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## ***Interactive comment on “Estimating carbonate parameters from hydrographic data for the intermediate and deep waters of the Southern Hemisphere Oceans” by H. C. Bostock et al.***

**H. C. Bostock et al.**

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We would like to thank the two anonymous reviewers for their valuable and constructive feedback and address the major comments from each referee below.

Referee#1 The first reviewer asked us to clarify the data and corrections that we used to develop the algorithms, and we would like to thank the reviewer for the clarification of the differences between the WOCE and CLIVAR and GLODAP and CARINA/PACIFICA. We used the original measured alkalinity and DIC data from south of 25°S and deeper than 200 m from the WOCE/CLIVAR voyages, rather than the GLODAP or CARINA/PACIFICA data products, which we will state more explicitly in the

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revised text. We did not recalculate the data, but we did quality control these original WOCE/CLIVAR data as discussed in the text.

“We undertook quality control of the carbonate and hydrographic data using two approaches. Any data that was larger or smaller than typical oceanographic values were removed (Table 2). The data were then plotted against each other, e.g. temperature vs salinity, DIC vs oxygen. These were plotted against data of similar potential density to determine any outliers greater than 3 standard deviations from the mean (Pearson, 2002). Outliers were not removed if there was a cluster of points from one voyage, or in one region, that could represent a real feature. . . . . In total  $\sim 150$  samples ( $<1\%$ ) were removed from the overall dataset of  $\sim 20,000$  data points. Most of the outliers were due to erroneous alkalinity and DIC measurements, but several were due to high oxygen and salinity data.” If this is unclear, we are happy to clarify further in the text.

The reviewer states that the “deeper values are relatively strongly overestimated. I am missing a quantitative discussion on what this means for the derived parameters like the saturation states”. Yes, we agree that the deeper values are overestimated, but his appears to have little impact on the calculated saturation states as stated in the text “...  $\Omega_{\text{aragonite}}$  and  $\Omega_{\text{calcite}}$  give an  $R^2 = 0.99$ ,  $RSE = \pm 0.05$  and  $\pm 0.08$  respectively (Fig. 5). This is just greater than the overall uncertainties of the aragonite and calcite saturation state calculations of  $\pm 0.03$  and  $\pm 0.05$ , respectively (Mucci, 1983; Millero, 1995; Feely et al., 2012). The high  $R^2$  for  $\Omega_{\text{aragonite}}$  and  $\Omega_{\text{calcite}}$  suggests that the errors in the alkalinity and DIC are offset in the calculation of the saturation states.”

The reviewer asks us to explain why there are two distinct regimes the way you define them. More regimes might be discerned as well. The reviewer is also “not convinced that the minimum in chi square for DIC is at 27.5 from the figure I read 27.4”. We have chosen to just use two distinct regimes for waters  $>200$  m. The Monte Carlo simulation shows that there is a distinct change at a potential density of 27.4-27.5 (27.5 is chosen as both the alkalinity and DIC display peaks at this density). The data between 27.45 and 27.55 is an average of both the intermediate and the deep water algorithms. This

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potential density agrees well with the transition between intermediate and deep waters in the Southern Oceans. We comment in the text that the Pacific Deep Waters should probably be a separate regime as they have the highest residuals. But Pacific Deep Waters cannot be separated using potential density alone and would require another parameter such as oxygen to be used to define them. Each major basin would probably have several different regimes if analysed individually. However, we have chosen to keep it simple with just the two, and the algorithm still appears to work relatively well.

The reviewer asks “Are the oxygen data referred to spurious? In that case, they should be discarded.” We mentioned the anomalous oxygen data, which was not removed by our original quality control, because when we used this oxygen data it provided estimates of DIC and deep water alkalinity that were significantly offset from the rest of the P06 line and transects crossing it. Therefore, we suggest that there may have been an issue with the oxygen calibration for several stations during this P06 voyage. The point we were trying to make is that you need good, well-calibrated, hydrographic data for these algorithms to work well. As we have also discovered with our own data from around New Zealand.

