

## **ANSWER TO REVIEWER 1**

*First of all, we would like to thank reviewer #1 by his/her work and valuable comments that have improved the quality of our initial manuscript.*

*As indicated below, we have checked all the general and specific comments and the technical indications provided by the reviewer and all of them have been changed accordingly to his indications.*

### **General comments:**

The manuscript “Carbonate system buffering in the water masses of the Southwest Atlantic sector of the Southern Ocean during February-March 2008” by Gonzalez-Davila et al. describes the distribution of DIC, total alkalinity, pH and CFCs on a transect between Cape Town and 57°S. Patterns are explained in the context of hydrographic properties. The manuscript presents new data which brings new insights about the magnitude and timescale of CO<sub>2</sub> uptake by the Southern Ocean.

The authors use the data to estimate the buffering capacity of the water masses and present an estimate of when these water masses will be undersaturated with respect to aragonite, one of the currently most discussed questions in the marine carbon cycle community.

While the methods are state-of-the-art and the description of the carbonate system distribution is detailed, the last part “3.3 Sensitivity of carbonate system to increasing CO<sub>2</sub>” needs to be treated more carefully (see specific comments). After an attentive revision of language and style (abbreviations, units), I recommend the manuscript to be published in Biogeosciences.

### **Specific comments:**

1. Page 436, Line 12: A<sub>T</sub> and C<sub>T</sub> are abbreviations which need to be explained before being used.

*We have included the whole words for all the abbreviations.*

2. Page 436, Line 18: Ω<sub>arag</sub> has not been defined.

*It has been done.*

3. Page 437, Line 18: It is not clear what you mean with buffer factors at this stage of the manuscript.

They will not be explained until part 3.3. Use either „Revelle factor“ or „the buffering capacity“ or explain what you mean with buffer factors.

*We agree with the reviewer and we have changed our presentation*

4. Page 438, Line 14f: the buffer capacity is the method to describe the sensitivity to the increase of CO<sub>2</sub>; it is enough to mention one of them here.

*It has been done*

5. Page 439 2.2 pH measurements: indicate uncertainty associated with pH measurements.

*It has been included*

6. Page 439, Line: 19: give reference to Andrew Dickson for CRMs.

*It has been included*

7. State whether you corrected your measurements by the offset of the CRMs and if not, state why not. How often were they measured? Consider switching sections 2.3 and 2.4 as in 2.4 you explain the use of CRMs in more detail. This should come first.

*It has been changed and considered as indicated here and below*

8. Page 440, Line 12: NA<sub>T</sub> needs to be written out before using the abbreviation.

*It has been included*

9. Page 440, 2.5: Calcite and aragonite saturation states: State which constants you used in CO<sub>2</sub>SYS (for K<sub>1</sub>, K<sub>2</sub>, K<sub>sp</sub>, K<sub>SO4</sub>).

*It has been included*

10. Page 441, Line 13ff: following this definition (which is correct), you do not have data from the Weddell Gyre, as this starts south of 57°S. State that you have data from the subtropical domain, the ACC, and from the boundary region between ACC and Weddell Gyre/northern edge of Weddell Gyre.

*It has been changed following this comment.*

11. Page 443, Line 1: Noth that A<sub>T</sub> and C<sub>T</sub> are not shown. I suggest to show at least C<sub>T</sub> though as it is discussed in detail in the text.

*C<sub>T</sub> is now shown.*

12. Page 443, Line 19: Polar Front is mentioned for the first time here, do not use the abbreviation.

*It has been included*

13. Page 444, Line 13: Where did you get the chlorophyll data from? Mention here or better in section 2.

*It has been included in section 2*

14. Page 445, Line: 6: Did you use the equation within its definitions, i.e., did you only calculate  $A_T$  for SST < 20°C? The variations of  $A_T$  at 35°55'S are at SST > 20°C, aren't they? Hence it is not astonishing, that they differ from the calculated values. The upwelling of waters rich in  $A_T$  has already been discussed before, so this paragraph does not seem to bring any new information.

*The values have been recalculated using the valid range. The sentence has been removed.*

15. Page 446, Line 6ff: APF, UCDW, LCDW are not defined.

*They have been included*

16. Page 446, Line 21: Where would CDW mix with Ice Shelf Water? Ice Shelf Water is found on the shelves and is further altered and mixed until it comes close to the ACC.

