**Comment on bg-2021-42**

J.K.B. Bishop (Referee)

Referee comment on "Early winter barium excess in the Southern Indian Ocean as an annual remineralisation proxy (GEOTRACES GIPr07 cruise)" by Natasha René van Horsten et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2021-42-RC3, 2021

Review. van Horsten et al. "Early winter 1 barium excess in the Southern Indian Ocean as an annual remineralisation proxy".

The authors describe particulate Barium, O2, and potential density profile data from 7 stations in the Southern Ocean along from 59°S to 41°S crossing the Antarctic polar front (51°S) along 30°E south of Africa during GEOTRACES GIPr07 (in early wintertime conditions, June 28-July 13). This is a hard to get and interesting data set. The hypothesis is that since particulate barium should have only a short residence time (days to weeks) in the water column the inventory of particulate Ba would be far lower at times of low productivity that at other times of the year. The authors report particulate Ba concentrations as high as seen in other seasons and infer an active biological carbon pump year-round. The stocks are regressed against annual mean primary production. Comparisons are made with other data sets from the Southern Ocean.

What I like about the work is the heroic effort to achieve sampling in the wintertime and the excellent primary data arising from the expedition. Also, the goal of finding the correct transfer function relating the inventory of particulate barium in the mesopelagic (an indicator of export) to remotely sensed biomass or primary productivity would be a big plus.

That said, the paper falls short of its goals. The regressions in Figure 3, and manuscript discussion provide no insight. The data south of the polar front are aliased by cloud obscured retrievals of surface chlorophyll and primary productivity (See e.g., Ocean color monthly composites) and fall on a different slope than north of the PFZ. The STZ station is an outlier. The discussion does not sufficiently unify these divergent observations.

Response: We thank Pr. Jim Bishop for his review of our manuscript.

Please see below our responses to the revisions and comments (in blue) and the excerpts from the revised manuscript (in red).

We agree that remotely sensed PP does have inherent issues, as for any scientific methodology, that being said, we have confidence in our data as we made use of OC-CCI data which integrates all available sensors. This approach increases the chance of accurate measurements compared to a single sensor approach.

We checked the percentage of valid pixels for all stations of the compilation dataset in order to prove that remotely sensed data south of the polar front (82 ± 29 %; mean ± SD, n = 488) is as valid as north of the polar front (90 ± 20 %; mean ± SD, n = 370). This information has been added to the manuscript under section 2.5.

In order to assess the validity of the remotely sensed PP data and demonstrate no meridional bias across the SO, the percentage valid pixels were calculated for data north (90 ± 20 %; mean ± SD, n = 370) and south (82 ± 29 % mean ± SD, n = 488) of the PF.

Reflecting on other reviewer comments, I am convinced that a more comprehensive analysis of the data (now abundant) from multiple projects need to be considered. I am sure that everyone referenced would have data to share.

Response: In the initial manuscript, the $Ba_{xs}$ data were plotted against satellite-derived PP, integrated over months prior to sampling. At the time of previous cruises (e.g., INDIGO 3, ANT X/6 and EPOS 2, as suggested by the two other reviewers), there was no remotely sensed PP data available. The PP data, when available, were measured during the cruise and are not representative of integrated PP over months preceding the study. This is why these data were not initially included in our compilation.

Nevertheless, the mesopelagic $Ba_{xs}$ stock (μmol $m^{-2}$) is now plotted against day of year sampled (Figure 4, see below) in the revised manuscript, including the INDIGO 3, ANT X/6 and EPOS 2 data. However, as stated in the figure caption and the main text, these data must be considered with caution because these samples were not digested using HF. This can lead to an underestimation of aluminium concentrations and an overestimation of $Ba_{xs}$, where there are possible significant lithogenic inputs (e.g., close to Antarctica and downstream of the Drake Passage).