The reviewer is concerned about the calculation of aragonite and saturation states without using phosphate and silicate, especially in a high nutrient region like the Southern Ocean. These concerns are valid. We found that there is a 1-3% difference in the calculated aragonite and calcite saturation state if silicate and phosphate are assumed to be 0 in the calculation. The residuals are greater for calcite saturation states and at high latitudes. The latter is expected, as this is where deep waters with high concentrations of nutrients are upwelled. Therefore without silicate and phosphate data the ASH and CSH are slightly deeper than if the nutrient data are used for the calculation. The algorithms we have produced are primarily concerned with estimating alkalinity and DIC. We deliberately did not use nutrients in our final calculations of the aragonite and calcite saturation states as there are currently no sensors to measure these in-situ. Silicate and phosphate concentrations are analysed on bottle samples at the

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same depths as the alkalinity and DIC. Therefore the spatial and depth coverage of nutrient data in the oceans, while generally better than alkalinity and DIC, is still not as good as hydrographic data from CTDs (or in future Argo). The CARS climatology does not have nutrient data. Therefore we suggest that the ASH and CSH developed from the CARS climatology are slightly deeper than if we had used phosphate and silicate concentrations in our calculations, but the spatial and depth resolution is significantly increased. We would recommend that, if available, the nutrient data is used for these calculations of the other carbonate parameters in CO2Sys. A statement along these lines will be added to the manuscript.

We chose to use CARS rather than WOA, as CARS data is provided at a resolution of  $0.5^\circ$ , while WOA09 is only at a resolution of  $1^\circ$ , i.e., the same as GLODAP data set, so maps of saturation state would be equally sparse in the deep ocean. To provide more context for the introduction and discussion, we will provide a map of the southern hemisphere/Southern Ocean with all the topographic features, basins, currents and fronts mentioned in the text. We will reassess the abbreviations used throughout the paper. The figures will be enlarged, and we will address the minor typo and grammar comments from this reviewer.

Referee#2 The second reviewer has recommended that we address the issue of the anthropogenic carbon perturbation (also mentioned by Referee#1) explicitly for three reasons: 1) Although the mean biases may be small, they will be non-linear in nature and have a spatially coherent structure along isopycnal surfaces. 2) While DIC has an anthropogenic signal, alkalinity does not, which could lead to a non-linear bias in the prediction of the aragonite and calcite saturation horizons from these two variables. 3) It would allow this technique to be applied in the future with newer datasets.

This point is also related to the reviewer's recommendation that we also look separately at the algorithms for the 1990's and 2000's in order to infer changes in the anthropogenic input to the carbonate system.

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In order to assess the magnitude of the biases due to changes in anthropogenic carbon storage in the ocean interior, we used the simple scaling argument proposed by the reviewer, along one line in the Pacific (P16S). We scaled the GLODAP anthropogenic carbon (calculated using  $C^*$ ) by 20%, based on the additional anthropogenic carbon storage that would be predicted from the atmospheric CO<sub>2</sub> increase between 1995 and 2005 (analogous to the scaling used in Mikaloff Fletcher et al 2006). This is a simple perturbation test that neglects the fact that the spatial distribution of anthropogenic carbon storage is likely to have changed slightly, but gives us a first pass estimate of the expected magnitude of decadal change. Figure 1a shows the anthropogenic carbon increase that would be expected along P16S based on this scaling argument. We see less than 9 micromol/kg increase, and along P16S for waters deeper than 200m (e.g. the depth range included in this study). This is similar to the residual standard error for DIC for the algorithms ( $\pm 7.3$  micromol/kg). The residuals between the observed and estimated DIC from our algorithms are shown in Figure 1b. Contrasting these two figures shows both that the magnitude of the anthropogenic carbon perturbation is small compared to other sources of error in the method, and that the spatial structure of the residuals from our algorithms does not appear to reflect a strong influence from the anthropogenic carbon input. After careful consideration of the errors introduced by the anthropogenic carbon, we still consider this to be minor for intermediate and deep waters. However it is an interesting issue, and future work will look to address this as discussed below.

The reviewer's second point is that since the anthropogenic carbon accumulation effects the DIC but not the alkalinity, a non-linearity is introduced that could cause larger errors in the calculation of other aspects of the carbonate system from these two species such as the ASH and CSH. Feely et al. (2012) show a relatively modest change in aragonite saturation state south of 25°S along line P16 between 1992 and 2006 of  $\pm 0.1$  in the upper 500 m (with a similar story for P18). This will not affect the depth of the calculated ASH, which is >500 m. Also, there is currently little evidence that the deeper waters have had enough anthropogenic carbon input to affect

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the calculated CSH.

