

On the barium-oxygen consumption relationship in the Mediterranean Sea: implications for mesopelagic marine snow remineralization

Authors: Jacquet et al.

Response to Referee #1

Jacquet et al. present new data of Baxs concentrations, O<sub>2</sub> consumption rates from direct measurements and prokaryotic heterotrophic productions (PHP) from the ANTARES station in the Mediterranean Sea. The aim of this research is to investigate the connections between these three parameters (Baxs concentrations, O<sub>2</sub> consumption rates and PHP) in order to validate the Baxs-O<sub>2</sub> consumption transfer function first proposed by Dehairs et al. (1997) in the Southern Ocean. The authors found higher Baxs concentration associated to deeper PHP and to greater O<sub>2</sub> consumption rate. Finally, they found a relatively good agreement between O<sub>2</sub> consumption rates estimated by the Ba<sub>xs</sub> transfer function from the Southern Ocean (Dehairs et al., 1997) and by direct measurements, confirming the use of this transfer function in the Mediterranean Sea.

Previous studies used Ba<sub>xs</sub> as a tracer of O<sub>2</sub> consumption and thus as a tracer of POC remineralisation, but they either assumed the universality of the Southern Ocean transfer function (e.g. Cardinal et al., 2005) or proposed new transfer function without direct O<sub>2</sub> consumption measurements (e.g. Lemaitre et al., 2018). It is therefore of interest to investigate the conformity of this transfer function by directly measuring O<sub>2</sub> consumption rates and PHP. For that reason, the findings of this study are highly valuable for the community.

Reply: great!

However, the authors report data from only one station (only one data added in both the PHP/Ba<sub>xs</sub> and JO<sub>2</sub>-Ba<sub>xs</sub>/JO<sub>2</sub>-opt correlations) which is weak to support their conclusions. Statistical analyses (p-values, errors on the slopes, etc) are needed.

Reply: we agree that statistical analyses are needed to reinforce conclusions.

Also, a direct comparison of the Ba<sub>xs</sub>/JO<sub>2</sub>-opt correlation from this study (where the authors show 4 data points; Fig. 3a) with the one proposed by Dehairs et al. (1997) in the Southern Ocean would be very useful and more convincing, to me.

Reply: we added Dehairs data.

Many details are also missing in the methods to really understand how Ba<sub>xs</sub> concentrations, O<sub>2</sub> consumption rates and PHP were measured. Moreover, I would appreciate if there was a discussion about the variations found between ANTARES, PAP and DYFAMED stations, about the differences observed between the Southern Ocean and Mediterranean Sea correlations (Baxs background for example) and about the implications of this study in the water column C budget of the Mediterranean Sea. Finally, all the data (Ba<sub>xs</sub> concentrations, O<sub>2</sub> consumption rates and PHP) should be presented in a Table.

Reply: suggestions are clearly made in the specific comments to improve results presentation and discussion. We'll do our best to answer each of them in the revised ms.

Overall, the manuscript is well written and will be a good fit for publication in Biogeosciences, but considering the lack of details and comparisons, considering the relatively large error bar associated to the JO<sub>2</sub>-opt, and considering that this study adds only one data point to the JO<sub>2</sub> correlation, I would suggest the authors to soften their conclusion on the 'universal validity' of the Dehairs's transfer function.

Reply: we should indeed moderate our conclusion.

## A. Specific comments

### 1-Introduction

In general, this section should be developed and should mention all the studies on Baxs concentrations as a tracer of POC remineralisation but also all the recent studies investigating barite formation and the role of barite on the Ba cycle

Lines 55-61: Please develop the paragraph about the use of Baxs as a geochemical proxy: more studies have worked on Baxs in the past (e.g. Bishop, 1988; Collier and Edmond, 1984; Ganeshram et al., 2003; Gonzalez-Munos et al., 2003). Moreover, there are some recent studies that should be mentioned/discussed about lab experiments and Ba isotopes giving extremely interesting new insights on the formation of barites and on their role in the Ba cycle in the ocean. Please, see for example the studies of Martinez-Ruiz et al. (2018, 2019), Horner et al. (2015), Cao et al. (2020), Hsieh et al. (2017).

Reply: the present ms. is a “short” paper focusing on the link between Ba and oxygen consumption and on the comparison between SO and MedSea data to test Dehairs equation. That’s why we don’t go into any more details on isotopes or lab experiments for examples. However, as further requested, few references have been added in the ms.

