

*We would like to thank Reviewer #2 for his/her comments and suggestions that have improved the initial manuscript.*

Comments and recommendations from referee

#### **General comments**

The manuscript “Carbonate system buffering and the water masses of the Southwest Atlantic sector of the Southern Ocean during February-March 2008” by González-Davila et al. presents an interesting and important study of the carbonate system and the sensibility of the buffer capacity due to changes in the addition of carbon dioxide (CO<sub>2</sub>), as an effect of increased CO<sub>2</sub> in the atmosphere, in the climatically sensitive Southern Ocean (SO). The manuscript describes the hydrography in the Atlantic sector of the SO and the influence on the carbonate system parameters. However, in its present form the manuscript is hard to follow and need to be rearranged. Perhaps the manuscript was written in a rush, and is also in the need of a language check (e.g. tempus). Important information on the methods of some of the parameters is not described sufficiently or is missing. Results and discussion section is unclear and results are not explained enough. Additional figures on data should be added. Part of the conclusion is redundant and some information is already presented in the abstract. The objective mentioned in the conclusion is highly speculative and is not possible to resolve in this work. In my point of view, the manuscript is recommended for publication after moderate to major revision.

*We have considered the general comments by reviewer #2 in order to re-write more specifically our objectives and the results presented here. The paper has been restructured as indicated below.*

#### **Specific comments**

Title: in the title, “buffering” is suggested to be eliminated; “Carbonate system and the influence of water masses of the Southwest Atlantic sector of the Southern Ocean during February to March 2008”

*The title has been changed as indicated.*

In the entire manuscript, sometimes pHT25 is presented, sometimes pH in situ, sometimes both. A consequent use of the two parameters would be preferable, for example present both and with one in parenthesis. The same non-consequence is used in the figures, where it would be better to present both pH in situ and pHT25. There is no explanation to why you use pHT25 or pH in situ at different sites

*We have changed many sentences in order to present the results as indicated here (also for other normalized carbonate variables). We considered that the pH in total scale, both at 25°C and at in situ conditions, are needed for the scientific community in order to be sure which are the real pH values and the changes in which the organisms are now living and how it will be affected in a next future.*

Use carbonate system consequently throughout the manuscript instead of carbon system that is sometimes used, which is confusing. In other case, explain the definitions.

*We agree with the reviewer and we have always used carbonate system.*

The structure of the manuscript is unclear and difficult to follow and to get the important information. I recommend to add a new section to the introduction such as “Study area – hydrography” as background to the study, where the description of the water masses, surface and deep, fronts and eddies are presented with position, salinity and SST, instead of in the result section. In results and discussion section, the carbonate system parameters can be related to the specific areas and water mass characteristics already described in the study area. That would make the results of the carbonate system more clear and easier to follow.

*As indicated above, we have followed this comment and we have included both a section about the study area and also a section about calculations and the normalization procedure in the Data and Methods section.*

For the calculations in the manuscript, add a new section in data and method section: here, add the calculations of the calcite and aragonite saturation, CO<sub>2</sub>sys calculations (omega, pH in situ, fCO<sub>2</sub>), normalization of AT and CT.

In this section, also add calculations of buffer coefficients: add formulations and explanations.

*It has been done*

#### **Abstract**

Page 436, line 15 to 18: “...UCDW was recently mixed with ventilated waters...”, which means that also anthropogenic CO<sub>2</sub> should be higher, than in older, deeper water. Why is this ventilated water “...high carbonate concentration” water?

*This has been explained in the Hydrography section and references have been included. In the abstract, only a sentence is given related to the CFC values.*

Page 436, line 20, 21: According to figure 4, the value should be 900m or 1000m instead of 600m, so that "...deepen from 600m to 1500m" should be changed to "...deepened horizon from 1000m to 1500m". It is difficult to see in the figure what value. The same question for south of 57.5°S, where it looks like it is 900m or 1000m instead of 700m in figure 4.

