Biogeosciences Discuss., 10, 6225–6257, 2013 www.biogeosciences-discuss.net/10/6225/2013/ doi:10.5194/bgd-10-6225-2013 © Author(s) 2013. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Biogeosciences (BG). Please refer to the corresponding final paper in BG if available.

# Estimating carbonate parameters from hydrographic data for the intermediate and deep waters of the Southern Hemisphere Oceans

# H. C. Bostock, S. E. Mikaloff Fletcher, and M. J. M. Williams

National Institute of Water and Atmospheric Research Ltd., Private Bag 14-901, Wellington 6241, New Zealand

Received: 31 January 2013 - Accepted: 25 February 2013 - Published: 2 April 2013

Correspondence to: H. C. Bostock (helen.bostock@niwa.co.nz)

Published by Copernicus Publications on behalf of the European Geosciences Union.



# Abstract

Using GLODAP and CLIVAR ocean carbon data, we have developed several multiple linear regression (MLR) algorithms to estimate alkalinity and dissolved inorganic carbon (DIC) in the intermediate and deep waters of the Southern Hemisphere (south of 25° S) from only hydrographic data (temperature, salinity and dissolved oxygen). A Monte Carlo experiment was used to identify a potential density ( $\sigma_{\theta}$ ) of 27.5 as an optimal break point between the two regimes with different MLR algorithms. The algorithms provide a good estimate of DIC ( $R^2 = 0.98$ ) and alkalinity ( $R^2 = 0.91$ ), and excellent agreement for aragonite and calcite saturation states ( $R^2 = 0.99$ ). Combining the algorithms with the CSIRO Atlas of Regional Seas (CARS), we have been able to map the calcite saturation horizon (CSH) and aragonite saturation horizon (ASH) for the Southern Ocean at a spatial resolution of 0.5°. These maps are more detailed and more consistent with oceanography than the gridded GLODAP data. The high resolution ASH map reveals a dramatic circumpolar shoaling at the Polar Front. North of 40° S the CSH is deepest in the Atlantic (~ 4000 m) and shallower in the Pacific Ocean

40° S the CSH is deepest in the Atlantic (~ 4000 m) and shallower in the Pacific Ocea (~ 2750 m), while the CSH sits between 3200 and 3400 m in the Indian Ocean.

#### 1 Introduction

Our understanding of the carbonate concentrations and saturation in the oceans has been considerably advanced by the collection of large global datasets such as
 GEOSECS (1960–1970s), GLODAP (1990's; Lamb et al., 2002; Key et al., 2004) and more recently CLIVAR/CO<sub>2</sub> Repeat Hydrography Program, also known as CA-RINA/PACIFICA (2000's; Tanhua et al., 2008; Sabine et al., 2009). However, there are still large gaps, with many areas of the globe that have had little sampling for carbonate parameters. Some of these regions have significant topographic features, such as
 plateaux and ridges that produce complex currents, thus it is not possible to extrapolate or grid the global datasets across these regions to provide meaningful local estimates.



There may also be temporal variability in these parameters due to seasonal (Feely et al., 1988; Juranek et al., 2009, 2011; McNeil, 2010; McNeil et al., 2011; Alin et al., 2012) or interannual variations caused by phenomenon like El Niño Southern Oscillation (ENSO; McNeil, 2010) or the Pacific Decadal Oscillation (PDO; Kim et al., 2010),
<sup>5</sup> which will not have been captured by the one off or decadal repeat transects across the global oceans.

In contrast, there are vast repositories of hydrographic data, which have been compiled to produce ocean climatologies (e.g., World Ocean Atlas (WOA), 2009; CSIRO Atlas of Regional Seas (CARS), 2009). If it was possible to use the detailed hydro-10 graphic data to estimate the carbonate parameters in areas where there has been limited sampling for alkalinity and DIC, we could potentially provide detailed carbonate saturation estimates for all areas of the global oceans, with more realistic values in areas where there are complex topography and currents that are not well represented by interpolation of sparse carbon data.