Lines 66-68: Lemaitre et al. (2018) do not use the Southern Ocean transfer function proposed by Dehairs et al. (1997). These authors proposed a new function specific to the North Atlantic. Consequently, they (sort of) ‘revised’ the validity of this transfer function at least for the GEOVIDE study area. You could also use this study as an additional reason to check the validity of the Southern Ocean transfer function in the Mediterranean Sea.

Reply: discussion on the relationship reported in Lemaitre et al. is now mentioned and discussed.

Line 67: Instead of Lemaitre et al. (2018), you could also cite Cardinal et al. (2005), Dehairs et al. (2008), Jacquet et al. (2008 a, b, 2011, 2015), Planchon et al. (2013).

Reply: ok added

### 2-Sampling and Analyses

This section must be developed. The reader needs more information and details on how and how well you measure Baxs, O<sub>2</sub> consumption rates from optodes and prokaryotic heterotrophic productions. Also, please show all your new data in Figures and Tables. Reply: ok for references and Figures. Tables are not necessary.

Line 115: Please show the full Baxs, pAl and bio Ba depth profile, i.e. from surface to 2000m, in Fig.2a. This will also confirm that the Baxs background stays at around 130pM at depths > 500m.

Reply: sampling was done in the upper 1000 m. We added it section 2.2.

Lines 115-116: If I am correct, the samples used for the data presented in Fig. 2a have not been collected on the same day or exact location. Please prove that there was no evolution of water mass or biology between each sampling. If there was any change, could this influence your Baxs or pAl concentrations?

Reply: Thirteen depths between surface and 1000 m were sampled by combining different casts sampled closeby in time and space (total of 28 samples) and having similar potential temperature – salinity data profiles. No major change in water mass characteristics occurs over the 3-day sampling period (Figure 1c). If there was any change, the risk is that concentrations would reflect another Ba-Al story from a different water mass, e.i. they could reflect an “external” input (lateral, advection, etc...) of particles, or a no local-remineralization-linked signal.

Lines 120-121: Please give the precision and accuracy of your analyses.

Reply: ok added

Lines 124-125: 'sea-salt particulate Ba contribution was found negligible'. What is negligible? Please give numbers.

Reply: done - <0.1%

Line 125: Give more details on the Ba/Al ratio you are using to correct the lithogenic fraction. I suppose it is from the UCC but how does this value compare to the lithogenic inputs at ANTARES? This station is relatively close to the coast and is likely subject to lithogenic inputs, it is therefore important to be sure about the Ba/Al ratio used to correct the lithogenic fraction. Without that, your estimation of Baxs concentrations may not be correct. For comparison, Lemaitre et al. (2018) do not take into account data from two stations where the pBa-litho accounts for 28 and 44% of total Ba. At ANTARES, the Ba biogenic fraction range from 50 to 80%, meaning the lithogenic fraction is not negligible.

Reply: ok we added details on the litho-Ba fraction calculation. We discuss the range of biogenic Ba contribution in session 3.1. The litho impact is negligible at mesopelagic depths (see the grey area in fig. 2a) where it remains <20%. Ba is mostly biogenic at these depth (>80%).

Line 126: How did you determine the standard uncertainty? From the RSD given by the Element for Ba? From error propagation, taking into account the RSD of Ba and Al?

Reply: yes, we obtain it by error propagation (by taking into account both RSD, uncertainties on Al/Ba ratio, etc..)

Lines 131-136: There is no reference at all in this paragraph – it is thus difficult to understand the technic for someone who is not familiar with this. Please explain, at least briefly, how you measure O<sub>2</sub> concentrations with this technic and how you calculate the O<sub>2</sub> consumption rates – an equation might help? Can you prove the precision/accuracy of this method? I suppose you need relatively precise measurements to determine an O<sub>2</sub> consumption rate. However the errors associated to this measurement and to the final calculation seem high (Fig. 3), why?

Reply: We re-wrote this paragraph. Errors bars seem high because we have 2 optodes per depth. We observe higher variability at upper-mesopelagic depths. Unfortunately we were not able to carry out more than 2 duplicates per depth. We mention it in the ms.

Lines 137-142: Same here, please give more details on the protocol you use for determining the PHP. Why do you use 3H-leucine? How do you then calculate the PHP (equation)?

Reply: the protocol is given in Tamburini et al. (2002). We refer to this paper for detail on protocol and equations.