*Reference is given in order to complete and give further information.*

17. Page 447, Line 6: AAIW is not defined.

*It has been included*

18. Page 447, Line 15: Please specify what you mean with South Atlantic here.

*It has been indicated.*

19. Page 447, Line 23: delete sentence, was already written in Line 17/18.

*It has been done*

20. Page 448, Lines 3-8 and Figure 3: CFC-12 values > 0.07 pmol/kg cannot be distinguished in Figure 3. Also AT and CT values south of the Sbdy cannot be read. Color shading would help.

*Color shading has been included*

The following points concern page 449ff, 3.3 Sensitivity of carbonate system:

21. It is not entirely clear how changes in  $\Omega$ , [H+], and [CO<sub>2</sub>] are calculated. An equation and the initial values of [CO<sub>2</sub>] and [H+] that you use for the calculations should be given.

*Following reviewer #2 a new sub-section has been included to explain the calculations and the equations*

22. Be aware of your regional constraints. On p. 450, Line 14 you say „South of 55°S...“, and later on, Line 19: „at high Southern Ocean latitudes“. South of 55°S you only have data until 57°S. This should be made clear here and speculations about what happens further south should be marked as hypotheses.

*It has been included*

23. You assume a 10  $\mu$  mol/kg increase in CT and cite ESTOC data. While these are certainly high-quality data, I suggest to use data of the same region to be more realistic. A decadal estimate on the Prime Meridian was done by Hauck et al. 2010, JGR, doi:10.1029/2009JC005479. The estimate should be put into perspective with other Southern Ocean studies on temporal CT increase (e.g. Levine et al., 2008, DOI: 10.1029/2007JC004153; Sabine et al., 2008, JGR, DOI: 10.1029/2007JC004577; Metzl 2009, DSR II, doi:10.1016/j.dsr2.2008.12.007), i.e., a range of possible yearly CT increases should be used instead of one number and this will also result in a range of years when the surface ocean will be undersaturated. Further south, CT increase can be considerably lower, compare e.g., Hauck et al. 2010, JGR, doi:10.1029/2009JC005479 and McNeil et al., 2010, GRL, doi:10.1029/2010GL044597, therefore you should include lower values into your range.

*Most of the references provided here have been included and commented in this new version. According to the references, a range of values is now considered.*

24. Please clarify how you calculated year 2045 as the year in which the surface ocean will be undersaturated with respect to aragonite. With the equation:  $\Omega(dt) = \Omega_{\text{initial}} + dCT / \omega_{CT} * \Omega_{\text{initial}}$  and

$$\Omega_{\text{initial}} = 1.47$$

$$dCT = 1 \mu \text{ mol/kg/year} * dt$$

$$dt = 1:50 \text{ years}$$

$$\omega_{CT} = -0.12 * 1e3 \mu \text{ mol/kg}$$

I get undersaturation after 39 years after 2008, i.e., 2047. Would it make a difference if you would calculate the buffer factor again each year or each ten years?

*Your calculations are correct. The results are based in an estimation of an increase in  $C_T$ , and for that reason we rounded down to 2045. In this version we used a range of rates of increase in  $C_T$  and a range of years is also given. Of course, it is estimative as the rate of change can vary as emissions do.*

25. The buffer factors don't have any unit until page 450, Line 10, it's important to know that they are in mmol/kg though, please add when they are first mentioned.

*It was included in the experimental section and in the legends.*

26. Page 450, Line 10: You probably mean  $\omega_{CT}$  instead of  $\Omega$ . Add unit.

*It has been changed*

27. Page 451 - Conclusions: Do not use abbreviations in the conclusions or define them again within this section.

*It has been changed*

### **Figures**

Figure 1: What does C.I=0.2 m mean? Define unit of color coding (label colorbar). What do the dotted lines mean? Black letters are hard to read on dark blue. The ship is very hard to see.

*We have improved the figure 1*

Figure 2: Mark the Agulhas rings.

*It has been done*

Figure 3: pHT<sub>25</sub> is not in  $\mu$  mol/kg. (see comment (20) above: CFC-12 values > 0.07 pmol/kg cannot be distinguished in Figure 3. Also AT and CT values south of the Sbdy cannot be read. Color shading would help.)

*We agree with reviewer. We only wanted to indicate that proton concentration is in molinity scale. We have now presented all plots in colors.*

Figures 3-5: Label y-axis (depth in m).

*Done*

Figure 5: Give units and use  $\omega$  CT instead of  $\Omega$  CT. Same for AT.