<sup>15</sup> One potential solution would be to develop relationships between carbonate species and hydrographic data using a multiple linear regression (MLR) fit to the existing carbonate data, and then use these relationships and the more widely available oceanographic data to obtain high spatial and temporal resolution information. This MLR approach was first used to predict carbonate species by Wallace (1995), based on obser-

- vations that carbon exhibited strong correlations with other oceanographic parameters (Brewer et al., 1995). Over the last few years, several publications have used MLR techniques to estimate the carbonate parameters (or carbonate saturation), and changes in anthropogenic carbon uptake from hydrographic measurements (Archer, 1996; Brewer et al., 1997; Millero et al., 1998; Sabine et al., 1999; Lee et al., 2000, 2006; Wallace et
- al., 2001; McNeil et al., 2001; Friis et al., 2005; Sabine et al., 2008; Juranek et al., 2009, 2011; Kim et al., 2010; McNeil, 2010; Wanninkhof et al., 2010; Peng and Wanninkhof, 2010; Feely et al., 2012). Many of these studies have augmented the hydrographic data with nutrients and/or one of the carbon parameters, hence restricting the usability of these MLR algorithms to regions where this extra data also exists.



Many of the previous efforts to undertake this kind of work have focussed on the surface waters of the oceans (e.g. Millero et al., 1998; Lee et al., 2000, 2006). We focus on the intermediate and deep waters and the depth of the calcite (CSH) and aragonite saturation horizons (ASH), as our interest is in understanding how carbonate ion concen-

- trations of bottom waters, which interact with the seabed, affect the distribution of deep water carbonate organisms and sediments. For example, the global depth distribution of deep sea habitat-forming, aragonitic, stony (Scleractinian) corals have been found to be controlled by the aragonite saturation state, with 95% of the organisms found above the ASH (Guinotte et al., 2006). With the ASH currently shoaling at 1–2 m yr<sup>-1</sup> in the
- <sup>10</sup> Southern Hemisphere oceans (Feely et al., 2012), and predicted to shoal considerably in the Southern Ocean by 2100 (Orr et al., 2005; McNeil and Matear, 2008), this could significantly reduce the habitat for these aragonitic organisms.

In this paper, we develop MLR algorithms to estimate carbonate parameters for intermediate and deep waters of the Southern Hemisphere, using hydrographic data (tem-

<sup>15</sup> perature, salinity and dissolved oxygen) and carbonate data (alkalinity and dissolved inorganic carbon – DIC) collected during the WOCE/GLODAP and CLIVAR campaigns from the Southern Ocean. After testing the MLR algorithms with detailed CTD hydrographic data from the WOCE transects, we then apply the algorithms to the CARS (2009) climatology database to produce detailed maps of the CSH and ASH for the Southern Hemisphere oceans.

#### 2 Oceanography

25

The oceanography of the Southern Hemisphere oceans is dominated by the Southern Ocean (Orsi et al., 2005). The Southern Ocean links all the large ocean basins of the world via the Antarctic Circumpolar Current (ACC), and acts as an important biogeochemical exchange venue, orchestrating the transfer of nutrients between deep and surface waters and the exchange of carbon between the ocean and atmosphere



masses south of the SAF, although there are subtle differences in the water chemistry at depth due to the influence of deep waters entering the Southern Ocean and the formation of intermediate waters that flow north into the adjacent Pacific, Atlantic and Indian basins.