*Following your comments and reviewer #1 comments figures are now in colors. The values have been checked and the ones presented in the text are correct. In any interpolation procedure, assumptions are done (like in figures and in models). We used the computed values from the experimental data.*

### **Introduction**

Page 438, line 15: change "ocean" to "Southern Ocean". This manuscript does only show the sensitivity in one part of the ocean. As you mentioned on page 450, line 28 and 29; "...results presented in this work provide a basis for comparing.....to other oceans".

*It has been done.*

### **Data and methods**

Page 438, line 22: dissolved oxygen is mentioned here but not shown elsewhere in the manuscript. Delete "dissolved oxygen" or add the oxygen measurements in results and discussion as figure and interpretation in discussions, and add method description. For nutrients, method description is missing and figure on data should be added since nutrients are discussed in the manuscript, to explain deep water and primary production etc. Add chlorophyll-a to the measurements here, and describe the methods for the measurements in data and method section.

*Here, we only mentioned the chemical parameters which were measured together with the carbonate system variables. We have included references to papers related to this cruise where these parameters are described in detail. We have not included a detailed description of nutrients as this paper is part of a special issue about the many studies carried out during this cruise. However, as indicated by the reviewer, we have included some nutrient data to clarify the comments.*

Page 439: Both nutrients and chlorophyll-a are referred to in the manuscript but the method descriptions are missing. Data on nutrient would be useful to present in the results to explain some of the results, especially when you refer to "high nutrients" or "low nutrients". I assume that nutrient concentrations of phosphate and silicate were used for the CO<sub>2</sub>sys calculations.

*As indicated above, references have been included. The nutrient concentrations were used in the computation of carbonate variables.*

Page 439, pH measurements: What was the precision and accuracy of the measurements? What cell length was used? For 1-cm cell, correction for the effect of indicator pH needs to be done.

*The precision for the pH determination has been included together with a detailed reference of the location of our pH system. We removed the dye effect for each pH determination. We used four pH readings at different dye concentrations and the readings are extrapolated to zero dye concentration to get the real pH for the seawater.*

Page 440, lines 11 to 13: Move to description of the total alkalinity on page 439.

*It has been done.*

Page 440: add new section "Calculations", with sub sections, where calculations for calcite and aragonite saturation state, CO<sub>2</sub>sys calculations, pH in situ, fCO<sub>2</sub>, calcium concentration, , normalization of AT and CT, and buffer activity are formulated described.

*We considered this comment including a new section.*

Page 440, CO<sub>2</sub>sys calculations: clarify what constants were used for the calculations of omega and fCO<sub>2</sub>, and if nutrients were used or not (and what nutrient concentrations).

*It has been done. We had phosphate and silicate concentrations for each sample.*

Page 440, How was calcium concentration estimated from salinity? Explain how and give method or reference. How was normalization of AT and CT done?

*In the new section about calculations, the normalization procedure has been described in detail.*

### **Results and discussion**

In general, more explanations to the results presented in the manuscript are needed. For example use data in property-property plots, such as T-S plots, AT:CT plots, and add new section plots on nutrients and pH in situ.

*We have tried to explain most of these aspects better. As the nutrient discussion is presented in other papers related to the cruise, we have not included any special section. However, some indications are presented.*

The sensibility of carbonate system to increasing CO<sub>2</sub> is difficult to follow and needs more explanations. *The presentation has been improved.*

Add the reference and information from Bakker et al., (2008), Biogeosciences, 5. There are some overlaps in the ACC area, which could be interesting to compare the results in this manuscript with. *This paper has been referenced and the overlap (we only reached 57.5°S) was considered.*

Page 441, surface distribution: move lines 13 to 22 to new section describing the hydrography, SST and salinity. As mentioned above, extraction of the water mass description parts from the results would make the results and discussion of the carbonate system parameters more clear.