*Done*

### **Technical corrections**

*As indicated above, we have considered all the technical corrections in this new version.*

p. 436, Line 6 (and throughout the manuscript): pH in situ

*done*

General use of tenses: present tense should be used to report background that is already established. Use past tense to describe results of a specific experiment, especially your own.

*The use of tenses has been checked along the text*

p. 436, Line 7: **were** observed

*It has been changed*

Line 8: was **at** a minimum

*It has been changed*

Line 8ff: stick to one tense within the sentence (past as it is one of your results)

*It has been changed*

Line 10: **nutrients** / nutrient **concentrations**

*It has been changed*

Line 10 Do you mean: spread out **across** the fronts?

*It has been modified.*

Line 16: revealing **that** mixing with ... **took place** / **that it was mixed** with...

*It has been changed*

Line 18: carbonate concentrations.

*It has been changed*

Line 19: **polar front** or **Polar Front**

*It has been changed*

Line 20: substitute „ $\Omega$  arag = 1 “ by „the aragonite saturation horizon “ deepens

*It has been substituted.*

Line 22: Buffer coefficients related ... **had minima** in the Antarctic Intermediate Water ... (delete: showed the minimum values are found)

*It has been changed*

Line 25: decrease pH and carbonate saturation states (delete: the)

*It has been changed*

Line 27: undersaturated **with respect to** aragonite

*It has been changed*

p. 437, Line 7: delete „ocean “: Since preindustrial times, uptake of CO<sub>2</sub> **has**

*It has been changed*

Line 8: ions ... latitudes **being** one ...

*It has been changed*

Line 10: delete: been observed to have

*It has been changed*

Line 11: decline **by** around 0.3 **until** the year 2100.

*It has been changed*

Line 13: **undersaturation**

*It has been changed*

Line 16: suggest that **wintertime** Souterh Ocean aragonite undersaturation

*It has been changed*

Line 18: total inorganic **carbon** concentration

*It has been changed*

Line 27: surface layer (not layers)

*It has been changed*

Line 28: showed **that**

*It has been changed*

Page 438, Line 2: ... cycling, **compared to temperature driven differences in solubility** or biological processes.

*It has been changed*

Line 12: southwest

*It has been changed*

Line 13: ... work **is** to ... carbonate system

*It has been changed*

Line 14: ... defining **their** buffer ...

*It has been changed*

Line 17: southwest

*It has been changed*

Line 17 and throughout the manuscript: no space between ° or ' and S: 33°58'S

*It has been changed*

Line 20: completed **on** 17

*It has been changed*

Line 26: pH **on the** total scale

*It has been changed*

Page 439, Line 3: pH **from** 1609 samples, **from 1559** samples for AT and **from 1504** samples for CT.

*It has been changed*

Line 7: and **were overfilled**

*It has been changed*

Line 8: **At** shallow stations and **when** samples could ...

*It has been changed*

Line 12: **We measured pH on the total scale (pHT)** at a constant temperature of 25°C.

*It has been changed*

Line 17: standardized

*It has been changed*

Line 19f: ... certified reference **material** for oceanic ... **titration system. Measurements of CRMs were within ...**

*It has been changed*

Page 440, Line 3: titration **of total** dissolved (delete „the “)

*It has been changed*

Line 5: each **new** titration cell

*It has been changed*

Line 6: (**once** a day), **in total 31 CRMs were analyzed.**

*It has been changed*

Line 7: **We measured** 1996.0 ...

*It has been changed*

Line 9: temperature **at which CT is determined which was 25°C in our case.**

*It has been changed*

Line 9f: **Raw data were corrected for this offset by multiplying with** the factor ...

*It has been changed*

Line 15: delete: „degree of “

*It has been changed*

Line 16: as **the product of the calcium and carbonate ion concentrations at in situ ...**

*It has been changed*

Line 21: from salinity (delete „the “)

*It has been changed*

Page 441, Line 2: hydrocast

*It has been changed*

Line 13: divided **into** three

*It has been changed*

Line 17: frontal systems **were** described

*It has been changed*

Line 23: substitute „correlated “ by „accompanied “; surface **dissolved inorganic carbon concentrations (Fig. 2).**

*It has been changed*

Page 442, Line 1: By **using** Sea Surface ... (SSS) **data** from this work ...

*It has been changed*

Line 2: south

*It has been changed*

Line 7: **from**

*It has been changed*

Line 8: **north**

*It has been changed*

Line 8ff: I don't understand the sentence.