- Subantarctic Mode Waters (SAMW) and the low salinity Antarctic Intermediate Waters (AAIW) have high oxygen and low alkalinity, as they are formed by the subduction of Antarctic surface waters (AASW) at the SAF (Fig. 1; e.g. McCartney, 1977, 1982; Talley, 1996, 1999; Sloyan et al., 2010). The primary region of formation is the southeast Pacific, but there is subduction at several other locations in the Southern Ocean (Sallée Context).
- to et al., 2010; Bostock et al., 2013). These cool AASW are subducted between potential density ( $\sigma_{\theta}$ ) surfaces of 26.9 and 27.3 and have low alkalinity and intermediate DIC (Gonzalez-Davila et al., 2011; Bostock et al., 2013; Fig. 1). The aragonite saturation horizon (ASH) sits at the base of the AAIW in the majority of the South Pacific basin (Bostock et al., 2013).
- <sup>15</sup> Below the intermediate waters is the Circumpolar Deep Water (CDW). The CDW is commonly split into lower (ICDW,  $\sigma_{\theta} > 27.75$ ) and upper (uCDW,  $\sigma_{\theta} = 27.3$  to 27.75) components. The uCDW has a low oxygen signature, with high alkalinity and DIC in the Pacific Sector due to the influence of old Pacific Deep Water (PDW; Bostock et al., 2011; Fig. 1). These deep waters upwell at the Polar Front (PF; Fig. 1), where old carbon rich waters release CO<sub>2</sub> back to the atmosphere. The ICDW also has high alkalinity and DIC (Fig. 1) but has higher salinity and oxygen than the overlying uCDW due to the influence of Antarctic Bottom Water (AABW) (Fig. 1; Orsi et al., 1999). CDW also has a large influence from North Atlantic Deep Water (NADW), especially in the South Atlantic, with its slightly higher salinity of 34.72–34.73 (Warren, 1981) and lower alkalinity and DIC (Gonzalez-Davila et al., 2011).

There is some variability in the intermediate and deep waters below the subtropical gyres in the different ocean basins. In the southeastern Pacific, there is significant upwelling in the Peru/Chile Current, which extends from 43° S to 10° S. This results in the shoaling of the ASH to < 500 m (Feely et al., 2004; Bostock et al., 2013). These



waters overlie the low salinity, well oxygenated AAIW, which has recently formed in the southeast Pacific (McCartney, 1977).

The circulation in the southwest Pacific is complex due to the topography. There are multiple types of AAIW in the southwest Pacific (Tomczak and Godfrey, 1994; Hamilton,

- <sup>5</sup> 2006; Bostock et al., 2013). Beneath the AAIW in the central South Pacific sits the highly corrosive PDW, with very high alkalinity and DIC, which causes the CSH to shoal to 2700 m between 130° W to 180° (Bostock et al., 2011). These waters have excess alkalinity due to the dissolution of carbonate (Feely et al., 2002). The PDW is also the main water mass that enters the South Fiji and New Caledonia Basins in the
- southwest Pacific, as the complex topography of this region blocks the flow from the south, and the only entrance is via the Solomon Sea in the north (Sokolov and Rintoul, 2000). In contrast, the Tasman basin only receives CDW, with lower alkalinity and DIC, directly from the Southern Ocean. Therefore the deep waters in the Tasman basin have a deeper CSH at ~ 3100 m (Bostock et al., 2011).
- The AAIW flows into the South Atlantic along the western boundary under the Malvinas Current at 500–1200 m, but then continues north under the western boundary Brazil Current (Tomzcak and Godfrey, 1994). A tongue of uCDW lies immediately below the AAIW, but is only found as far north as 22° S (Stramma and England, 1999; Gonzalez-Davila et al., 2011). NADW, which has lower DIC and alkalinity than other
   deep waters, dominates the deep waters of the South Atlantic (Stramma and England, 1991)
- 1999). The NADW mainly flows down the Southwest Atlantic, with smaller amounts in the Southeast Atlantic (Stramma and England, 1999). Below the NADW are a number of weak tentacles of northward flowing AABW, all of which are topographically constrained by seafloor features, especially in the southeast Atlantic where AABW is
- <sup>25</sup> prevented from flowing north of 25° S by the Walvis Ridge (Tomzcak and Godfrey, 1994; Stramma and England, 1999).

In the Indian Ocean the AAIW, with its conspicuous salinity and alkalinity minimum, overlies the Indian Deep Water (IDW). The IDW is characterised by a salinity maximum, intermediate alkalinity and DIC. These IDW have been influenced by mixing with



NADW, especially in the deep western boundary current (Ganacharud et al., 2000). In the east, the CDW/AABW enters via the Australian-Antarctic Discordance and then moves north along the western boundary of the Ninety East Ridge (Tomczak and Godfrey, 1994).

