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Interactive comment on "Rapid acidification of mode and intermediate waters in the southwest Atlantic Ocean" *by* L. A. Salt et al.

L. A. Salt et al.

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We would like to thank both reviewers for their helpful comments towards improving the manuscript. Each comment has been addressed and the revised manuscript is attached as a supplement.

Anonymous Referee #1 Received and published: 11 June 2014 Review of Salt et al. " Rapid acidification of mode an intermediate waters in the southwest Atlantic Ocean".

This paper is comparing carbon and related biogeochemical variables along a repeat section in the southwest Atlantic Ocean that was occupied in 1994 and repeated in 2012. The paper focuses on the uptake of anthropogenic carbon, the decrease in pH, and on a discussion on buffer factors in the various water masses and a quantification

of the sensitivity to increasing DIC concentrations in the ocean. The paper is generally well written and scientifically relevant questions are being addressed. The manuscript deserves to be published in BG but some deficits needs to be addressed; most seriously is some probably erroneous calculations of one of the buffer factors.

Response: We would like to thank both reviewers for pointing this out. The final buffer factor has been recalculated. Whilst the distribution does not change the numbers, however, quite significantly do. Having said that, this does not affect any of our conclusions.

Another deficit is the neglect to utilize data from this section occupied in other years (2002, 2003 and 2013 by the Spanish ship Hesperides).

Response: This was considered, however, we though the analysis would then become more focused on the temporal trends in changing Cant over the two decades, elucidating trends between irregular time steps, which would most likely lead to large scale atmospheric and physical processes – as seen in Brown et al. 2010 and Perez et al. 2014. Instead we wanted to specifically examine the effects of Cant on the aforementioned buffering capacities and pH. With further analysis of another three cruises, we felt the paper would shift focus away from this. However, we do agree that such an analysis would be interesting and valuable work in the examination of Cant uptake in the southwest Atlantic.

In the discussion section the authors argues that the eMLR results is reliable in the surface waters. This is first of all surprising since the eMLR results indicates zero carbon uptake in the tropical North Atlantic, and secondly it is a different view from most previous studies that used eMLR. On pages 6771-2 the calculated (from AT and DIC) pCO2 between the two repeats is presented, with a difference in the DeltapCO2 (i.e. the ocean / atm. gradient) of 11 ppm. This is a large difference in the dis-equilibrium, and not "relatively consistent" as the authors suggest. However, and most importantly, the authors are trying to deduce sensible differences in the air-sea disequilibrium from the difference between two cruises in an area of significant seasonal variability (about +/- 20 ppm, [Takahashi et al., 2009]). The authors admit to "changes in temperature or other physical processes may exert controls undetectable to our analysis", and to " variations in chemical stoichiometry which could not be accounted for" with regard to eMLR results in surface waters. Based on the evidence presented in the manuscript, the consistency between the eMLR data and "what can be expected from increase in pCO2" is coincidental, with large areas where there is no such consistency. In the current version of the ms. I see no evidence for eMLR being any better than the expected DIC increase calculated from TA, sal etc. and the atmospheric increase in pCO2. To be able to state that "the surface ocean uptake of CO2 is less/more than expected" regular sampling over the year will be needed. I suggest to modify the discussion of the validity of the eMLR analysis in the surface waters.

Response: In light of this comment, and a similar one by the other reviewer- pointing out that further analysis of the surface waters is not mentioned in the manuscript, we have chosen to delete this section from the manuscript. Whilst the anticipated increase in Cant from atmospheric increase is in line with that calculated with eMLR in the subtropics, the tropics do show greater variation from that expected. This has been observed in the Eastern Tropical Atlantic by Shneider et al., 2012, and this is now briefly mentioned in the text, however, still no reason can be found for the calculation of 0 ΔCant from the eMLR method in the tropical Atlantic. As such, we have restrained from trying to draw any conclusions from this result.

For the discussion on buffer-factors it would be very helpful to: 1) have the density intervals separating the water masses marked on the sections in Figure 5,

Response: We tried to include density intervals on Fig. 5, however, as contour lines are already plotted, the addition of density intervals makes the plot quite difficult to read. But we agree that a visual aid of the density intervals would be helpful in distinguishing the water masses and regions, and as such we have added the density intervals to Figure 3(a) and labeled the water masses in Figure 3(b), which we believe is sufficiently

helpful.

and 2) a table with the values of the buffer factors for each water mass.