### 3-Results and Discussion

The authors should give more details to convince the reader about the validity of this Baxs-JO<sub>2</sub> function in the MedSea. A direct comparison of the slope of the transfer function you obtain here (Fig. 3a) with the one from the Southern Ocean would be helpful. Some statistics would also help. Moreover, I think this section would get more interesting if there was some comparison with the literature and some explanations on why some of your results slightly differ compared to those of other study areas (essentially, more explanation on the story of the MedSea data – not only about the use of Baxs in this area to trace O<sub>2</sub> consumption). The figures could be clearer as well.

Ok

Line 149: 'pAl concentrations are low...' 170nM is not low! On the contrary, it clearly shows a lithogenic input and this makes your Baxs estimations doubtful as the lithogenic correction may not be perfectly constrained. How much is the pBa lithogenic fraction in the depth layer that is interesting for this study (i.e. 100-500m)? Can it be considered as negligible? If yes, why? Please see my previous comment about the Ba/Al ratio and discuss more about the lithogenic correction at

ANTARES station.

Reply: pAl are not low but It is the global lithogenic contribution to the total Ba signal that is low. We corrected the sentence. 170nM was measured in surface. As reported above, we consider that the contribution is negligible at mesopelagic depths. For comparison, pAl measured during the PEACETIME cruise (excluding dust deposits) are in the same range of values at mesopelagic depths as reported here.

Line 156: You mention the pBa biogenic fraction in the interested depth layer is >80% but is it high enough to be assured of a good Baxs estimation? What is the error associated to this correction (this could go to the methods section)?

Reply: yes, it is what is usually assumed. We added details on this correction in the method section.

Lines 157-160: How do you explain the difference between the Baxs background observed in the Southern Ocean and in your study? For example, Lemaitre et al. (2018) also observed a Baxs background at 180pM in the North Atlantic. What is different in the MedSea?

Reply: the difference in Ba background is linked to the saturation level in the MED which is very low compared to other sectors. We discuss it in session 3.1

Lines 165-166: How do you explain the difference of adsorption between ANTARES and DYFAMED stations? Is it related to different bloom timing or intensity?

Reply: it could also be related to a different composition of phytoplankton material (different species)

Lines 168-169: Please show the full depth profile, i.e. from the surface to 2000m, in Fig. 2a. That would be useful to clearly see the background level.

Reply: sampling was done in the upper 1000 m at ANTARES. We added it section 2.2

Lines 169-170: At DYFAMED station, Baxs concentrations seem to keep decreasing for depths >600m, why is it not stabilised at 130pM?

Reply: The Ba background corresponds to a range of value around which Ba concentrations oscillate at depth.

Lines 180-183: Please, discuss the result of the PAP station if you present it. It is below the trend, why? Moreover, what is the p-value of this trend? Is it a significant correlation with and without the new ANTARES and PAP data? Is it possible to add data from DYFAMED?

Reply: ok. Results at the PAP site reflect a similar situation as observed during KEOPS2 at Plateau site and in a meander of the polar front area (not show in Figure 2b), indicating the temporal evolution and patchiness of the establishment of mesopelagic remineralization processes within a same area. The correlation is reported for KEOPS1, and confronted to KEOPS2, PAP and ANTARES, as given in Jacquet et al. 2015.

Line 184: Are these PHP profiles similar to the one at ANTARES station? Could you plot them all in a figure and add the ANTARES data in a table?

Reply: PHP profiles will add nothing to discussion, because it is ratios of integrated values that are important to be confronted (gradients).

Lines 185-189: 'Indeed, mesopelagic Baxs...' These lines repeat your sentence lines 181-183 '..indicating higher DWA Baxs in situations where a significant part..'. Please re organise this section to avoid repeating things.

Reply: ok done.

Lines 189-190: 'Our MedSea results are located..'. You provide only one new result from ANTARES

station, please change the plural to singular form in this sentence. Also, this sentence repeats what you say lines 180-181. Maybe you should delete it.

Reply: ok. We reformulated the sentence.

Lines 190-195: Please develop this section according to the new literature (e.g., Martinez-Ruiz et al., Horner et al., Cao et al., Hsieh et al..) and find a transition with your previous sentence.

Reply: references are added. However, according to personal data (a similar work as Martinez-Ruiz et al. we performed during the BONUS SO cruise) and following Martinez-Ruiz et al., (2018, 2019), it is still unclear, to our understanding, whether barite formation at mesopelagic depths is (directly or indirectly) bacterially induced or bacterially influenced.