#### 5 3 Data

This study uses all the WOCE/GLODAP, CLIVAR voyages for which alkalinity and DIC were measured on bottle samples, and the associated hydrographic data were also collected (temperature, salinity, dissolved oxygen) (Table 1; Fig. 2). We used all the data south of 25°S and deeper than 200 m. as the intermediate and deep water masses formed in the Southern Ocean lie beneath the subtropical gyres. In total there 10 are  $\sim 20\,000$  bottle sample data for alkalinity and DIC. The sampling and analyses of the hydrographic and carbonate parameters were performed following standard protocols. Total alkalinity was determined by potentiometric titration and calculated using the Mehrbach et al. (1973) carbonate constants as refitted by Dickson and Millero, 1987, while DIC was analysed using coulometric titration; U.S. Department of Energy (DOE), 15 1994) and using certified reference material (CRM; Dickson, 2001). The accuracy of the carbonate parameters is estimated at  $\pm 3 \mu$ mol kg<sup>-1</sup> for DIC and  $\pm 5 \mu$ mol kg<sup>-1</sup> for alkalinity (Lamb et al., 2002; Dickson et al., 2007). A secondary quality control is performed by comparing the deep water (> 2000 m) hydrographic, nutrient and carbonate data where they cross other transects, and most of the data is within measurement 20

error (Key et al., 1996, 2002; Lamb et al., 2002; Sabine et al., 2009; Tanhua et al., 2010). We excluded one voyage (P15S 1996), due to a larger offset in the alkalinity data ( $-5 \mu$ mol kg<sup>-1</sup>; Key et al., 2002).

We undertook a further 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 obvious 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. For example, a cluster (24 data points) of very low oxygen samples exists immediately offshore the west

- <sup>5</sup> coast of South America on WOCE line P06E. This is an oxygen minimum zone, thus these data points represent a real oceanographic feature and have been retained in the dataset. In total ~ 150 samples (< 1 %) were removed from the overall dataset of ~ 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.
- The data was collected over several decades 1990s and 2000s. We found that there were subtle variations in the MLR algorithm coefficients when only the 1990's GLO-DAP data is used compared to the 2000's CLIVAR data and therefore we have not made any corrections for the uptake of anthropogenic carbon in the intermediate and deep waters. The anthropogenic signal is considered to be minor in the intermediate and deep waters, with only 5–10 μmol kg<sup>-1</sup> changes in DIC estimated between 200–
- and deep waters, with only 5–10 µmorkg<sup>-1</sup> changes in Dic estimated between 200–1000 m (Sabine et al., 2008; Sallée et al., 2012). This is small relative to the natural variability in the oceans and of similar order of magnitude to the combined uncertainty associated with the measurements (±2 µmol kg<sup>-1</sup> when using a CRM) and our algorithms. Furthermore, any approach we might take to correct for the anthropogenic signal would introduce its own errors.

Once we had developed and tested the algorithms using the GLODAP/CLIVAR data, we applied them to the CSIRO Atlas of Regional Seas (CARS, 2009) climatology (Dunn and Ridgway, 2002; Ridgway et al., 2002). This database provides temperature, salinity and dissolved oxygen that have been subjected to consistent quality control and have

<sup>25</sup> been interpolated taking into account both bathymetry and land. CARS provides mean values and annual and semi-annual cycles, but does not provide information about temporal variability over longer timescales. The annual and semi-annual modes allow monthly climatological fields to be derived. In the Southern Ocean, research vessel logistics and operations have led to a summer bias in oceanographic measurements,



so here we use only the CARS data temporally interpolated for January (Austral Summer).

