surface layer. Further decrease of  $Ba_d$  in the surface layer occurs due to Ba  
12 uptake as a consequence of phytoplankton activity, complemented by barite formation in sea-  
13 ice. Within the voluminous deep Weddell Gyre,  $Ba_d$  is enriched compared to the source water  
14 of the gyre. This is effectuated by two processes; first, barite dissolution in the undersaturated  
15 deep water, with barite originating from the depleted surface layer; and second by  $Ba_d$  mixing  
16 into the deep water from the strongly  $Ba_d$  enriched bottom layer.  $Ba_d$  influx from the bottom  
17 layer seems to occur predominantly in the southeastern part of the Weddell basin, in exactly  
18 the same region where bottom layer enrichment of silicate occurs. Water movement and  
19 circulation further redistribute  $Ba_d$  through the Weddell-Enderby basin. Tentative calculations  
20 showed that enrichment of the deep water due to  $Ba_d$  originating from the surface layer is  
21 likely to be larger than through  $Ba_d$  supply from the bottom layer. Locally this may certainly  
22 be variable.  
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38 Summarizing, a mechanism appears to exist in which the Weddell Gyre acts as an efficient  
39 conduit for  $Ba_d$  export to the deep and abyssal world oceans. In the surface layer  $Ba_d$  is  
40 subtracted due to phytoplankton activity and barite precipitation within sea ice. This  
41 particulate, absorbed and adsorbed Ba is subsequently exported from the surface layer by  
42 gravitational action and redissolves in the deep Weddell Gyre. The deep water, classified as  
43 Antarctic Bottom Water, thus enriched in  $Ba_d$  abandons the gyre to replenish the abyssal  
44 ocean basins to the north.  $Ba_d$  depleted surface water leaves the gyre northwards through  
45 Ekman transport.  
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## Figure captions

### Figure 1

Map of the Weddell Sea and environs with station locations during cruise ANT-XXII/3. Arrows denote the schematic surface circulation in the region.

### Figure 2

Section at the Prime Meridian cutting the Weddell Gyre and the southernmost part of the Antarctic Circumpolar Current, contoured for potential temperature ( $^{\circ}\text{C}$ ) at cruise ANT-XXII/3 in 2005.

### Figure 3

Sections contoured for dissolved barium ( $\text{nmol kg}^{-1}$ ) during cruise ANT-XXII/3 in 2005, A) at the Prime Meridian cutting the Weddell Gyre and the southernmost part of the Antarctic Circumpolar Current; and B) across the Weddell Sea from Kapp Norvegia (right) to Joinville Island at the tip of the Antarctic Peninsula (left).

### Figure 4

Sections contoured for dissolved silicate ( $\mu\text{mol kg}^{-1}$ ) during cruise ANT-XXII/3 in 2005, A) at the Prime Meridian cutting the Weddell Gyre and the southernmost part of the Antarctic Circumpolar Current; and B) across the Weddell Sea from Kapp Norvegia (right) to Joinville Island at the tip of the Antarctic Peninsula (left).

### Figure 5

1 Plots of silicate ( $\mu\text{mol kg}^{-1}$ ) vs. salinity (A, B) and dissolved Ba ( $\text{nmol kg}^{-1}$ ) vs. salinity (C, D)  
2 for the Weddell and the Prime Meridian sections to investigate property maxima in the deep  
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4 water.  
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9 Figure 6

10 Barite saturation state  $\Omega$  (ion product of Ba and sulfate divided by the solubility of barite) for  
11 the sections along the Prime Meridian (A) and across the Weddell Sea (B). If  $\Omega > 1$  the water  
12 is supersaturated with barite.  
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21 Figure 7

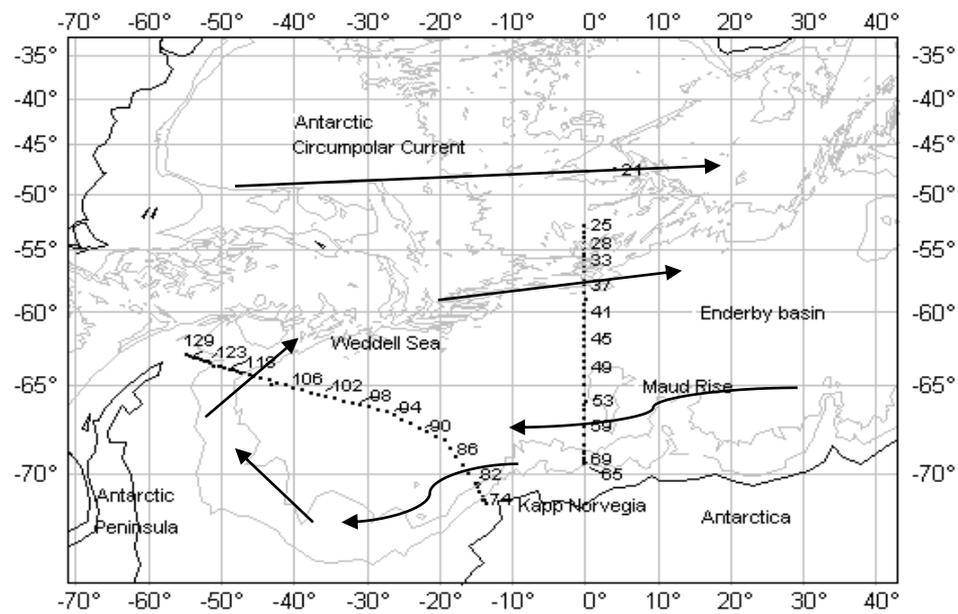
22 Dissolved Ba ( $\text{nmol kg}^{-1}$ ) plotted against silicate ( $\mu\text{mol kg}^{-1}$ ) for data from the Prime Meridian  
23 and Weddell sections combined. Also shown is the regression for a section at  $30^\circ\text{E}$  (1993,  
24 CIVA1 cruise, WOCE I6 line) where only stations south of the Polar Front were included.  
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33 Figure 8

34 Dissolved barium concentration difference between the temperature minimum layer and the  
35 near-surface in the surface layer vs. latitude at the Prime Meridian (A), and vs. longitude at  
36 the Weddell section (B). The same Ba difference plotted against the potential temperature of  
37 the temperature minimum layer at the Prime Meridian (C) and at the Weddell section (D).  
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48 Figure 9

49 Dissolved barium plotted against potential temperature. Data are from the Prime Meridian  
50 section only; surface layer data are excluded.  
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Source: GEBCO.