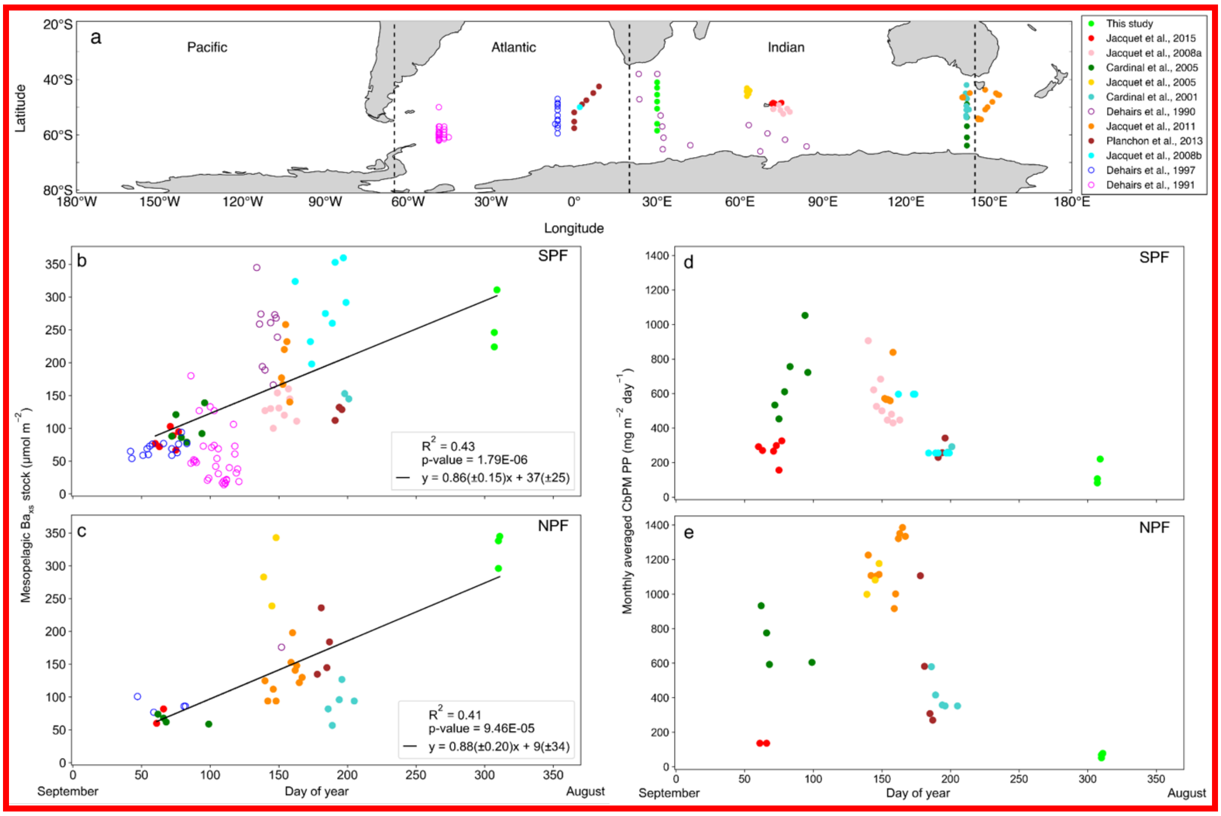


**Figure 4: (a) Positions of $Ba_{xs}$ observations compiled from all known SO studies, on a cylindrical equal-area projection of the SO, the three SO basin cut offs are indicated by the dashed black lines, from left to right, Pacific, Atlantic and Indian. Integrated mesopelagic $Ba_{xs}$ stock plotted against day of year sampled, with the 1st of September set as day 1, for all available literature data and winter data from this study. Data was split into two zones using the Polar Front (PF) to divide the SO; (b) South of the PF (SPF) and (c) North of the PF (NPF). Monthly averaged remotely sensed PP plotted against day of year, for locations and dates of the SO compilation dataset and winter data from this study; (d) SPF and (e) NPF. Open circles are data points from studies which did not use HF in the particulate sample digestion procedure, regressions did not include these data.**

I echo a need for a fuller hydrographic and dissolved phase framework for data interpretation – the supplemental data are very sparse.

Response: The hydrographic data was originally available on an ftp site (address given on page 19, line 30). Unfortunately, we have been made aware of problems with the ftp site and we apologize for that.

Temperature, salinity and nutrient data have now been included in the supplementary as Table S5. Unfortunately, no dBa data are available (nor were samples collected for this parameter).