## 4 Approach

10

In this approach, we treat the observed DIC and alkalinity (Alk), from the GLO-5 DAP/CLIVAR cruises as a linear combination of temperature, (T), the salinity, (S), with a background salinity of 35 removed, oxygen, ( $O_2$ ), and a constant offset, (C),

 $DIC = \alpha T + \beta(S - 35) + \gamma O_2 + C$ Alk =  $\alpha T + \beta(S - 35) + \gamma O_2 + C$ ,

where *T* has units of °C and DIC, Alk, and O<sub>2</sub> have units of  $\mu$ mol kg<sup>-1</sup>. Then, a Singular Value Decomposition (SVD) is used to determine the best values of the parameters  $\alpha$ ,  $\beta$ ,  $\gamma$ , and *C* to fit the observations.

Initially, this optimization was undertaken with all of the data below the surface layer (depth > 200 m). Analysis of the residuals, e.g. the difference between the modelled and observed values, as a function of potential density ( $\sigma_{\theta}$ ) revealed that there were likely to be two distinct regimes with different relationships between carbonate parameters and *T*. *S* and  $\Omega_{\tau}$ . We were able to substantially improve the fit by dividing the

eters and T, S, and  $O_2$ . We were able to substantially improve the fit by dividing the data into two different density regimes and fitting them separately.

The optimal break point between the two regimes was determined objectively using a Monte Carlo simulation. We generated a random normal distribution of 5000 possible break points centred around  $\sigma_{\theta}$  = 27.6 with a standard deviation of 0.1 and calculated

<sup>20</sup> the best fits to equations 1 and 2 for each of these 5000  $\sigma_{\theta}$  break points. Then, we evaluated the goodness of fit using the reduced  $\chi^2$ . The results of this Monte Carlo simulation show a clear, fairly flat minimum in the reduced  $\chi^2$  over a  $\sigma_{\theta}$  range of about 27.45 to 27.55 for Alkalinity and 27.4 to 27.6 for DIC (figure 2). At  $\sigma_{\theta}$  higher than 27.65, the reduced  $\chi^2$  begins to increase steeply.



For this analysis, we chose to use a break point of  $\sigma_{\theta} = 27.5$  throughout, because it represents a minimum reduced  $\chi^2$  for both DIC and Alkalinity. This is also fits with the oceanography as it sits at the boundary between intermediate and deep waters. In order to avoid discontinuities at the density boundary between the two regimes when calculating values of DIC and Alkalinity from these regressions, we take  $\sigma_{\theta}$  averaged weighting of the two fits for data over the density range of  $\sigma_{\theta} = 27.45-27.55$ .

5

The residual standard error (RSE) for the MLR fit is  $\pm 7.3 \,\mu$ mol kg<sup>-1</sup> for DIC and  $\pm 9.8 \,\mu$ mol kg<sup>-1</sup> for alkalinity, based on all the data used in the optimisation. If we remove the alkalinity and DIC measured-estimated residuals greater than 3 standard deviations from the mean (about 1% of the total data), considered outliers (Pearson, 2002), there is a minor improvement in the RSE, from  $\pm 7.3 \,\mu$ mol kg<sup>-1</sup> to  $\pm 6.8 \,\mu$ mol kg<sup>-1</sup> for DIC and  $\pm 9.8 \,\mu$ mol kg<sup>-1</sup> to  $\pm 9.2 \,\mu$ mol kg<sup>-1</sup> for alkalinity. In general, 70% of the DIC and alkalinity estimates are within 1 standard deviation of the data, and the *R*<sup>2</sup> of the measured *v* estimated alkalinity and DIC was greater than 0.9 (Table 3).

- <sup>15</sup> The MLR picks out temperature and oxygen as the main controllers of DIC (Table 3). This is not surprising as DIC is affected by organic matter formation (or break down) in the water column which produces (or requires oxygen). Lee et al. (2000) previously determined that surface DIC can be determined from temperature and nitrate (the latter closely related to oxygen in the oceans). The temperature factor may also be acting
- as a proxy for depth, with an increased  $\alpha$  coefficient for deeper waters as oxygen decreases (Table 3). Alkalinity, on the other hand, is primarily influenced by salinity and temperature (Table 3; Millero et al., 1998; Lee et al., 2006). Alkalinity is also affected by carbonate dissolution and precipitation. Thus the measured v estimated correlation for alkalinity ( $R^2 = 0.91$ ) is slightly lower than DIC ( $R^2 = 0.98$ ), as none of the parameters
- <sup>25</sup> (*T*, *S* or dissolved O) are directly affected by carbonate dissolution. Temperature and oxygen may be playing a proxy role in predicting depth, as the coefficients  $\alpha$  and  $\gamma$  increase for estimating alkalinity in the deep waters.