FIGURE 1

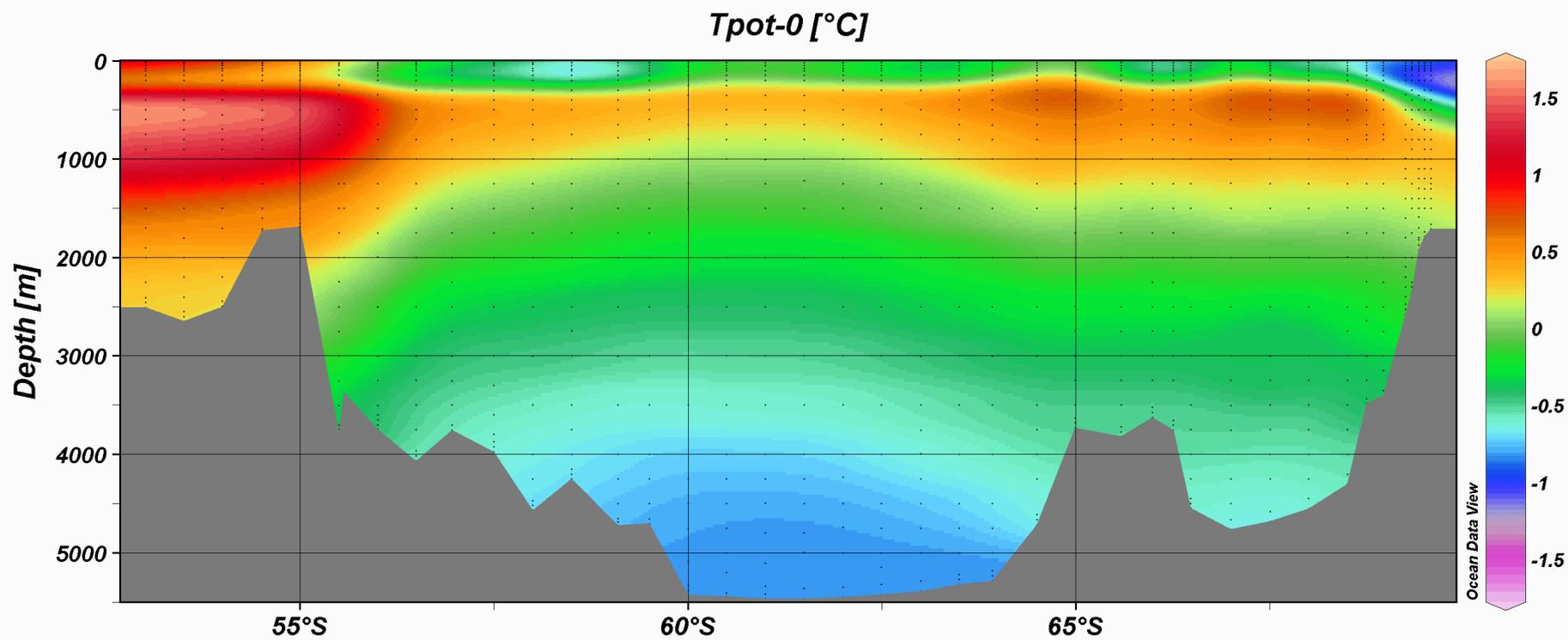


FIGURE 2

Ba [nM/Kg]