Response: We agree that this would be a nice way to summarize the results, and we have added Table 3, with the average buffer factors for each water mass and some characteristics relevant to the buffer factors.

Maybe this is a personal preference, but in the discussion on buffer capacity of various water masses, I think the discussion is incomplete without including the Revelle factor.

Response: We have added a plot of the Revelle factor to Figure 5, and incorporated it in the text as well.

The discussion on buffer factor will have to be modified once the correct omegaDIC values have been calculated (if in error, which I think they are). Specific comments: Page 6756, line 20: Consider removing the word "current" in light of the text in the next sentence.

Response: Done.

Page 6757, line 10: This statement is probably not true for the global ocean. For instance see paper by Yool et al. [2010].

Response: We agree with the reviewer that this statement is too broad, thus we have specified that we refer to the Atlantic Ocean and adjusted the text accordingly.

Page 6758, line 6: If the decrease is -0.1 unit, does that mean that pH increased? Please reformulate.

Response: Done.

Page 6760, line 2: I do not think the expression "no longer present" is correct. Maybe it would be better to say "is unstable", or "will dissolve". There are also kinetics to dissolution of sinking particles that needs to be considered.

Response: We agree that this sentence is not clear and has been modified as suggested.

Section 2.1: It is common practice, and a requirement, that the data used for a publication is publically available for other scientists to reproduce the results. Where are the Dutch 2011 data publically available? If the date are not publically available it would be appropriate not to publish this paper in BG.

Response: Yes, the intermediate data product from both cruises used in this study is now available as part of the GEOTRACES Intermediate Data Product: http://www.geotraces.org/dp/idp2014. This has now been included in the text as well.

Section 2.1: The 1994 data have been subject to so called secondary quality control in order to identify any systematic biases in the data (not only the carbonate system variables). Is this the case for the Dutch data as well? Biases in auxiliary variables can bias the eMLR analysis.

Response: No, at current time, the Dutch data has so far not undergone any additional investigation into systematic biases. However, our comparison between the auxiliary variables of the two datasets indicate good conformity thus we anticipate minimal bias in the eMLR results.

Page 6763, line 23: It is mentioned that pressure is used in the regression. Why is P not in equation 2? Please correct equation and discussion below eq 2.

Response: Thank you for pointing this out, this was an oversight and has now been included in the equation.

Page 6764, equation 5: This is most likely in error. Due to editorial errors in the paper by Egleston et al. (2010) this equation is not correct. This is unfortunate, and not easy to spot by the authors. It was noted for the first time in a recent paper by [Álvarez et al., 2014] Please see either the thesis of Egleston or the paper by Álvarez et al. [2014] for the correct expression. This will obviously have consequences for the discussion in

the paper that needs to be correspondingly modified.

Response: Yes, thank you for bringing this to light. The correct equation from Alvarez et al., 2014 has now been applied and we have changed equation 5 accordingly.

Figure 3: The font-size of the text in these panels is too small to read. Please modify.

Response: Done.

For the discussion it would be very useful to include iso-lines of density corresponding to the water mass divisions on these plots. Same is valid for the other sections in other figures, e.g. Figs 4 and 5.

Response: This has been done for Figure 3(a), also please see above comment.

Page 6765, line 16: Why "below 1000 meter"? The discussion is about AABW (below 4500 m), or not?

Response: This depth was included to make it clear that the AT 'maximum' that we were discussing was not the maximum in the entire section, but a subsurface/deep maximum. To make this clear we have rephrased this in the text and placed the depth specification in brackets.

It would be useful to have the characteristics of the water masses in a table.

Response: This has now been done to sufficient degree in Table 3, with the accompanying buffering capacities.

Page 6767, line 21: The discussion on warm surface water is not correct in this context; high temperatures as in the tropical Atlantic leads to high buffering capacity and potentially high Cant concentrations. That the eMLR shows zero Cant concentrations at the surface must have other reasons.

Response: This discussion has now largely been deleted and the remaining parts modified.