Line 200, Fig. 3a and b: It seems that there is a mistake with the units. They do not correspond to those in Jacquet et al. (2015), would it not be mmol/m<sup>2</sup>/d instead? If I am correct, please change all your JO<sub>2</sub> data in umol/L/d and compare the slope you obtain in Fig. 3a with the one from the Dehairs et al. (1997).

Reply: data presented in Jacquet et al. (2015) are integrated values (from 3 to 4 measurements). Each point corresponds to a station. At ANTARES we have only one station (and 4 measurements). This explains the difference of unit. We added a Fig 3c to compare results with Dehairs data;

Lines 201-203: I agree this is a very interesting feature confirming your background Baxs concentration! Could this result give an insight on why there is a different Baxs background in the MedSea compared to other areas?

Reply: as reported above, the difference in Ba background is linked to the saturation level in the MED which is very low compared to other sectors. We discuss it in session 3.1

Line 209: Why do you use a factor of 17450 here while it is 17200 in Jacquet et al. (2008) or Lemaitre et al. (2018)?

Reply: according to data presented in Dehairs et al., 1997, the ratio is 17450. We added it in Fig3c. No idea why 17200 is used elsewhere (we removed points in the correlation?).

Lines 214-219: There is a large error bar associated to your ANTARES data point for JO<sub>2</sub>-opt (Fig. 3b), why? I agree that considering this large error bar, your data fits the trend observed during KEOPS. However, this large error bar and the poor distributions of the data points (either low JO<sub>2</sub> for KEOPS or high JO<sub>2</sub> for ANTARES) make this correlation too weak to state that there is no difference between both regions. What is the p-value of this correlation with and without ANTARES? Is it possible to add data from PAP or DYFAMED stations? I would be more convinced by a comparison of your Baxs-JO<sub>2</sub> trend with the one of the Southern Ocean. For now, the slope in Fig. 3a is very different from the one of the Southern Ocean (100 versus 17450). After fixing the unit problem, please discuss about this comparison.

Reply: data are not available for PAP or DYFAMED (no JO<sub>2</sub> measured). As reported above the error bar is obtained from error propagation following Dehairs equation. Comparison with Dehairs's data is given in Figure 3c.

Line 226: Please indicate what is Z in this study.

Reply: ok 175-450 m.

Lines 228-229: Please give the range of the fluxes from the literature and discuss them according to the one you estimate at ANTARES.

Reply: done

Lines 239-241: Expand a bit the discussion here. How does your study contribute to the MedSea carbon budget? Does it help balancing the water column budget?

[Reply: done](#)

## **B. Line notes**

Abstract:

Lines 25-27: These are not new observations/conclusions. Please make it clear here that you are confirming what has been observed earlier in another area (Jacquet et al., 2015).

[Reply: done](#)

Line 25: 'higher Baxs (409 pM; 100- 500 m) [occurs] in situations where integrated PHP (PHP100/500= 0.90) is located deeper'

[Reply: ok added](#)

Line 26: 'higher Baxs [occurs] with increasing JO2-Opt'

[Reply: ok added](#)

Introduction:

Line 63: 'highly resolved, precise..' seems a bit exaggerated as a sampling resolution of 50m depth is good but not high for me and I suppose the technics may be more precise today compared to 1997.

[Reply: ok deleted](#)

Line 70: I would delete this sentence as it repeats the sentence line 68 ('Yet its validity has never been tested..') and it separates two linked sentences.

[Reply: ok deleted](#)

Line 70: 'These advancements..' refer to the results of Jacquet et al. (2015) I suppose? Please make it clearer.

[Reply: ok](#)

Line 83: Which fluxes are you referring here? Primary production, export, remineralisation?

Line 83: Please give a range of the fluxes determined by Santinelli et al (2010) and Ramondec et al. (2016). [Reply: remineralization and fluxes are given in discussion](#)

Methods:

Line 111: I would name this whole section 'Methods' and would name the sub-section 2.2 'Sampling and Analyses'

[Reply: OK done](#)

Line 107: 'and [(3)] Levantine Intermediate Water...'

[Reply: ok added](#)

Line 117: 'total digestion of filters using a [concentrated] tri-acid mixture..'

[Reply: ok added](#)

Line 130: 'The background (or residual value) is considered as "preformed" Baxs at zero oxygen consumption left over after transfer and partial dissolution of Baxs produced during degradation of previous phytoplankton growth events. [The background is set at 130pM in this study].'