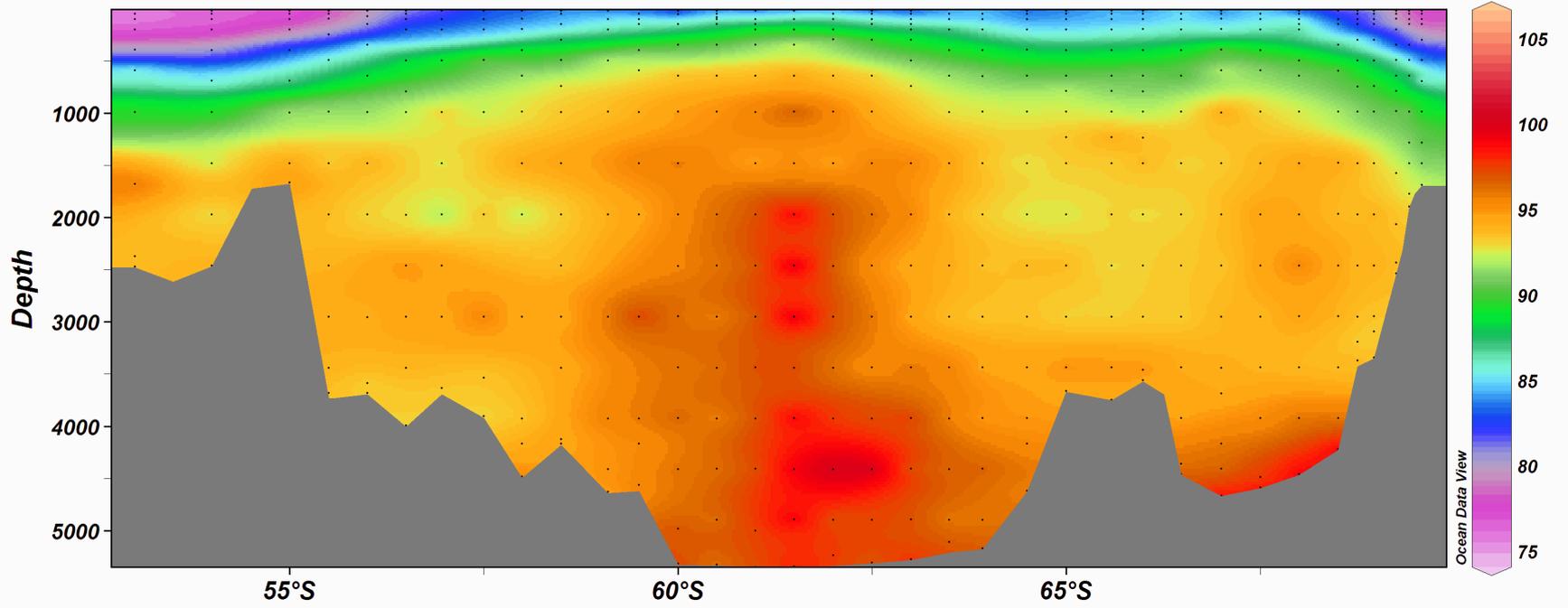


FIGURE 3A

Ba [nM/Kg]