Page 6768, line 22: This is inconsistent with the analysis above, see point made above. Either you use the eMLR analysis and discuss temporal variability (using more than the 2 repeats you report on) both on seasonal, annual and decadal time-scales, or you accept that the eMLR on surface waters is unreliable and base your calculations solely on expected changes of surface water based on atmospheric CO2 change.

Response: In light of previous comments, the section dealing with surface Cant increases has been deleted.

Section 4.2: The same discussion about close to surface waters does apply to this section as well.

Response: This discussion has now been modified (see above comments).

Page 6770, line 15: An acidification rate of -0.0005 /y means that the pH value increases. Please exchange "acidification" to Delta-pH, or change the sign.

Response: Done.

Page 6773: The discussion on the relative sensitivity on pH to DeltaDIC is a bit of circular evidence since you have calculated DeltapH from DeltaDIC, but obviously with different TA etc. This is obviously the buffer capacity (betaDIC) that is different, as the authors explore later. Also, the difference in DeltaDIC and DeltapH is only meaningful if you add uncertainties to those numbers. With any realistic uncertainty to those numbers I doubt that you will find a significant difference.

Response: DeltaDIC is given with uncertainty (Table 2). We admit when calculating pH from AT, and DIC there will inevitably be an error introduced, simply by the calculation, however, as we use the same calculation for both datasets and focus on the change in pH between time periods we believe that the error introduced, should be minimal.

References: Álvarez, M., H. Sanleón-Bartolomé, T. Tanhua, L. Mintrop, A. Luchetta, C. Cantoni, K. Schroeder, and G. Civitarese (2014), The CO2 system in the Mediterranean Sea: a basin wide perspective, Ocean Sci., 10(1), 69-92. Takahashi, T., et

al. (2009), Climatological mean and decadal change in surface ocean pCO2, and net sea-air CO2 flux over the global oceans (vol 56, pg 554, 2009), Deep-Sea Res. I, 56(11), 2075- 2076. Yool, A., A. Oschlies, A. J. G. Nurser, and N. Gruber (2010), A model-based assessment of the TrOCA approach for estimating anthropogenic carbon in the ocean, Biogeosciences, 7(2), 723-751.

Referee #2; Marta Alvarez REVIEW of Salt et al. (2014): Rapid acidification of mode and intermediate waters in the southwest Atlantic Ocean

This work quantifies the increase of anthropogenic carbon (CANT) and the derived pH decrease in the water column of the southwest Atlantic Ocean using data from two occupations of the WOCE A17 section in 1994 and 2010/11. Although the CANT increase / pH decrease in the ocean is always a relevant issue, this work suffers from major methodological problems and presents a quite simplistic approach to tackle this question. My first conclusion was rejection, but if several MAJOR IMPROVEMENTS are done, it might be finally accepted in Biogeosciences.

MAJOR ISSUES 1) Literature references. Some references are wrongly used (Levine et al., 2011, page 6756, line 21), others are omitted (page 6757, last phrase, e.g., Mikaloff-Flecher et al. (GBC 2011), Lovenduski et al. (GBC 2011)), and on the other hand too many are cited for specific issues. Please read the manuscript again with new eyes.

Response: We have corrected the references mentioned as suggested and modified other references in-line with the adjustments made to the manuscript. I am working on the assumption that the Mikaloff Flecher reference was the 2006 paper, which has been included, and the Lovenduski, 2007 paper (I think this is the one you were referring to) has also been included in the discussion.

2) Data. The data section needs to be reorganized (combine and reorganize current sections 2.1, 2.2 & 2.3). Many details for the 2010/2011 CO2 data, which is good, but none for the 1994 data (TA was corrected, DIC was measured but also pH, state which

CO2 parameters you used). Not all the 1994 stations shown in Fig 1 were measured for CO2 data, please show just the stations with CO2 data used. The legend in Fig 1 is wrong.

Response: The data and methods sections have now been split into two different sections, and the sections rearranged into a more logical order. Furthermore, we have gone into more detail regarding the data used from the WOCE 1994 dataset, however, we refrain from going into as much detail as for the GEOTRACES dataset, as the WOCE dataset is already well-documented in the literature, whereas the GEOTRACES dataset is not. We have corrected Figure 1 to represent only the stations from which DIC and AT data was used for the analysis and the caption has been corrected and the incorrect "cruise track" for 1994 has also been removed.