*It has been changed*

Line 13: **was** injected **into** the region

*It has been changed*

Line 14: ... **Bank) as is proven both by ...**

*It has been changed*

Line 18: **Bank**

*It has been changed*

Line 19: **dropped**

*It has been changed*

Line 20: **fell**

*It has been changed*

Line 21: **were** found **to be** related ... centered at **40°S**

*It has been changed*

Line 24: delete: „the pHT at 25°C, “

*It has been changed*

Line 25: increased pHT,**25** (delete „the “)

*It has been changed*

Line 28: pHT,**25** increased (delete „the “)... 8.00, **following** the ...

*It has been changed*

Line 29: **Total alkalinity is strongly correlated with salinity.**

*It has been changed*

Page 443, Line 1: **from ... to ... at the N-STF. ... dropped ...**

*It has been changed*

Line 3: delete: „area “

*It has been changed*

Line 6: delete: „important “, „clearly “, „upwelling “ instead of „mixing “? ... deep **CO2-rich** waters takes place... overcompensates

*It has been changed*

Line 13: **dropped**

*It has been changed*

Line 14: **fell**

*It has been changed*

Line 15: decreased **by**

*It has been changed*

Line 16: **dropped**

*It has been changed*

Line 17: increased

*It has been changed*

Line 19f: There **were only weak** surface ...

*It has been changed*

Line 25: decreased

*It has been changed*

Line 26: increased  
*It has been changed*

Line 26ff: **The position of ... is seen more precisely in the pH gradient, pHT,25 decreased ...**  
*It has been changed*

Line 28: increased  
*It has been changed*

Page 444, Line 1f: **In the region studied, the southern boundary of the ACC is located at 55°xx.**  
*It has been changed*

Line 8: deep **and salty water**  
*It has been changed*

Line 9: **western part** of the Weddell Gyre **to the Prime Meridian**  
*It has been changed*

Line 12: **deep waters rich in alkalinity**  
*It has been changed*

Lines 13, 15, 17, 24, 25, 29: **pHT,in situ**  
*It has been changed*

Line 16: a mean **pHT,in situ** value  
*It has been changed*

Line 18: subtropical zone with **fCO<sub>2</sub>**  
*It has been changed*

Line 25: fCO<sub>2</sub> **was at a maximum** and pHT,in situ was **at a minimum**  
*It has been changed*

Line 26: implies **that**  
*It has been changed*

Line 26ff: **EITHER:... takes place ... are located ... spreads out across the fronts ... increases ... decreases OR: took place ... were located ... spread out across the fronts ... increased ... decreased**  
*It has been changed considering the first option.*

Line 27: **CO<sub>2</sub>-rich (low pH and high nutrient) water**  
*It has been changed*

Line 28: nutrient **input**  
*It has been changed*

Line 29f: **was** observed south of 40°S **at** the southern ...  
*It has been changed*

Page 445, Line 2: was **detected** together  
*It has been changed*

Line 3f: of **a chemical** ... which **was over at the time of sampling (... was...)**  
*It has been changed*

Line 5: area **between** 30°S **and** 70°S  
*It has been changed*

Line 11: **were**  
*It has been changed*

Line 15: delete „the “; **is**  
*It has been changed*

Page 446, Line 1f: south, north  
*It has been changed*

Line 9f: **UCDW is characterized by a pHT,25 as low as 7.56 (... low oxygen...) and LCDW by high salinity... ()**  
*It has been changed*

Line 11: Both Circumpolar Deep Water masses ... **by maxima** ...  
*It has been changed*

Line 16: **NCT in the range of xxx .**  
*It has been changed*

Line 19: Circumpolar Deep Water masses ... **waters coming from** ...  
*It has been changed*

Line 24: Weddell Sea **Deep Water**  
*It has been changed*

Line 25: **We found a pHT,25 value of 7.62 and CT around xxx ... in WSDW.**  
*It has been changed*

Line 26: **Close to the seafloor** ...  
*It has been changed*

Line 29: **characterized by** (instead of presenting)

*It has been changed*

Page 447, Line 1: **and higher pHT,25 values (7.63) than in WSDW.**

*It has been changed*

Line 8: AAIW **in this region** is characterized by low pHT,25 levels, **ranging between 7.65 and 7.68 ...**

*It has been changed*

Line 11: where **it** met

*It has been changed*

Line 10: Cape **Basin**

*It has been changed*

Line 11f: In the Cape **Basin, salinity values were 0.2 units higher and temperature was 2°C warmer** than...

