

## 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 González-Dávila 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.
2. Page 436, Line 18: Ω<sub>arag</sub> has not been defined.
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.
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.
5. Page 439 2.2 pH measurements: indicate uncertainty associated with pH measurements.
6. Page 439, Line: 19: give reference to Andrew Dickson for CRMs.
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.
8. Page 440, Line 12: NA<sub>T</sub> needs to be written out before using the abbreviation.
9. Page 440, 2.5: Calcite and aragonite saturation states: State which constants you used in CO2SYS (for K1, K2, Ksp, KSO4).
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.
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.
12. Page 443, Line 19: Polar Front is mentioned for the first time here, do not use the abbreviation.
13. Page 444, Line 13: Where did you get the chlorophyll data from? Mention here or better in section 2.
14. Page 445, Line: 6: Did you use the equation within its definitions, i.e., did you only calculate A<sub>T</sub> for SST < 20°C ? The variations of A<sub>T</sub> 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<sub>T</sub> has already been discussed before, so this paragraph does not seem to bring any new information.

15. Page 446, Line 6ff: APF, UCDW, LCDW are not defined.
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.
17. Page 447, Line 6: AAIW is not defined.
18. Page 447, Line 15: Please specify what you mean with South Atlantic here.
19. Page 447, Line 23: delete sentence, was already written in Line 17/18.
20. Page 448, Lines 3-8 and Figure 3: CFC-12 values > 0.07 pmol/kg cannot be distinguished in Figure 3. Also  $A_T$  and  $C_T$  values south of the Sbdy cannot be read. Color shading would help.

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

21. It is not entirely clear how changes in  $\Omega$ ,  $[H^+]$ , and  $[CO_2]$  are calculated. An equation and the initial values of  $[CO_2]$  and  $[H^+]$  that you use for the calculations should be given.
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.
23. You assume a 10  $\mu\text{mol/kg}$  increase in  $C_T$  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  $C_T$  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  $C_T$  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,  $C_T$  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.

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:  $\Omega(dt) = \Omega_{\text{initial}} + d_{CT}/\omega_{CT} * \Omega_{\text{initial}}$  and

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

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

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

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

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?

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.

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

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

## Figures

Figure 1: What does  $C.I=0.2 \text{ m}$  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.

Figure 2: Mark the Agulhas rings.

Figure 3:  $\text{pH}_{\text{T},25}$  is not in  $\mu\text{mol/kg}$ . (see comment (20) above: CFC-12 values  $> 0.07$  pmol/kg cannot be distinguished in Figure 3. Also  $A_{\text{T}}$  and  $C_{\text{T}}$  values south of the Sbdy cannot be read. Color shading would help.)

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

Figure 5: Give units and use  $\omega_{\text{CT}}$  instead of  $\Omega_{\text{CT}}$ . Same for  $A_{\text{T}}$ .

### Technical corrections

p. 436, Line 6 (and throughout the manuscript):  $\text{pH}_{\text{in situ}}$

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.

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

Line 8: was **at** a minimum

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

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

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

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

Line 18: carbonate concentrations.

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

Line 20: substitute „ $\Omega_{\text{arag}} = 1$ “ by „the aragonite saturation horizon“ deepens

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

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

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

p. 437, Line 7: delete „ocean“: Since preindustrial times, uptake of  $\text{CO}_2$  **has**

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

Line 10: delete: been observed to have

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

Line 13: **undersaturation**

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

Line 18: total inorganic **carbon** concentration

Line 27: surface layer (not layers)

Line 28: showed **that**

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

Line 12: **southwest**

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

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

Line 17: **southwest**

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

Line 20: completed **on** 17

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

Page 439, Line 3: pH **from** 1609 samples, **from 1559 samples for A<sub>T</sub> and from 1504 samples for C<sub>T</sub>**.

Line 7: and **were overfilled**

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

Line 12: **We measured pH on the total scale (pH<sub>T</sub>)** at a constant temperature of 25°C.

Line 17: standardized

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

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

Line 5: each **new** titration cell

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

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

Line 9: temperature **at which C<sub>T</sub> is determined which was 25°C in our case.**

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

Line 15: delete: „degree of“

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

Line 21: from salinity (delete „the“)

Page 441, Line 2: hydrocast

Line 13: divided **into** three

Line 17: frontal systems **were** described

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

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

Line 2: **south**

Line 7: **from**

Line 8: **north**

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

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

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

Line 18: **Bank**

Line 19: **dropped**

Line 20: **fell**

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

Line 24: delete: „the  $pH_T$  at 25°C,“

Line 25: increased  $pH_{T,25}$  (delete „the“)

Line 28:  $pH_{T,25}$  increased (delete „the“)... 8.00, **following** the ...

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

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

Line 3: delete: „area“

Line 6: delete: „important“, „clearly“ . „upwelling“ instead of „mixing“? ... deep **CO<sub>2</sub>-rich** waters takes place ... **overcompensates**

Line 13: **dropped**

Line 14: **fell**

Line 15: **decreased by**

Line 16: **dropped**

Line 17: **increased**

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

Line 25: **decreased**

Line 26: **increased**

Line 26ff: **The position of ... is seen more precisely in the pH gradient,  $pH_{T,25}$  decreased ...**

Line 28: increased

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

Line 8: deep and salty water

Line 9: **western part** of the Weddell Gyre to the **Prime Meridian**

Line 12: **deep waters rich in alkalinity**

Lines 13, 15, 17, 24, 25, 29:  $\text{pH}_{T,\text{in situ}}$

Line 16: a mean  $\text{pH}_{T,\text{in situ}}$  value

Line 18: subtropical zone with  $\text{fCO}_2$

Line 25:  $\text{fCO}_2$  **was at a maximum** and  $\text{pH}_{T,\text{in situ}}$  **was at a minimum**

Line 26: implies **that**

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**

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

Line 28: nutrient **input**

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

Page 445, Line 2: was **detected** together

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

Line 5: area **between** 30°S and 70°S

Line 11: **were**

Line 15: delete „the“; **is**

Page 446, Line1f: south, north

Line 9f: **UCDW is characterized by a  $\text{pH}_{T,25}$  as low as 7.56 (... low oxygen...) and LCDW by high salinity ... ()**.

Line 11: Both Circumpolar Deep **Water masses ... by maxima ...**

Line 16: **NC<sub>T</sub> in the range of xxx .**

Line 19: Circumpolar Deep **Water masses ... waters coming from ...**

Line 24: Weddell Sea Deep **Water**

Line 25: **We found a  $\text{pH}_{T,25}$  value of 7.62 and C<sub>T</sub> around xxx ... in WSDW.**

Line 26: **Close to the seafloor ...**

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

Page 447, Line 1: **and higher  $pH_{T,25}$  values (7.63) than in WSDW.**

Line 8: AAIW **in this region** is characterized by low  $pH_{T,25}$  **levels, ranging between 7.65 and 7.68 ...**

Line 11: where **it** met

Line 10: Cape **B**asin

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

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

Line 14: **in** the Cape **B**asin

Line 17: delete „level“

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.**

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

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

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

Line 9: aragonite

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

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

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

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

Line 21: shoaled

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

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

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

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  $\beta_H$ .**

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

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

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

Page 450, Line1: **were** observed

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

Line 9: saturation states

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

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

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

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

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

Line 13: a mean **pH** value

Line 16: **were** presented

Line 17: **was** governed

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

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

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

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

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

Page 452, Line 1: delete „also“

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

Line 5: maxima

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

Line 7ff: Eight buffer indices **that relate** changes in C<sub>T</sub> and A<sub>T</sub> **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>.

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

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

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

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