Section 2.3. The consistency of CO2 and ancillary data needs to be compared for both cruises if you are to use an eMLR approach. Why using the whole data set for waters below 400 dbars?. It would be better to choose the data corresponding to the water mass with lower temporal variability maybe CDW.

Response: The depth of 400dbar was chosen to select the waters beneath the winter mixed layer - as waters shallower would show greater variability. However, using a water mass of known lower variability is more logical, as such, we have now specifically mentioned the variability in lCDW, as suggested.

The statements in page 6762 lines 1-3 make me question the rest of the work. When comparing data to find any bias I would look not only at the mean difference but also the standard deviation.

Response: The standard deviation was actually included as the numbers following the average differences, however, as pointed out, this was not clear in the text. These numbers (now referring to lCDW) have now been rewritten in a more conventional way to make this much clearer.

Just using two data sets when there is a well document CO2 data set in the western AO (Rios et al, 2011) and the new 2013 FICARAM occupation is simplistic and should be justified.

Response: The use of two datasets was with the idea to look at the total changes of anthropogenic carbon over almost two decades, thus using the baseline measurements of WOCE and (at the time) the most recent GEOTRACES occupation. We recognize that using all available datasets would yield more insights, particularly into the temporal evolution of increasing anthropogenic carbon in the section, however, such an analysis would inevitably change the following discussion and we wanted to consider the changes in buffering capacity and pH accompanying the increasing Cant. We felt that trying to fit all this into one paper may be slightly ambitious and thus kept to a more focused story. (Please also see comment and response by Reviewer #1).

3) Methods. I would separate this section from the one dealing with the Data. Response: Done.

In general, I do not understand / accept why you calculate the CANT increase with the eMLR approach while to calculate the pH decrease you apply the backcalculation technique. It has no sense and it makes me think that something is hidden.

Response: The pH decrease from 1994 to 2011 is calculated using the ΔCant eMLR results. The (ÏŢCT) Cant method was applied only to obtain pre-industrial values of DIC, thus enabling us to calculate the pH change (driven by Cant) since pre-industrial times. This has been rephrased in the text to make it more clear which method we use for which calculation.

Regarding the eMLR method: clearly state if you use a forward or backward method and why. In Fig 2 the residuals for the 1994 seem to have a rmse (by the way, define this acronym in the text) higher than the 2010/2011 adjustment but in page 6763 lines 7-10, you say 1994 – 6.66 and 2010 – 9.87 umol/kg. The maximum residual in Fig 2 for the 2011 data is higher than 7 umol/kg.

Response: Thank you for calling our attention to this – the former values quoted for 1994 and the max. residual in 2011 were from the deeper waters and had not been corrected when the text was changed. Both mistakes have now been changed accordingly.

(page 6763 line 18). In Table 1 what rmse is shown, that for 1994 or 2011?. I think you should give the coefficients for each year and the corresponding rmse and R2. Response: Table 1 has been changed as suggested, to show the coefficients for each year (Table 1 (a) and (b)) and corresponding rmse and R2 for each regression.

CANT method: no proper references are used for the method use. Although I do not understand why you use it to calculate the pH decrease but not the CANT increase?.

Response: The Cant method is outlined and explained in Vazquez-Rodriguez et al., 2009a, however, we understand this paper was never published in Biogeosciences, only Biogeosciences Discussions, and have thus added a reference to the Thesis of M. Vazquez-Rodriguez for more detail. The Cant method was largely employed to obtain total Cant values to compare the change in pH from pre-industrial times to 1994, and then we would use the eMLR results to calculate the change in pH from 1994 to 2011. As Cant was calculated and used, we have now included the plot of Cant in 2011 (Fig. 4a) to complement the change in Cant calculated by eMLR.

Buffer factors: as commented by the other referee, please check them in Álvarez et al. (Oc. Sc. 2014). Although knowing about the typo in their Table 1, the Egleston et al did not bother to write a correction in GBC, and it took me a few months to get the correct Table. State clearly that the buffer factors related to DIC only consider DIC changes at constant TA, so CO2 air-sea exchange.

Response: The buffer factors have been recalculated using suggested Matlab script, which was very much appreciated, thank you. We have also stated in the text that only the buffer factors relating to DIC have been calculated.