*It has been done.*

Page 442 to 448, information and references about the hydrography, SST and salinity are recommended to move to new hydrography section.

*It has been done*

Page 442, line 5: add that “CT was normalized to salinity 35 (?) to remove the effect of salinity on CT”. What salinity was CT and AT normalized?

*It has been described.*

Page 443, line 18: “...strong mixing occurs, affected the surface inorganic carbon distribution”. How? Explain.

*It has been explained*

Page 444, line 18: atmospheric value; add number.

*It has been included*

Page 444, lines 22 to 24: add numbers of the “very low values in Chl-a, minima in fCO<sub>2</sub> and maxima in pH in situ”. Explain why the values were lowest and highest, respectively at the position of the rings and of either side of the frontal zone.

Southern Ocean surface waters are usually rich in nutrients but low in chlorophyll-a, and are often referred to as “high-nutrient-low-chlorophyll, HNLC”, waters. It would be preferable to use this notification in the manuscript to explain why the primary production is not able to take up macronutrients in certain areas. In Southern Ocean, there are several explanations to why; e.g. iron limitation, unstable surface water stratification (mixing). Eddies and rings may provide either of these environment factors to promote primary production. There are references from studies in HNLC waters, such as in the North Pacific Ocean; Deep-Sea Research, 52 (2005) on Haida eddies.

*We have included some new sentences and references explaining the observed values.*

Page 445, line 3,4 : explain why primary production was favored in the rings compared to outside. Could it be an effect of iron availability within the rings, transported with the rings from land? There are references from studies in HNLC waters, such as in the North Pacific Ocean; Deep-Sea Research, 52 (2005) on Haida eddies.

*This feature observed in many other eddies, has been explained and referenced.*

Page 445, line 10: “large differences”: how large?

*It has been indicated*

Page 445, lines 12, 13: “variations are mainly due to input of CaCO<sub>3</sub>”: how do you know? Do you have evidence of CaCO<sub>3</sub> input? Could you show this from your data? Could it be due to other processes? Maybe the Lee et al. (2006) formulation is not suitable for eddies?

*In an integrating procedure, many mesoscale effects cannot be captured. Frontal zones, eddies, upwelling cells and filaments alter the surface distribution at local areas that, in many cases, cannot be described in general multilinear regression procedures.*

Page 446, lines 9, 10: “...low pHT<sub>25</sub>, 7.56...high salinity and pHT<sub>25</sub> = 7.61”, relative to what? Is pHT<sub>25</sub> = 7.61 high?

*It has been clarified.*

Page 447, line 18: “as a signature of age”, what more specifically?

*It has been defined.*

Page 447, NADW: there is no description on the carbonate system in NADW. You should add something about CT, AT and/or pH.

*It has been included.*

Page 448, line 7: “becoming older”, than what?

*It has been described.*

Page 448, lines 20, 21: in figure 4, the depth of 600m at 49.57°S is difficult to see as well as the depth of 700m at 50.37°S. It rather looks like 900m.

*The values presented in the text correspond to those determined experimentally.*

Page 448: mention why  $\Omega = 1$  is a critical point.

*It has been done.*

Page 448, line 19: what is “eddy M effect”? Define, explain.

*It has been explained*

Page 448, line 24: Do you mean upwelling due to winter cooling and strong persistent winds?

*It has been corrected as indicated.*

Page 448, lines 27, 28: show from your own data of AT and CT and explain more.

*It has been indicated.*

Page 448, line 28: what is “Polar sector”? Define.

*It has been corrected.*

Page 449 to 452: This section is difficult to understand and needs elaboration. Explain why you perform such exercise. What is the significance of  $\beta$  and  $\Omega$ , what is critical and why? In the text you sometimes you write “7 buffer coefficients”, sometimes “eight buffer indices”. Be consequent.

*We have corrected this fact and tried to explain the information provided by the different coefficients in more detail*

Page 449, lines 17 to 19: What are acid constants? Explain what you mean with “presence of borate”.