[Reply: ok added](#)

Results and Discussion:

Line 145: Maybe modify to '[Particulate Baxs] vertical distribution' to avoid any confusion for the reader.

Reply: ok done

Line 160: 'For comparison, the [Baxs] background value...'

Reply: ok added

Line 173: 'the particulate excess Ba (>BKG)' is confusing for me. You never expressed Baxs like this before. Please keep the same wording all along the manuscript, maybe modify to 'The maxima Baxs concentrations are centred..'

Reply: ok modified

Line 174: 'in this depth layer' instead of 'at these depths'

Reply: ok modified

Lines 174-175: Explain what is the depth-weighted average, as you did for example in Jacquet et al. (2015): 'i.e. the Baxs inventory divided by the depth layer considered Z'.

Reply: ok added

Line 175: 'over the 100-500m depth layer' instead of 'this entire depth layer'. It will avoid any confusion with Fig.2b and all the different depth integrations.

Reply: ok

Line 176: Figure 2b shows [the] column-integrated PHP at 100m over the [one] at 500m (PHP100/500). Our PHP100/500 ratio at ANTARES station is of 0.90 and is compared to results obtained during KEOPS1...'

Reply: ok modified

Line 180: 'ResultS at the ANTARES..' Are there more than one result? On Fig.2b, there is only one data from ANTARES station.

Reply: yes there is only one point because it is an integrated data for 1 unique station

Line 181: '...follow the trend previously reported in the Southern Ocean [(blue dashed line in Fig.2b; Jacquet et al., 2015)]...'

Reply: ok

Lines 181-182: Please make it clear that the ANTARES data confirms the conclusions found in Jacquet et al. (2015) and that it is not a new conclusion.

Reply: ok done

Line 204: '[In Figure 3b,] we applied..'

Reply: ok added

Line 217: 'Overall, our results indicate [a] similar Baxs-JO2 relationship..'

Reply: ok added

Lines 257-258: You also show the DYFAMED station in this figure. Please mention it is for comparison and cite Sternberg et al. (2008).

Reply: ok added

Line 258: '[c] potential temperature-salinity-depth plots...'

Reply: ok

Line 269: Could you integrate the DWA Baxs between 100-500m as well (to match with the PHP

integration)?

Reply: it is a mistake in the text; integration is done at 100m and not 150m. We corrected it.

Lines 269-271: 'Regression of the same ratio is reported for KEOPS1 ([light blue symbols;] out plateau stations) and KEOPS2 ([dark blue symbols;] Southern Ocean; Jaquet et al., 2015) and #DY032 ([red square;] PAP station, NE-Atlantic; pers. data) cruises.'

Reply: ok

Lines 269-271: Please clarify what the blue dashed line represents. Is it from Jaquet et al. (2015) or does it take into account all data points including the new ones from ANTARES and PAP stations?

Reply: It is KEOPS2 only. We specified it in Fig2.

Line 275: mmol/m<sup>2</sup>/d instead?

Reply: no, it is the correct unit umol /L/d

Lines 275-276: '..optode measurements (this study; [green square]), dark community respiration DCR (winkler titration; [red triangles]; JO<sub>2</sub>-DCR; Jaquet et al., 2015; KEOPS1)'

Reply: ok added

Lines 277-278: It is not clear if you speak about the y-axis or the black line. I propose to re write as '...and [Baxs contents (Southern Ocean transfer function from Dehairs et al. (1997); JO<sub>2</sub>-Ba]. The black line corresponds to the correlation found in Jaquet et al. (2015)'. If this is correct, please also mention that this correlation excludes some data points from A3 and E stations.

Reply: ok modified

Figure 2a, in the legend: Ba[<sub>xs</sub>] ANTARES; Ba[<sub>xs</sub>] DYFAMED; [p]Al ANTARES. Reply: ok And please show the full depth profile (until 2000m). Reply: profiles are limited to 1000m depth.

Figure 2b: Please indicate from where the blue line comes from. And indicate the p-value.

Reply: done

Figure 3a: Please check the units and indicate JO<sub>2</sub> in umol/L/d. And show the trend from Dehairs et al. (1997) in the Southern Ocean. Give the p-value.

Reply: units are correct. Done

Figure 3b: Please indicate JO<sub>2</sub> in umol/L/d. Also, indicate from where the black line comes from. And indicate the p-value.

Reply: ok

### C. References:

Reply: thank you for the references