4) Results As they are written now, discussion is also included.

Response: The results and discussion section have been merged in light of the other changes made.

5) Discussion A great deal of the discussion is about the eMLR method in the surface ocean when the title of the work is about intermediate and mode waters.

Response: In light of the other reviewers concerns as well, the section dealing with eMLR in surface waters has been removed.

The part dealing with the buffer factors is obviously questioned.

Response: The one buffer factor that was miscalculated has now been corrected, however, the conclusions are not affected by this.

Fig 6 is just a thermodynamic exercise. In the text there is no explanation for the DIC increase (by the way, either use CT or DIC) calculation for each water mass. It would be more interesting to check with real data (with all the temporal occupations of the W-SAO) how much the buffer factor changed by water masses.

Response: Whilst Figure 6 does largely show the results of a "thermodynamic exercise" the buffer values from 1994 use the WOCE data, thus it is an accurate demonstration of the change in buffering capacity over 17 years. We further feel that this is a clear and concise way of displaying such changes, not only as measured, but also projected changes. We have added some text to explain this figure a bit more, thus hopefully helping to highlight its significance. We have also added more explanation into the distribution of Cant in the Results section (5.1). We also now consistently use DIC, rather than a mixture of DIC and CT, although "Cant" remains, as it is so common in the literature that we felt that changing it to DICant could only lead to confusion.

I encourage the authors to answer the questions and improve the paper with the proposed suggestions. I provide a matlab script to calculate the buffer factors with the matlab version of CO2SYS as I did in the 2014 paper. Just copy the text below and change it accordingly to your data. This option is for DIC and TA input.

We would also like to thank you again for the matlab script – it definitely saved us time.

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/11/C4305/2014/bgd-11-C4305-2014-supplement.pdf

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Interactive comment on Biogeosciences Discuss., 11, 6755, 2014.

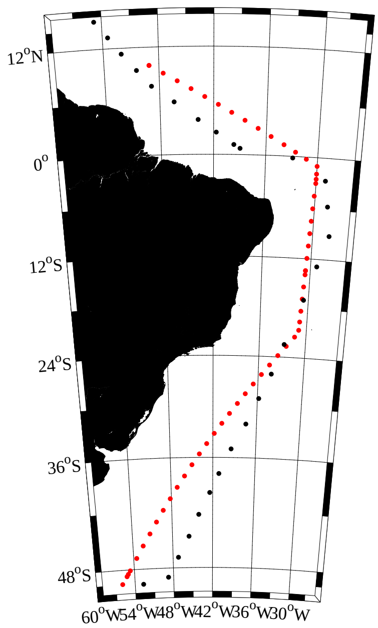
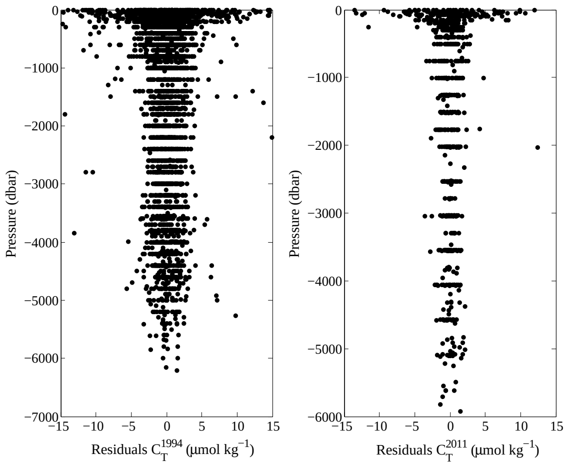


Fig. 1.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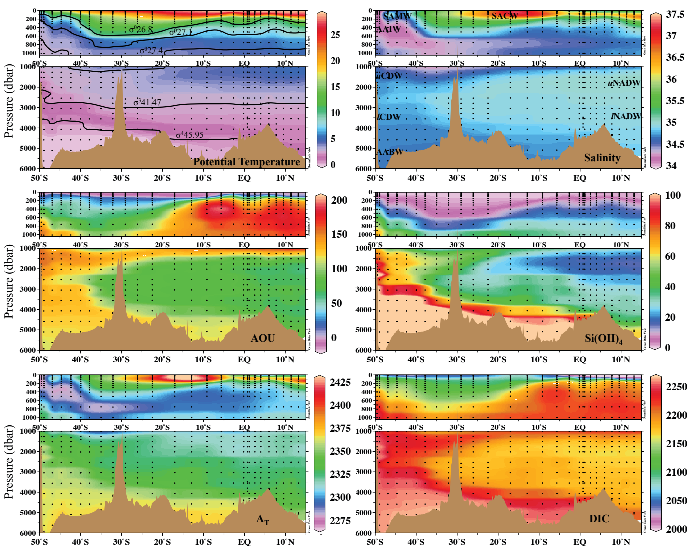
Residuals C_T^{1994} (μmol kg^{-1})
Residuals C_T^{2011} (μmol kg^{-1})