There are some issues: (1) methodology: bottle sampling and the missing large particle fraction,

Response: We are aware of the differences in sampling systems. Indeed, sampling spigots on Go-Flo bottles are located 4 cm above the bottom of the bottle, which precludes the extraction of water below that level, potentially leaving behind particles that settle below the point of extraction. Strategies to avoid, minimize, or account for these biases have been discussed (e.g., Planquette & Sherrell, 2012) and are recommended in the GEOTRACES cookbook protocols, which we strictly followed.

Moreover, all the data we are comparing have been generated from samples collected with bottles, not in-situ pumps making the comparison less biased in this aspect.

This is now included under section 2.3 of the revised manuscript.

Volumes of 2 to 7 L of seawater were filtered from the GO-FLO bottles onto acid-washed polyethersulfone filters (25 mm diameter, Supor, 0.45 µm pore size), mounted on swinnex filter holders, for pBa and pAl analyses. Filters were mounted in line on the side spigot of each Go-Flo bottle. Furthermore, bottles were mixed 3 times before filtration, as recommended by the Geotraces protocols. Although the large fast sinking fraction of particles may be under sampled by using bottles (Bishop and Edmond, 1976; Planquette and Sherrell, 2012), comparing data that were generated using the same, internationally validated sampling systems and protocols (Cutter et al. 2017) as we do in this study, minimizes the potential biases.

and (2) the hypothesis of expected low wintertime concentrations is premised on particle sinking rates that are far too high (50 m $d^{-1}$) for the micron sized particles that comprise the bulk of suspended barite (sinking speed ~0.1 m $d^{-1}$).

Response: The hypothesis of expected low wintertime concentrations was taken from literature (Jacquet et al., 2008b, 2011).

The sinking speed of 50 m $d^{-1}$ was referring to the sinking of aggregates from the surface layer, and not to the sinking speed of suspended barite. This value is within the range of sinking speeds reported in the literature for sub millimetre sized aggregates (50 - 100 m $d^{-1}$: Riebesell et al., 1991; 50 - 430 m $d^{-1}$ around South Georgia: Cavan et al. 2015; mean of ~ 100 m $d^{-1}$ in the Southern Ocean as reviewed in Laurenceau-Cornec et al., 2015; 10 - 150 m $d^{-1}$: McDonnell and Buesseler, 2010).

The sinking rates were used to estimate the maximum time needed by sinking aggregates to exit the mesopelagic zone, i.e., 1000m depth:

time = 1000 m / 50 m $d^{-1}$ = 20 days

With a mean current speed of 0.2 m $s^{-1}$ (Ferrari and Nikurashin, 2010), aggregates sinking through the mesopelagic zone (above 1000 m depth) in 20 days would have been displaced a maximum of 346 km eastward, towards the location of stations sampled for mesopelagic $Ba_{xs}$:

$0.2\ m\ s^{-1} \times 3600 \times 24 = 17280\ m\ d^{-1}$

$17280\ m\ d^{-1} \times 20$ days = 345 600 m = 346 km eastward

This distance was used to define the area of the sampling window where we estimated surface PP that was likely to have formed the aggregates that were further responsible for the release of the mesopelagic $Ba_{xs}$ signal measured within the mesopelagic zone.

The low sinking speed of suspended barite (~0.3 m $d^{-1}$, Sternberg et al. 2008), once produced in the mesopelagic layer, implies that the residence time of barite is indeed long, as suggested by Pr. Bishop in the last comment of the review. To sink from 300 m depth (~peak of production) to the bottom of the mesopelagic layer (1000 m depth), it would take (1000-300) / 0.3 = 2300 days, i.e., ~ 6 years. This supports our hypothesis, that the $Ba_{xs}$ signal in the mesopelagic layer may represent remineralisation activity over more than a few days to weeks, contrary to what was previously reported in SO studies (Dehairs et al., 1997; Cardinal et al., 2005; Jacquet et al., 2007, 2008a). It also further explains how mesopelagic $Ba_{xs}$ concentrations increase from spring to a maximum in winter (see new Figure 4b and c).

These explanations are now included in the text, and we thank Pr. J. Bishop for this comment that assisted us in clarifying this part.

The seasonal signal of PP over the growing season (Figure 4d and e) clearly shows that the highest values occur between January and February (day 125 to 175 of the year), thereafter steadily decreasing to minimal values in July (~ day 310 of the year, i.e., during our study). The mesopelagic $Ba_{xs}$ accumulation over time can, therefore, not be matched with the remotely sensed PP measured during the month of sampling.