The third point is around creating an approach to handling the anthropogenic carbon storage that will allow this method to be used to explore decadal changes in the ASH and CSH between the 1990's and 2000's. Such an approach could also be applied to new datasets in the future as the anthropogenic carbon storage effect increases. During the development of these algorithms, we were interested in exploring the role of decadal change. "We found that there were subtle variations in the MLR algorithm coefficients when only the 1990's data is used compared to the 2000's data". The changes in the algorithms between the decades were relatively modest compared to, for example, grouping the data by basin. Furthermore, we concluded that it would require a much more sophisticated approach to handle this in a consistent fashion on a global scale, because the cruises are spread widely in time over the two decades. We are working towards developing a method to handle the anthropogenic CO<sub>2</sub> perturbation correctly in order to allow these methods to be used to look at past and future changes in the carbonate system. This work is underway, however it represents a substantial undertaking and is therefore beyond the scope of this manuscript.

Extra reference: Mikaloff-Fletcher, et al., 2006. Inverse estimates of anthropogenic CO<sub>2</sub> uptake, transport, and storage by the ocean. *Global Biogeochem. Cycles*, 20, GB2002, doi:10.1029/2005GB002530.

Figure 1: a) The expected increase in anthropogenic carbon between 1995 and 2005 for deeper than 200 m using a simple scaling argument that the atmospheric anthropogenic CO<sub>2</sub> increased by 20%, and thus the ocean uptake by increased by 20%, b) the difference between the measured DIC and the estimated DIC using our algorithms, which shows much larger errors than the anthropogenic input and with a different depth distribution.

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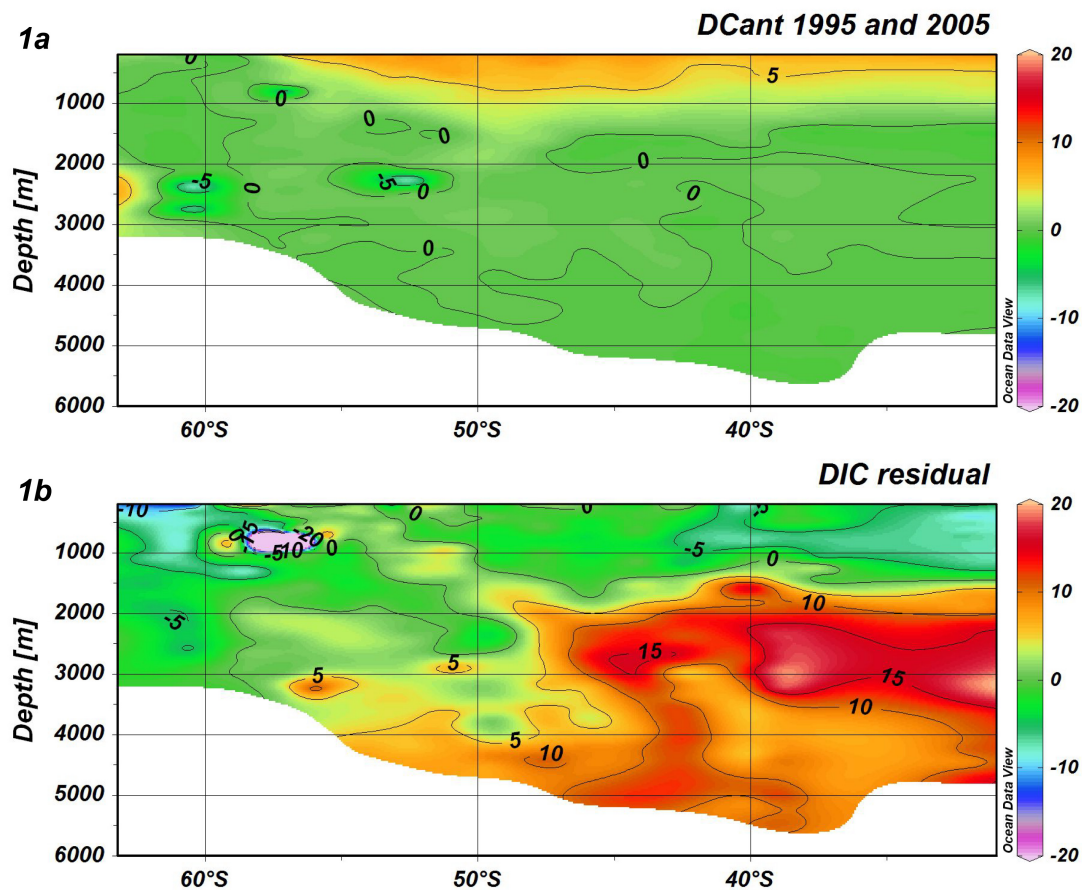
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**Fig. 1.** Figure 1: see text for rest of caption

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