Fig. 2.


Pressure (dbar)
Potential Temperature
Salinity
AOU
Si(OH)$_4$
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DIC
SAMW
SACW
AAIW
uCDW
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lCDW
AABW

Fig. 3.

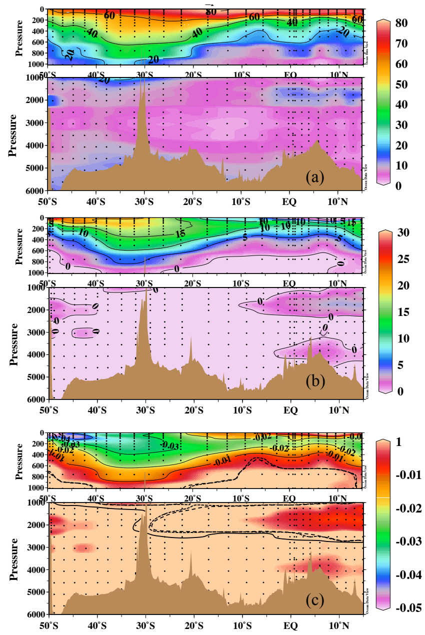

Fig. 4.

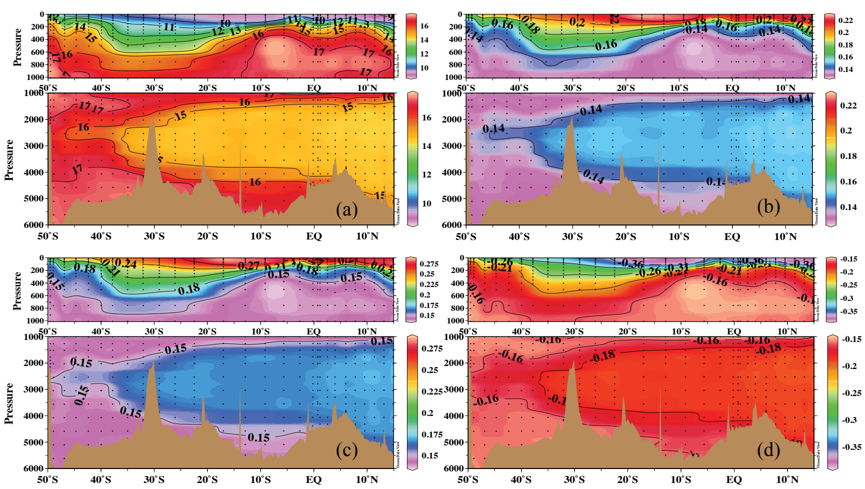

Fig. 5.

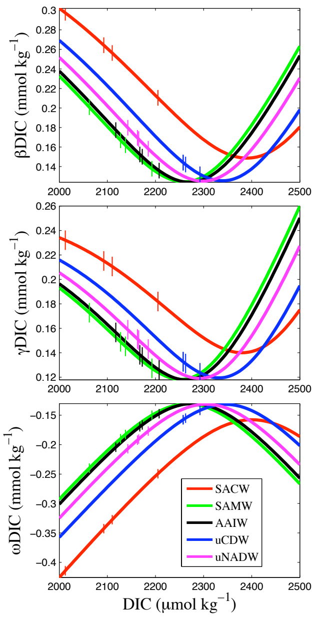
βDIC (mmol kg^{-1})
γDIC (mmol kg^{-1})
ωDIC (mmol kg^{-1})
DIC (μmol kg^{-1})
SACW
SAMW
AAIW
uCDW
uNADW

Fig. 6.