This strongly suggests that the $Ba_{xs}$ signal is not directly linked to synoptic measurements of PP at the time of sampling. In order to investigate this hypothesis, for the first time, we compiled a SO mesopelagic $Ba_{xs}$ stock dataset with all available literature data including data from this study (Figure 4a, Table S3). The mesopelagic $Ba_{xs}$ stock was integrated over the $Ba_{xs}$ peak depth range (as identified in each study). As can be seen on the map of the compilation dataset (Figure 4a), these data points were collected in the three basins of the SO, over 20 years. Despite this diversity, a statistically significant accumulation of mesopelagic $Ba_{xs}$ with time, SPF and NPF (Figure 4b and c) is still observed. Mesopelagic $Ba_{xs}$ accumulates at a rate of 0.86 (±0.15) µmol $m^{-2}$ $d^{-1}$, SPF ($R^2$ = 0.43, p-value < 0.05, n = 43; Figure 4b), and at 0.88 (±0.20) µmol $m^{-2}$ $d^{-1}$, NPF ($R^2$ = 0.41, p-value < 0.05, n = 31; Figure 4c), with no statistically significant difference between the two zones (Welch's t-test = 0.24; p-value = 0.80).
A possible link between the integrated mesopelagic $Ba_{xs}$ stock and the corresponding integrated remotely sensed PP was assessed for all studies conducted after September 1997, when remotely sensed PP data became available. To do so, we first estimated that sub millimetre sized aggregates, in which barite crystals produced, would take ~ 20 days to sink down to 1000 m (considered as the bottom of the mesopelagic zone, in this study), using a sinking speed of 50 m $d^{-1}$ that corresponds to an average literature value (50 - 100 m $d^{-1}$: Riebesell et al., 1991 ; 50 - 430 m $d^{-1}$ around South Georgia: Cavan et al. 2015; ~ 100 m $d^{-1}$ in the Southern Ocean as reviewed in Laurenceau-Cornec et al., 2015; 10 - 150 m $d^{-1}$: McDonnell and Buesseler, 2010). Assuming a maximum surface current speed of 0.2 m $s^{-1}$ (Ferrari and Nikurashin, 2010), it was estimated that these aggregates would have originated, 346 km west from the station that was sampled for mesopelagic $Ba_{xs}$, ~ 20 days prior. Using this distance, the dimensions of the sample area were set with the southernmost station (TM1) of this study, where degrees of longitude cover the

smallest area. For the sake of consistency this sampling area was applied to all sampling locations of the considered dataset. The integrated remotely sensed PP (see section 2.5) was then averaged spatially, positioned 6° upstream longitudinally, and 1° latitudinally centred around each sampled station, in order to capture the surface PP that is assumed to translate to the mesopelagic remineralisation and $Ba_{xs}$ stock.
The seasonal signal for PP over the growing season (Figure 4d and e) clearly shows that the highest values occur between January and February (day 125 to 175 of the year), thereafter, steadily decreasing to minimal values in July (~ day 310 of the year, i.e., during our study). The mesopelagic $Ba_{xs}$ accumulation over time can, therefore, not be matched with the remotely sensed PP measured during the month of sampling. A possible relationship between $Ba_{xs}$ and surface PP was further investigated by considering longer timescales. Integrated remote sensing PP of the preceding bloom was calculated using the month of September prior to sampling as the start of the bloom. This is in general agreement with previous bloom phenology studies for this region (Thomalla et al., 2011). The PP was integrated up to one month prior to the sampling date of the study, taking into consideration time needed for export, aggregate formation, and barite crystal release through remineralisation (~ 1 month). When remote sensing data was limited due to cloud cover and low sunlight during winter months, specifically at the southernmost stations, all available data was used for the duration of the season.

A couple of issues further complicating review is simply the lack of any access to the more complete data sets from the cruise beyond those used in figure 2 or the partially complete data sets used in figure 3. The cruise data should be available as supplemental data and also submitted to the GEOTRACES archives and DOI traceable.

Response: Data was made available on the SOCCO ftp site (see page 19, line 30 of the preprint) but as stated before, we were made aware of issues with the ftp, and we apologize for this inconvenience. We have now included these data in two tables in the supplementary material, Table S3 for this study and literature data, and Table S4 for nutrients, temperature, and salinity data for this study. Our data will be submitted to the GEOTRACES IDP once published.