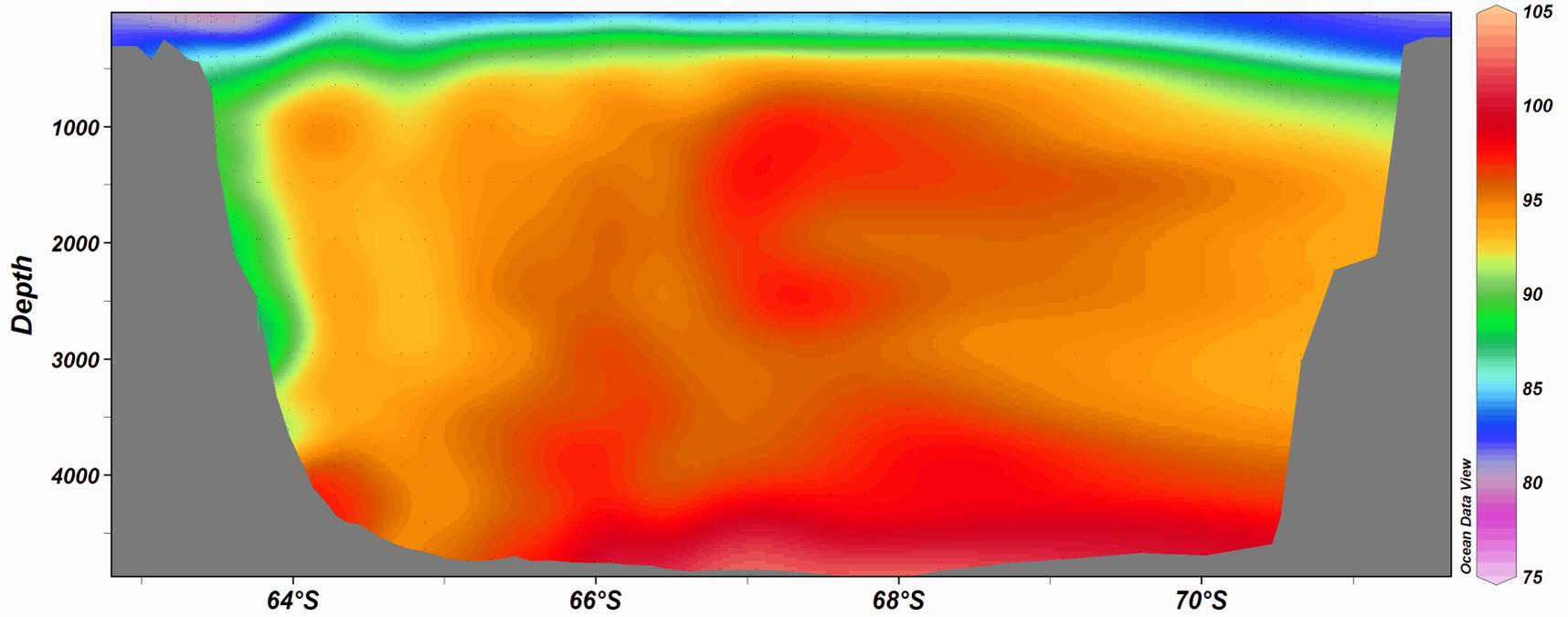


FIGURE 3B

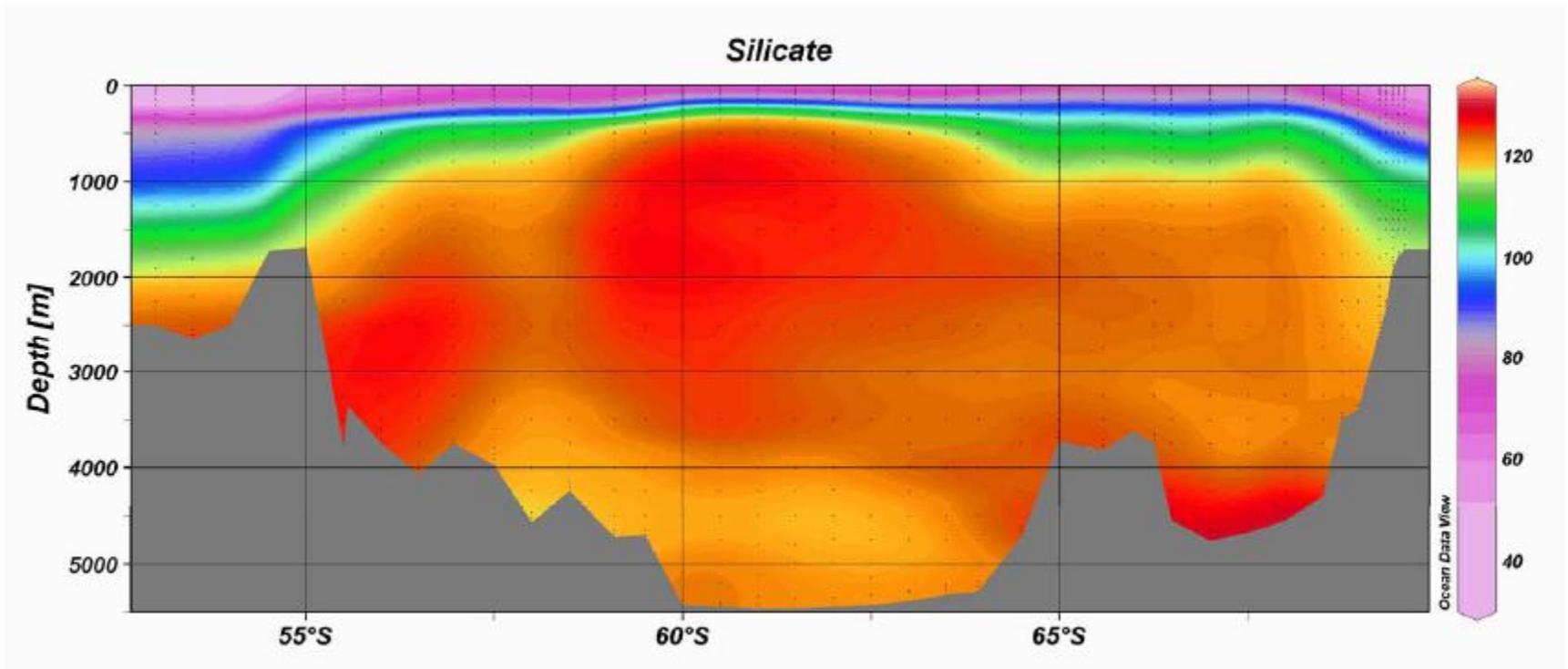


FIGURE 4A

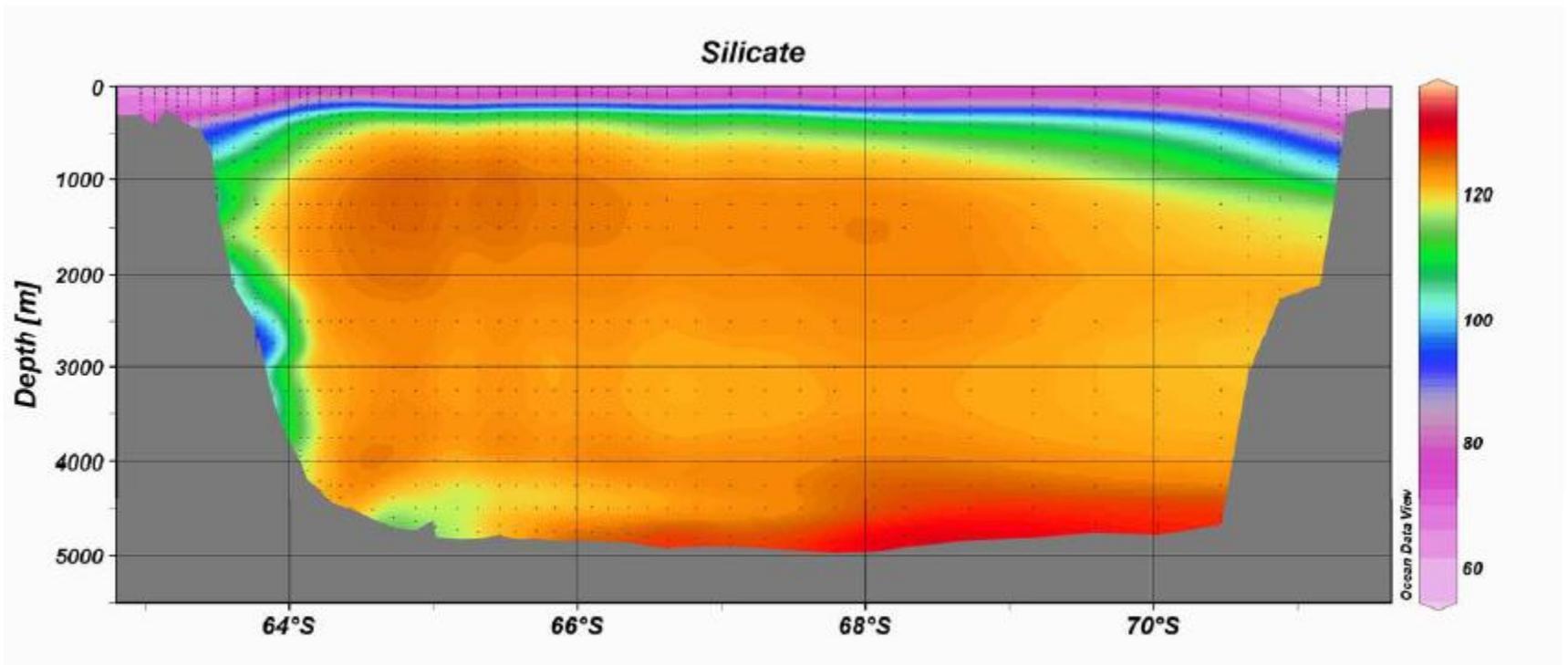


FIGURE 4B