*It has been changed*

Line 12f: AAIW **had also a higher dissolved inorganic carbon content, ranging**

*It has been changed*

Line 14: **in** the Cape **Basin**

*It has been changed*

Line 17: delete „level “

*It has been changed*

Line 19ff: **The present variety corresponds to the eastern NADW pathway, that has crossed ... (Arhan...). It is usually found in the Cape Basin and north of the SAF. It is characterized by salinity maxima higher than 34.83.**

*It has been modified.*

Line 29: are **in the range of xxx**

*It has been changed*

Page 448, Line 5: (...), **north of 36°S.**

*It has been changed*

Line 6ff: shown above south of **the** Sbdy, **indicating that** AABW ... and **is being** diluted with the overlying... south ... north

*It has been changed*

Line 9: **aragonite**

*It has been changed*

Line 10: **The isoline of  $\Omega_{cal} = 2$**  ...

*It has been changed*

Line 13: ... for the **isoline of  $\Omega_{arag} = 1.2$**

*It has been changed*

Line 18: **The aragonite saturation horizon is** at 1000 m ... (substitute  $\Omega_{arag} = 1$  by „the aragonite saturation horizon “ throughout the manuscript)

*It has been changed here and also throughout the manuscript.*

Line 19: ... eddy **M.** (delete „effect “)

*It has been changed*

Line 21: shoaled

*It has been changed*

Page 449, Line 3: continue **to affect**

*It has been changed*

Line 4ff: ... we **used the experimental data to compute** the fractional... **induced by** changes in...

*It has been changed*

Line 8: ... ocean to **hamper/delay changes in carbonate chemistry**

*It has been changed*

Line 10 (and throughout the manuscript): Don't start a sentence with an abbreviation: **The capacity of a chemical system to buffer changes in [H+] after the addition ... is denominated  $\beta_H$ .**

*It has been changed*

Line 11: Low values ... (delete „indices “)

*It has been changed*

Line 13 and throughout the manuscript: **seven** (write out numbers between one and twelve)

*It has been considered.*

Line 22: ... section, AT ... (delete „the “)

*It has been changed*

Page 450, Line 1: **were** observed

*It has been changed*

Line 2f: **were** found ... **were** located

*It has been changed*

Line 9: saturation states

*It has been changed*

Line 15: ... would increase [CO<sub>2</sub>] (delete „the “) by 7.1%, **and** [H<sup>+</sup>] (delete „the “)

*It has been changed*

Line 21f: **was** reported ... a period of ten years (delete „only “)

*It has been changed*

Line 24: ... by 2045 **surface waters south** of ...

*It has been changed*

Page 451, Line 2: The objective **of this study was** ...

*It has been changed*

Line 11: In other areas, pH and *f*CO<sub>2</sub> **were** ...

*It has been changed*

Line 13: a mean **pH** value

*It has been changed*

Line 16: **were** presented

*It has been changed*

Line 17: **was** govern

*It has been changed ed*

Line 19: **was** identified (delete „well “) ...

*It has been changed*

Line 20f: **In** the Cape Basin area...

*It has been changed*

Line 23: ... depths two (delete „the “) NADW branches **were** defined.

*It has been changed*

Line 23ff: The first one corresponds to the eastern NADW pathway with low CFC-12 concentrations (**<0.02 pmol kg<sup>-1</sup>**).

*It has been changed*

Line 27: in the **range of** 0.08 ...

*It has been changed*

Page 452, Line 1: delete „also “

*It has been changed*

Line 2f: **We could differentiate two varieties of circumpolar deep water.**

*It has been changed*

Line 5: maxima

*It has been changed*

Line 7: substitute „climate change “ by „changes in carbonate chemistry “

*It has been changed*

Line 7ff: Eight buffer indices **that relate** changes in CT and AT **to changes in** [CO<sub>2</sub>], [H<sup>+</sup>] and calcium carbonate saturation states showed low values, **i.e.**, low ...**sensitive** ... increase **of** CO<sub>2</sub>.

*It has been changed*

Line 10f: **The lowest values were observed in** the 1000-1500 ...

*It has been changed*

Line 11: **These depth ranges correspond to** ...

*It has been changed*

Line 13: ... decreases in pH (delete „the “) ... **calcium** carbonate saturation states

*It has been changed*

Line 15: **We predicted that** ...

*It has been changed*