I think the fundamental logic flaw (see comments below) lies on page 12 in the discussion of inferred barite residence times in the mesopelagic. I don't see a major advance beyond referenced work and don't support publication of this paper with its present interpretive framework. I encourage the Authors to look again at the results in a larger framework.

Response: Although we agree that further interpretation of data was required to improve the manuscript and support the study, we also believe that this work does go beyond what has been previously published. This is to our knowledge the first $Ba_{xs}$ dataset obtained during winter in the SO and we also use all available SO data and link it to remotely sensed PP, which has not yet been done.

We have included a more extensive assessment of the data in the revised manuscript that we believe to be more convincing.

Figure 4 is not needed. It is out of place. There is room for more figures.... Some detailed comments follow.

Response: As the three reviewers agree on this point, we have decided to remove this figure from the revised manuscript.

P4 line 08, R2=0.83... This seems like a bad validation of the O2 results.

Response: The slope (0.94 ± 0.10), intercept (0.07 ± 0.51) and p-value ($7 \times 10^{-10}$), of the calibration regression indicate that although the correlation coefficient is not as high as could be expected ($R^2 = 0.83$), the calibration is still valid. The sensor had also been calibrated by the manufacturer less than a year prior to the cruise (August 2016).

With this in mind, we do not use any absolute values of dissolved $O_2$, instead, the shape of the $O_2$ profiles were used to support evidence of mesopelagic remineralisation and oxygen consumption, and how it is linked to the $Ba_{xs}$ profiles.

This is now clearly stated in the manuscript.

Temperature (°C), salinity and dissolved $O_2$ (µmol $L^{-1}$) profiles were measured by sensors (SBE 911plus) which were calibrated by the manufacturer within a year prior to the cruise. At each cast discrete seawater samples were collected and analysed onboard for calibrating sensor salinity (8410A Portasal salinometer, $R^2 = 0.99$) and dissolved $O_2$ measurements (Metrohm 848 titrino plus; Ehrhardt et al., 1983, $R^2 = 0.83$).

Decreases in dissolved $O_2$ concentrations at intermediate depths, together with $Ba_{xs}$ concentrations, were used to define the mesopelagic remineralisation depth range.

p 4 line 10. The Python language did not exist in 1982. Please fix sentence.

Response: This sentence has been corrected, with the publication referring to the calculation.

Temperature and salinity measurements were used to calculate potential density ($\sigma_\theta$; Gill, 1982) to characterise water masses sampled and to identify the mixed layer depth (MLD).

P 5. Lines 18-20. I assume this was an in-line filter, directly connected to the side spigot of the bottle. State what was done. Also, state whether or not the large sinking particle fraction would be sampled.

Response: Indeed, there was an in-line filter (Supor) directly connected to the side spigot of the bottle. Bottles were mixed prior to filtering with the in-line filter as recommended by the Geotraces cookbook. Strategies to avoid, minimize, or account for these biases have been discussed (e.g., Planquette & Sherrell, 2012) and are recommended in the GEOTRACES cookbook. We strictly followed these protocols. This is now clearly stated in section 2.3.

Moreover, all the data we are comparing is generated from samples collected with bottles, not in-situ pumps making the comparison possible with studies included in the compilation dataset. This is also now clearly stated.

Filters were mounted in line on the side spigot of each Go-Flo bottle. Furthermore, bottles were mixed 3 times before filtration, as recommended by the Geotraces protocols.

Although the large fast sinking fraction of particles may be under sampled by using bottles (Bishop and Edmond, 1976; Planquette and Sherrell, 2012), comparing data that were generated using the same, internationally validated sampling systems and protocols (Cutter et al. 2017) as we do in this study, minimizes the potential biases.

p 5. line 29. If varying volumes of water were filtered, the blank will not be a constant value. (Ba(filter)-blank(filter))/volume filtered. to get Ba and error should be the s.d/filter blanks / volume filtered. Or is this what you did? I think the calculation was done correctly as error bars vary in size. Please clarify methods.

Response: Yes, this is indeed what was done. Unused filters were used to subtract the blank contribution. This is now explained in section 2.3.

Unused blank filters and filters containing the samples were acid reflux digested at 130°C in acid-cleaned savillex vials using a mixture of HF and $HNO_3$ (both Ultrapure grade, Merck) solutions (Planquette and Sherrell, 2012).