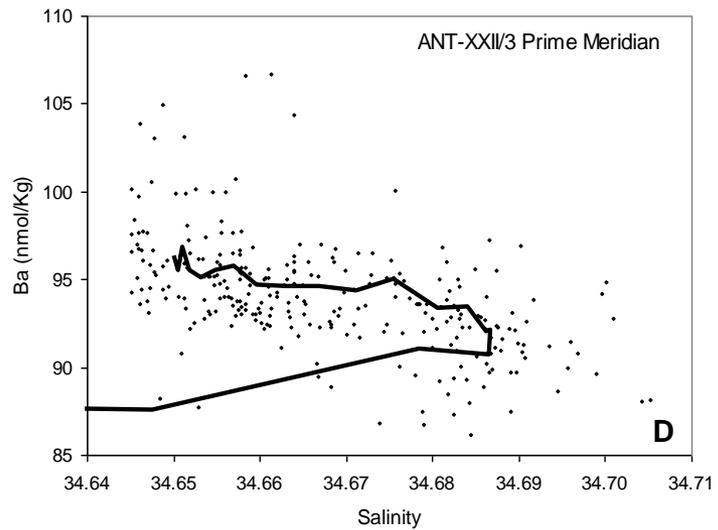
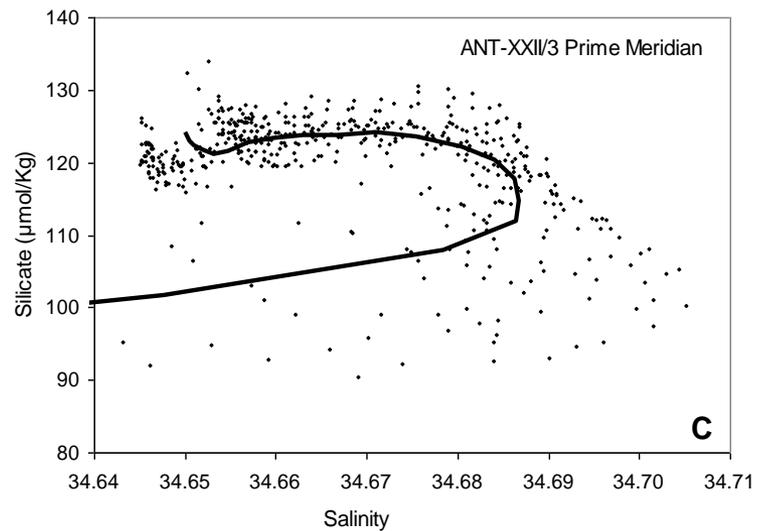
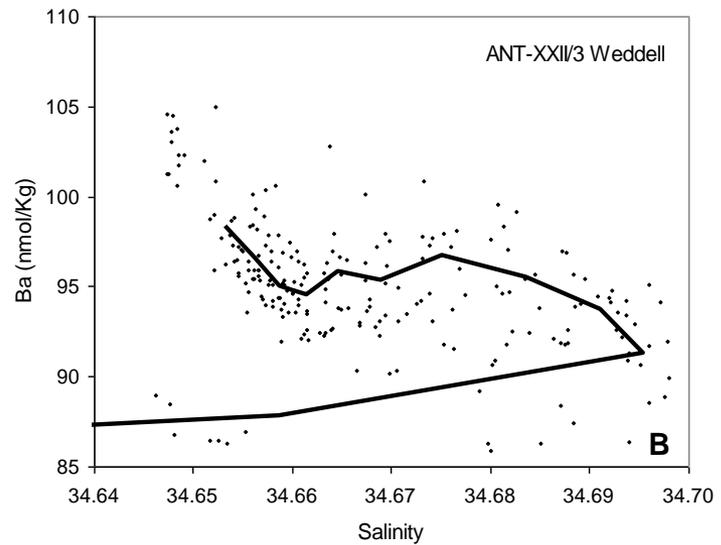
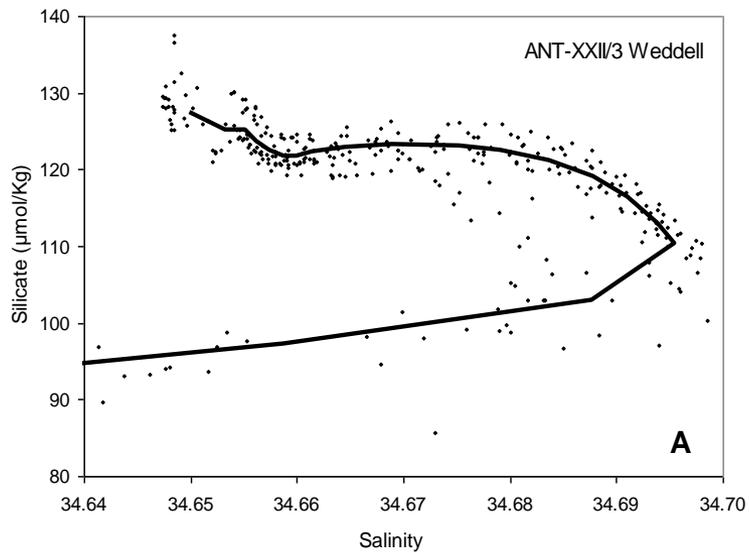