You write that “...B(OH)<sub>4</sub> are present at very low concentrations..”. Do you have data? How do you explain that, reference?

*We have included comments about these aspects .We used the CO2sys program output. At pH close to 7.5 we are at the lowest buffer capacity for the seawater, controlled by carbonate and borate systems. A new reference has been included.*

Page 450, lines 6 to 8: explain why the biological production is not able to use up the macronutrients. Is that because of “HNLC” waters, iron limitation or what (see above)?

*We used your comments to improve our description.*

Page 451 to 452, conclusion: I think this part is unnecessary. Most information is already in the abstract. The objective described on the first lines is not possible to resolve in this paper and should be removed.

*We have rewritten some parts as indicated by the reviewer..*

### **Figures and caption list**

Fig. 1 enlarge the fonts and abbreviations in the figure.

*It has been considered*

Fig. 2 add units for SST and Chlorophyll-a in figure caption. Fig 2A: change APF to PF.

*It has been done*

Fig.2 markers should be in different shapes, as complement to the different colors.

*We have modified the figure*

Fig.3 figure caption: pH has no unit, delete  $\mu\text{mol kg}^{-1}$  in caption and figure c). Dots cannot be seen in the figures. In a) add unit for T ( $^{\circ}\text{C}$ ).

*We know that (it was indicating in what units the  $[H^+]$  was expressed). As the reviewer knows, many of the pH data in a bibliography are difficult to follow because both scales and concentration units are not indicated. We have modified the figure and the definitions.*

Fig. 4 and 5: add a), b), c)...to figures and figure captions.

*It has been done*

Add new figure on pH (in situ) and nutrients.

*It has been considered.*

### **Technical corrections**

*All the technical corrections have been considered.*

Page 436, line 4: change February – March to February to March.

*It has been done*

Page 436, line: ...was at minimum.

*It has been done*

Page 436, line 23: add “that” between “showed” and “the minimum”.

*It has been done*

Page 437, line 3: Add “carbon dioxide (CO<sub>2</sub>)”, in case anybody does not know.

*It has been done*

Page 438, line 1: add “rich in CO<sub>2</sub>” as “... deep waters, rich in CO<sub>2</sub>, is the most...”

*It has been done*

Page 438, line 5: “carbon dioxide system parameters” is the same as carbonate system parameters. Add comment on that or use the same name.

*It has been done*

Page 438, line 14: change “carbon system” to “carbonate system”, or define carbon system.

*It has been done*

Page 440, line 15: add “( $\Omega$ )” after saturation state.

*It has been done*

Page 440, line 16: add “[Ca<sup>2+</sup>]” and “[CO<sub>3</sub><sup>2-</sup>]” after calcium and carbonate ion, respectively.

*It has been done*

Page 443, line 8: add “of CO<sub>2</sub>” as “reduction of CO<sub>2</sub> due to biological activity”.

*It has been done*

Page 444, line 13: add “fugacity of CO<sub>2</sub> (CO<sub>2</sub>)”.

*It has been done*

Page 444, lines 18, 19: change CO<sub>2</sub> to CO<sub>2</sub>.

*It has been done*

Page 444, line 27: change “rich CO<sub>2</sub>” to “CO<sub>2</sub> rich water”

*It has been done*

Page 445, line 1: change “CO<sub>2</sub>” to fCO<sub>2</sub>”.

*It has been done*

Page 446, line 6: change “APF” to “PF”

*.It has been done*

Page 447, line 16: what is “deep salinity maximum”? Do you mean “the salinity maximum of the deep water”?

*It has been corrected*

Page 448: where “carbonate” concentration is written, use “carbonate ion” concentration or abbreviation [CO<sub>3</sub><sup>2-</sup>].

*It has been done*

Page 450, line 14: add “assuming” after “...55°S,”.

*It has been done*

Page 451, line 4: delete “oxygen” or add more information.

*It has been corrected*