Mean amounts (in nmol) of a given element determined in unused filter blanks were subtracted from the amounts in the sample filter then divided by the volume filtered.

ALSO please state the assumed particle size fraction that has been sampled. There is no evidence that bottles adequately sample the sinking particle fraction.

Response: As stated above, we are aware that bottles may under sample the large fast sinking fraction of particles. There are unfortunately, also other potential sources of discrepancy such as filtration pressure (Gardner et al., 2003; Liu et al., 2005), filter type (Bishop et al., 2012), breakage or leakage of phytoplankton and other cells (e.g., Collos et al., 2014), creation of particles (Liu et al., 2005). Unfortunately, no sampling method is assumed to be perfect. Comparing data that were generated using the same, internationally validated sampling systems and protocols, as we do, minimizes the potential biases

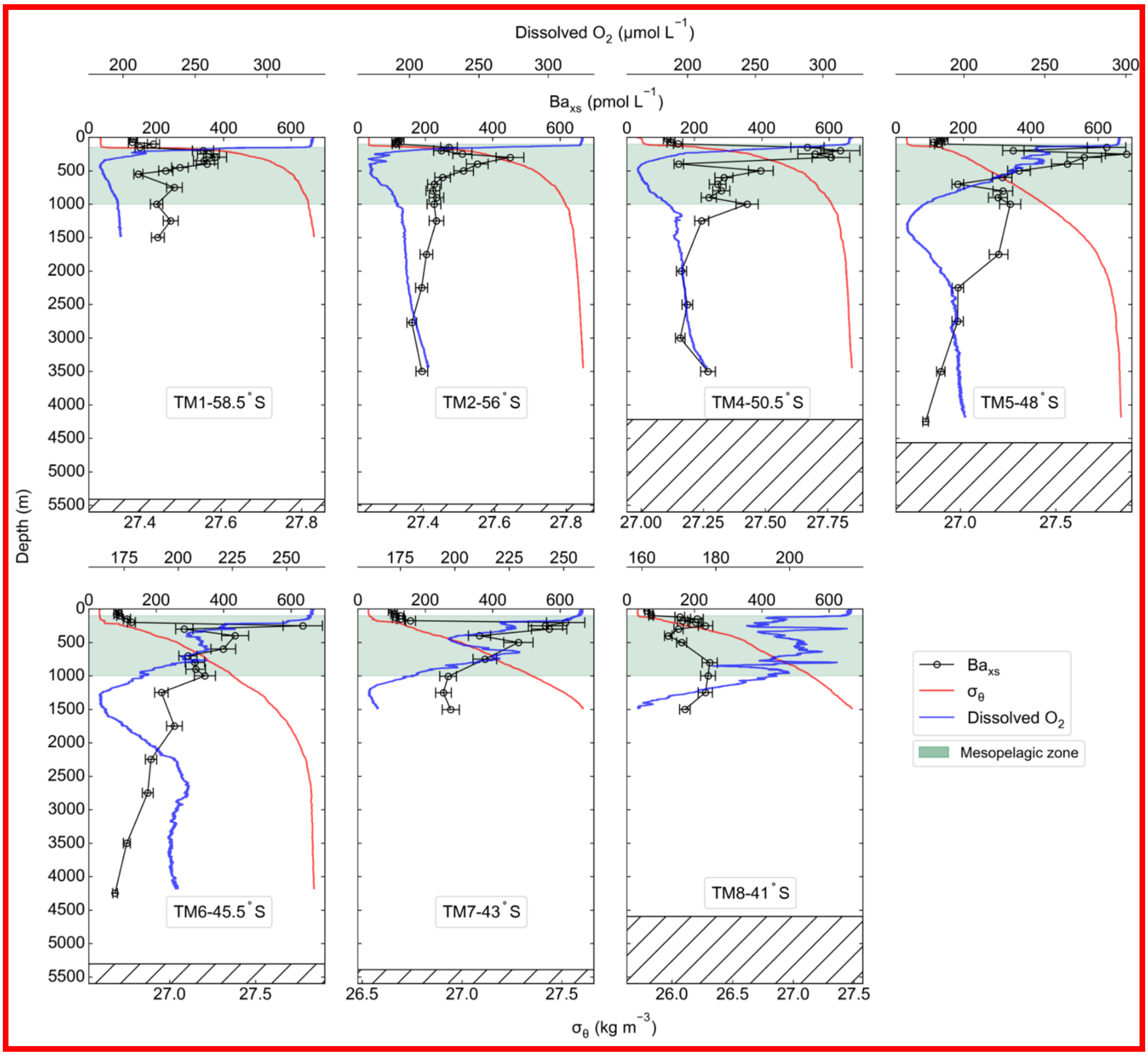
P 6 Line 63. "The data..." Which data?