FIGURE 5

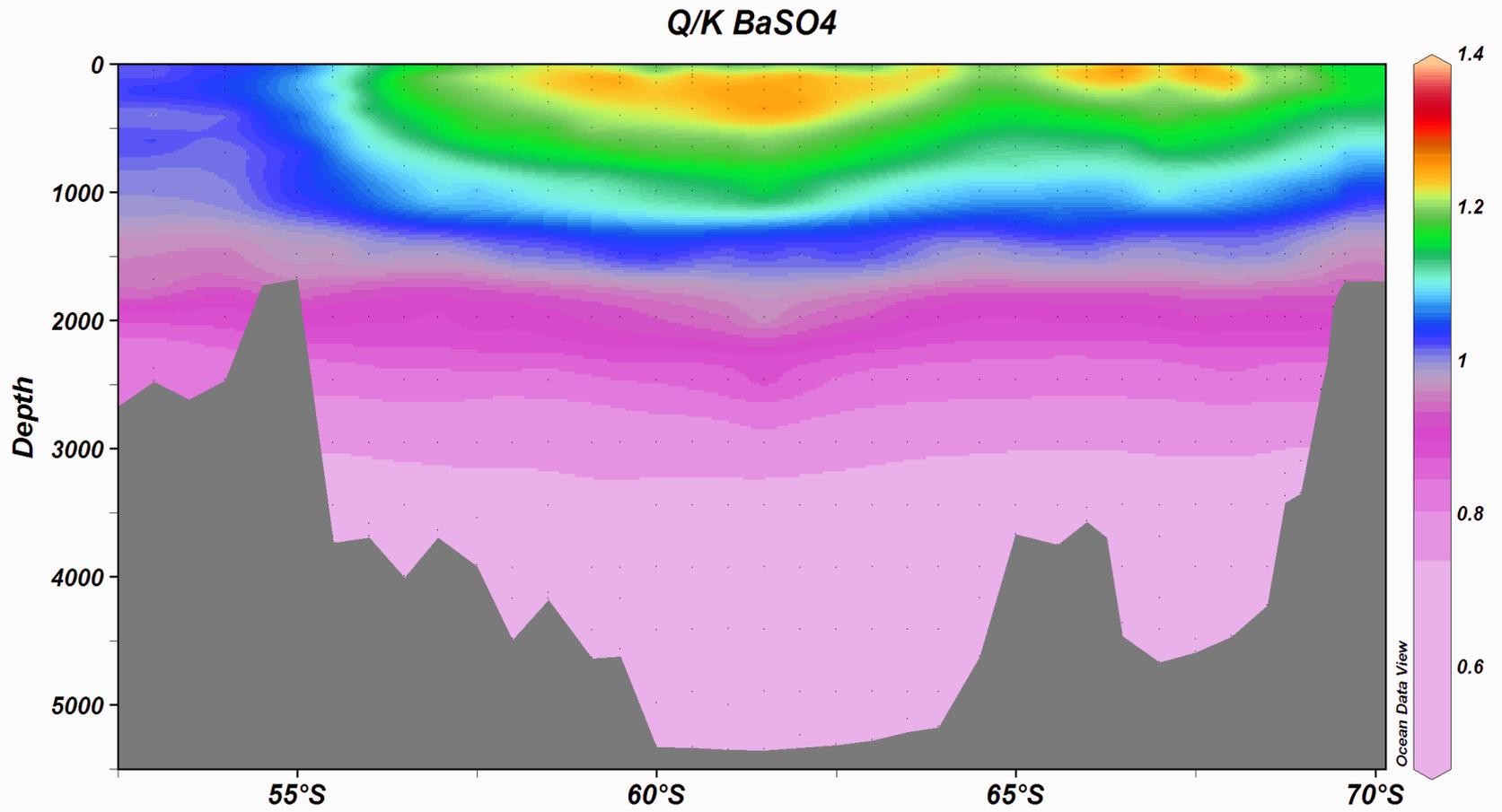


FIGURE 6A

# Q/K BaSO<sub>4</sub>