Response: The integrated remotely sensed PP data. This is now clearly stated in the revised manuscript.

The integrated remotely sensed PP data were regridded to 0.25° spatially, using bilinear interpolation, and averaged monthly.

P9. Fig. 2: O2 scale too compressed to be useful. Authors should provide complete data as supplemental (not just pAl, pBa, Baxs) and submit as soon as possible to GEOTRACES. Include T, S, sigma theta, o2, nutrients, dissolved Ba...

Response: Figure 2 has been amended to widen the dissolved $O_2$ scale. The temperature, salinity, and nutrient data has now been included in the supplementary (Table S5). We intend on submitting the complete dataset to GEOTRACES IDP once published.




p10... .Lines 31-33. “When taking into account....”. There is something wrong with this sentence.

Response: This sentence has been rephrased

A noticeable difference between profiles sampled early in the bloom season (Dehairs et al., 1997; Jacquet et al., 2015) versus those sampled later (Cardinal et al., 2001; Planchon et al., 2013), are the contrasted concentrations of Ba$_{xs}$ in the surface mixed layer.

p 10. Line 34. Very high values can be associated with Rhizosolienia blooms (Bishop, 1988).

Response: We agree that very high values can be associated with Rhizosolienia blooms, but also in most cases when productivity is high, specifically in the SO.

P 12. Lines 84 & 85. Line 94-95... “Residence time of barite in mesopelagic days to weeks. & Particle sinking speeds of 50 m d$^{-1}$”. The large particles comprising the flux do sink that fast; however, the subsurface barite is produced by fragmentation of these particles as they sink. The resulting micron sized barites sink at 0.1 m d-1. Thus, the premise of decay to background on the time scale of days to weeks is invalid. Barites in the mesopelagic would have a residence time (by sinking) of hundreds of days – if not years. The sink for these barites is dissolution and reaggregation. As grazing is reduced in the wintertime then dissolution and sinking would dominate.

Response: As explained at the beginning of the review, the sinking speed of 50 m $d^{-1}$ was indeed referring to the sinking of aggregates from the surface layer, and not to the sinking speed of barite crystals.

As stated above, the low sinking speed of suspended barite (~0.3 m $d^{-1}$, Sternberg et al. 2008), once produced in the mesopelagic layer, indeed implies that the residence time of barite is longer than a few days to weeks as generally postulated in the literature for the SO (Dehairs et al., 1997; Cardinal et al., 2005; Jacquet et al., 2007, 2008a). To sink from 300 m depth (~peak of production) to the bottom of the mesopelagic layer (1000 m depth), it would indeed take (1000-300) / 0.3 = 2300 days, i.e., ~ 6 years, without considering time needed for reaggregation and redissolution. This supports our hypothesis that the $Ba_{xs}$ signal in the mesopelagic layer represents remineralisation activity over more than a few days to weeks, as previously reported, and is not directly linked to synoptic measurements of PP during the same cruise. It also further explains how mesopelagic $Ba_{xs}$ concentrations increase from spring to a maximum in winter (see new Figure 4b & c) and suggests that the background value has to be measured at the transition between winter and spring, just before biological activity resumes.

These explanations are included in the text of the revised manuscript.

I've not addressed the detailed discussion further as this point and invalidates the key conclusion of the authors.

Response: We hope that our detailed responses and extensive revisions will convince Pr. Bishop of the validity of our hypothesis and manuscript.

jim Bishop (UC Berkeley).

p.s. have a look at Bishop 1989 (attached - since it may be hard to find). The mapped representation of barite stocks is virtually the same as sampled here.

Please also note the supplement to this comment:

https://bg.copernicus.org/preprints/bg-2021-42/bg-2021-42-RC3-supplement.pdf