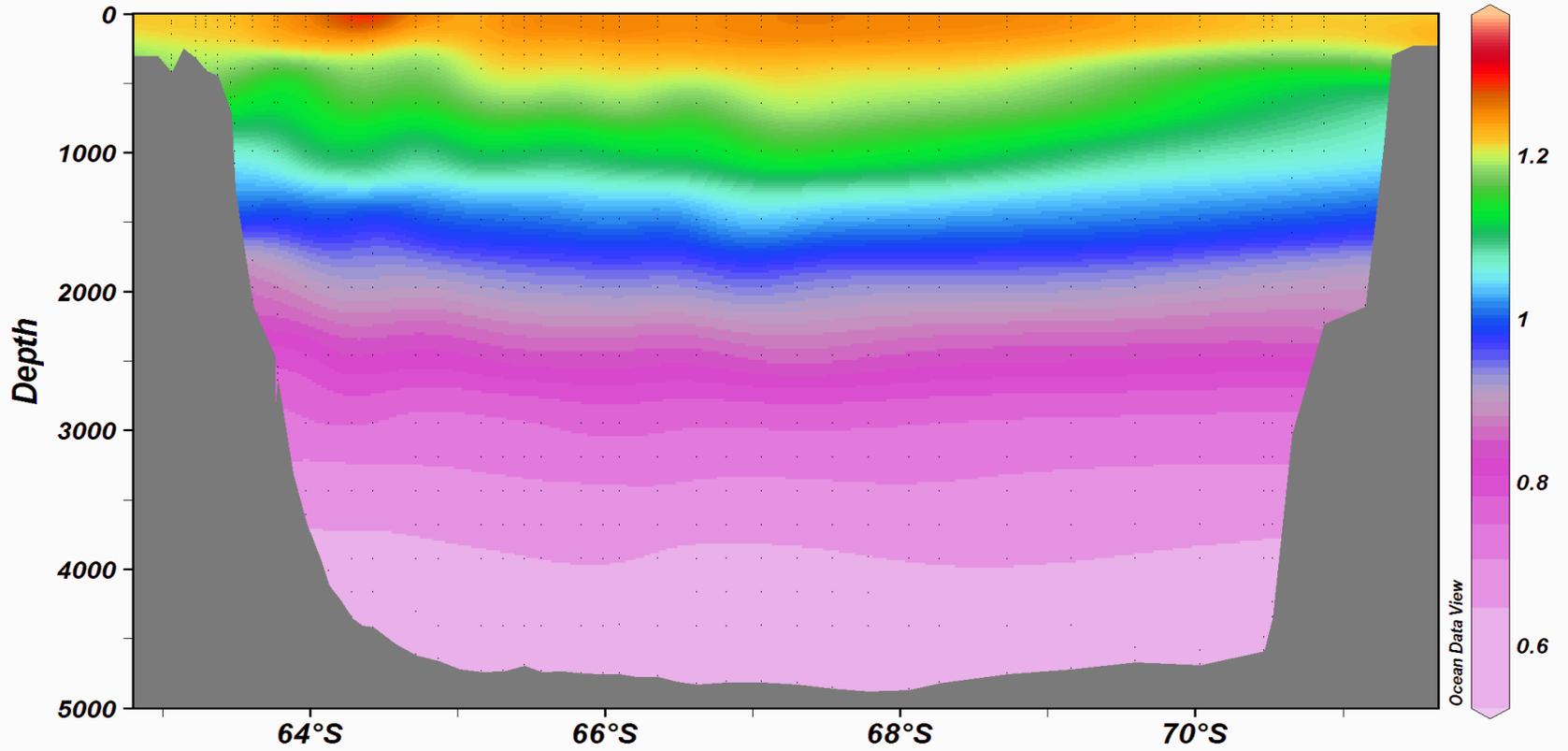


FIGURE 6B

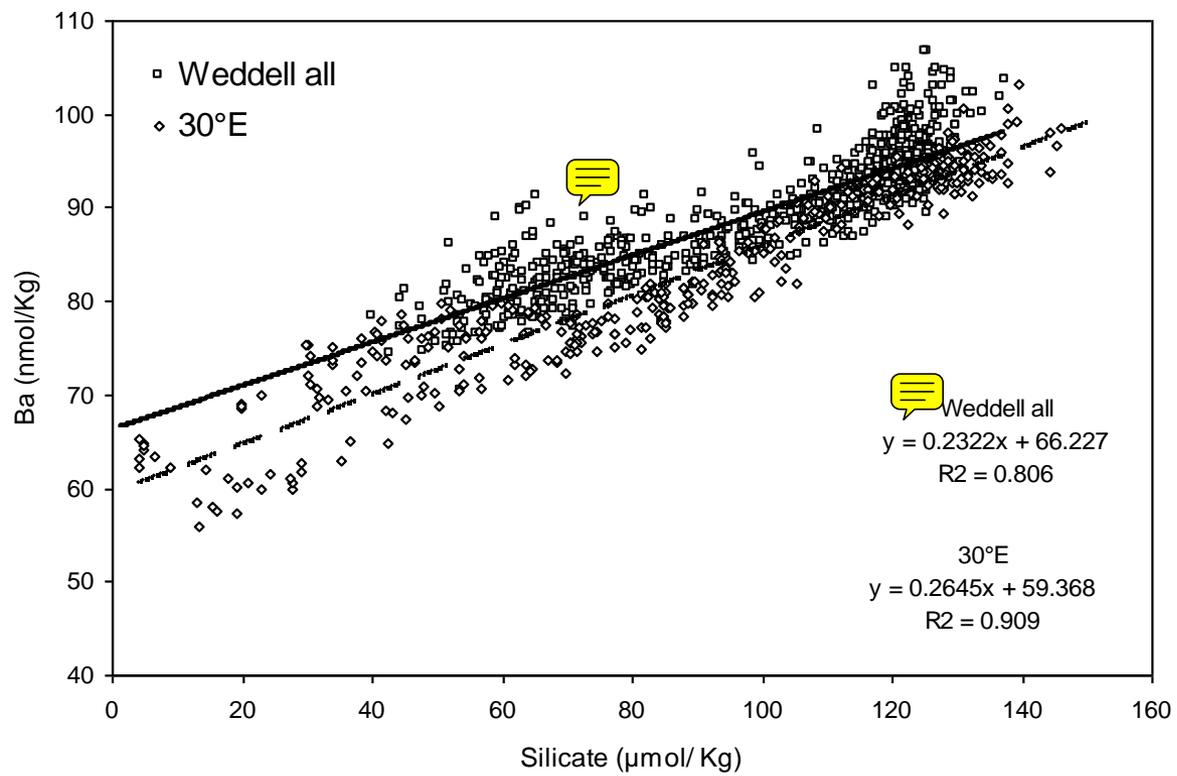


FIGURE 7

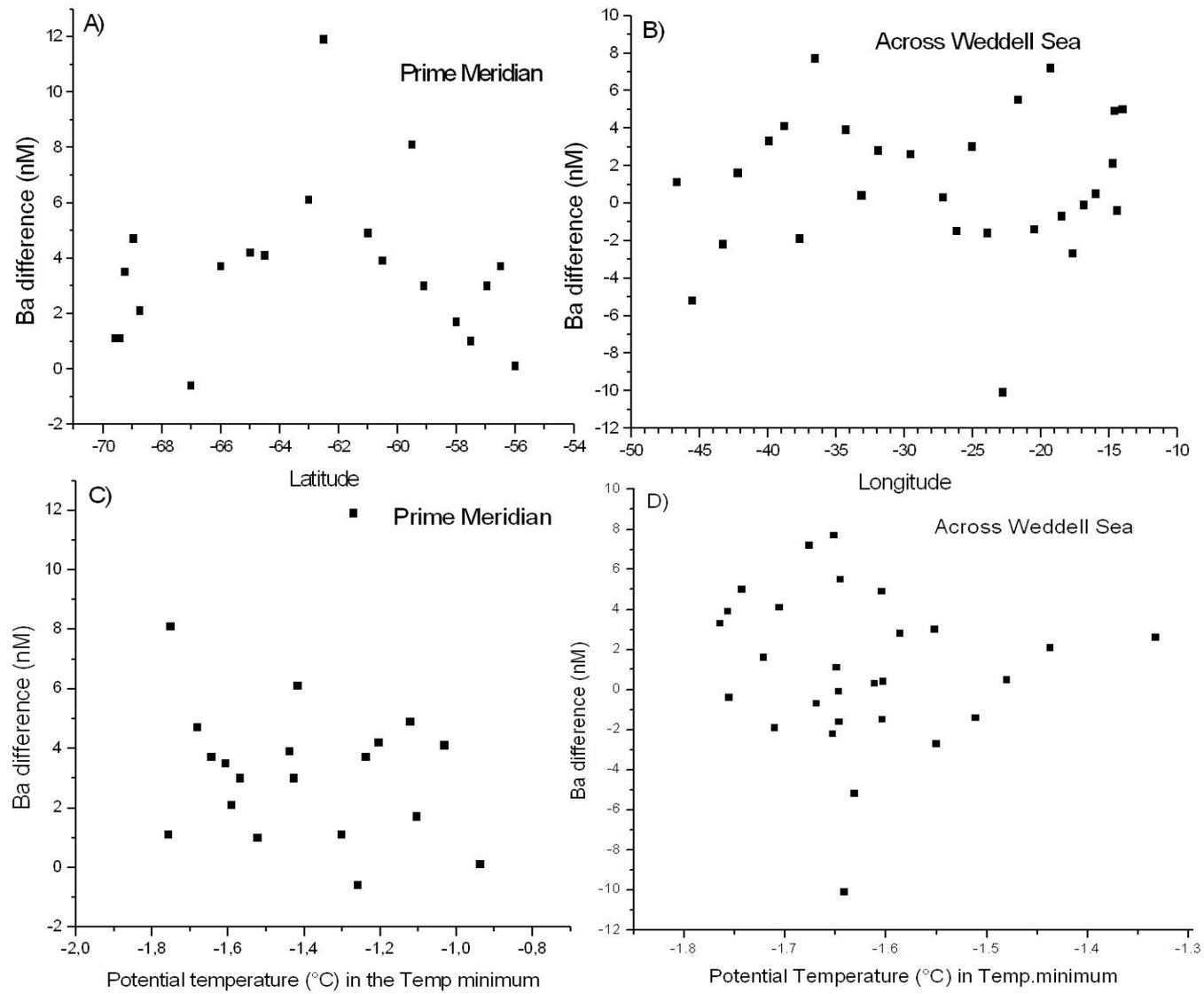


FIGURE 8

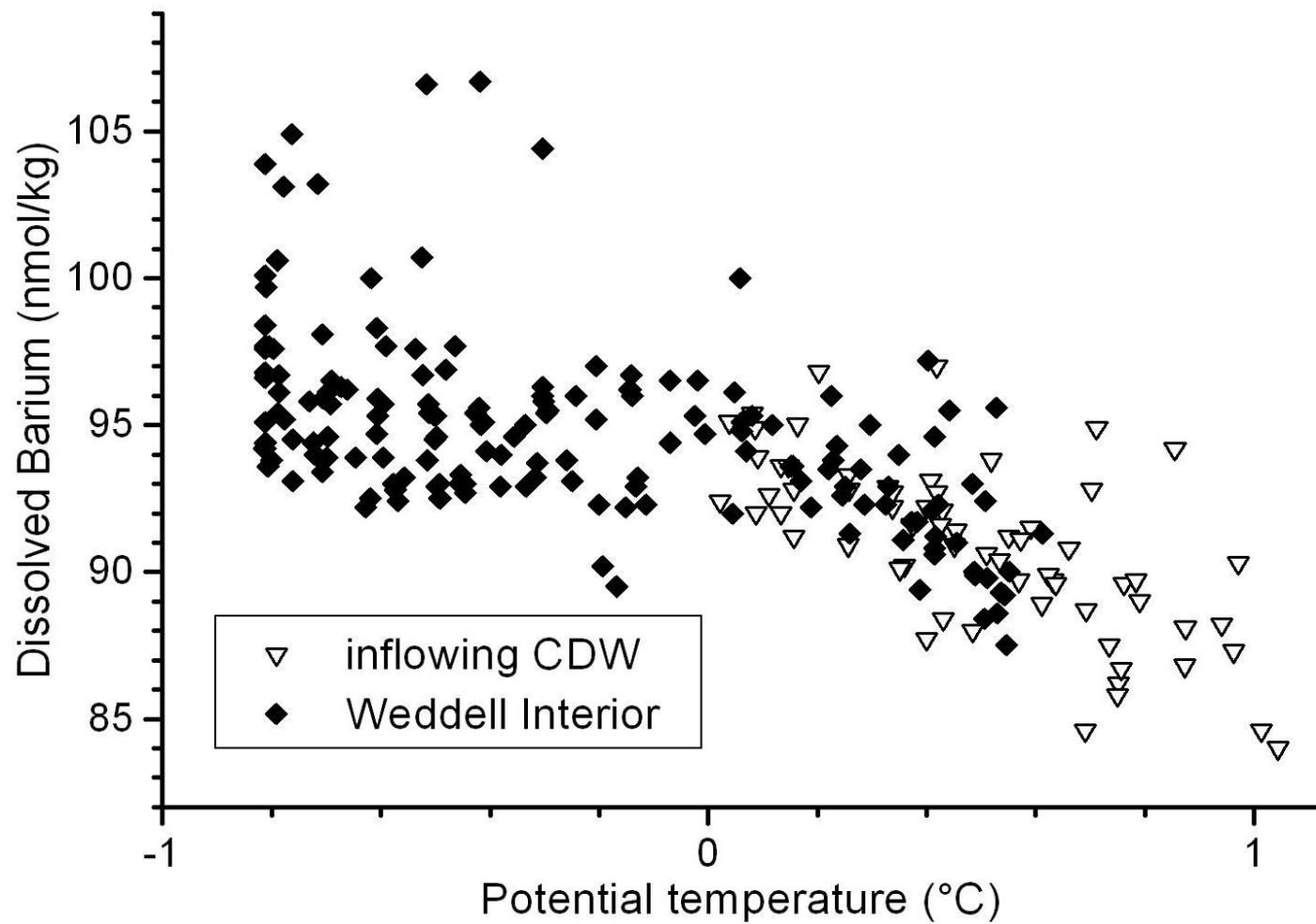


FIGURE 9