The largest residuals between the measured and estimated DIC and alkalinity are in the lower mixed layer/thermocline waters ( $\sigma_{\theta}$  = 25.5 to 26.5; 200–500 m) and the



deep waters ( $\sigma_{\theta}$  = 27.7 to 28; > 3000 m; Fig. 4). While both DIC and alkalinity are over and underestimated in the thermocline, the estimates for the deep waters are predominantly lower than the measured values. The high residuals are most commonly found in the PDW (1800–3500 m in P16S; Fig. 4). This is a region of excess alkalinity due

- to carbonate dissolution by these old corrosive PDW (Feely et al., 2002). A separate algorithm could be developed for the PDW, but this was not undertaken as the water mass could not be defined by potential density. It would therefore have to be defined by oxygen content and another parameter, increasing the complexity and usefulness of this deliberately simple approach.
- <sup>10</sup> South of the PF, the MLR overestimates alkalinity (and DIC to a lesser extent) in the upper 1000 m (Fig. 4). These very cold, dense waters are estimated by the deep alkalinity MLR algorithm as  $\sigma_{\theta} > 27.5$ . This region adjacent to Antarctica is controlled primarily by the cold temperatures, and it appears that a separate MLR algorithm may be required for the region between the PF and Antarctica.
- <sup>15</sup> There are anomalous residuals in both DIC and alkalinity between 145° W and 180° along P06 2003 (not shown). This seems to be related to lower oxygen values along this section of the P06 transect. This is especially evident in the DIC (which is more affected by oxygen) with residuals throughout the water column, while the alkalinity residuals are only higher in the deeper waters (where oxygen plays a larger role in the MLR; Table 3). This highlights the requirement of using well calibrated hydrographic data.

Previous researchers have used the MLR technique to directly determine aragonite saturation states (Juranek et al., 2009; Kim et al., 2010; Alin et al., 2012). Here we calculate the other carbonate parameters ( $[CO_3^{2^-}]$ ,  $\Omega$  aragonite,  $\Omega$  calcite) using CO2sys software (Lewis and Wallace, 1998) and the same temperature, salinity, pressure, alkalinity and DIC data. Silica and phosphate were assumed to be 0 in the CO2sys calculation as these parameters have a minimal effect on the calculation. A comparison of the  $[CO_3^{2^-}]$  calculated from the measured alkalinity and DIC with the estimated alkalinity and DIC gives an  $R^2 = 0.96$ , RSE = ±4 µmol kg<sup>-1</sup>, while  $\Omega$  aragonite and  $\Omega$ calcite give



an  $R^2 = 0.99$ , RSE = ±0.05 and ±0.08 respectively (Fig. 5). This is just greater than the overall uncertainties of the aragonite and calcite saturation state calculations of ±0.03 and ±0.05, respectively (Mucci, 1983; Millero, 1995; Feely et al., 2012). The high R<sup>2</sup> for  $\Omega$  aragonite and  $\Omega$  calcite suggests that the errors in the alkalinity and DIC are offset in the calculation of the saturation states.

## 5 Application and discussion

10

The development of the algorithm to determine alkalinity and DIC from hydrographic observations allows us to estimate the distribution of alkalinity and DIC where only hydrographic data has been collected. It also allows us to utilise oceanographic climatologies to provide more extensive coverage of the ocean.

Alkalinity and DIC values south of 25°S were estimated from CARS temperature, salinity and dissolved oxygen. From these,  $\Omega$  calcite and  $\Omega$  aragonite were determined using the CO2sys program. This provided saturation states at each 0.5° in latitude and longitude, and a vertical resolution of 250 m between 2000 and 5000 m, 100 m between

<sup>15</sup> 1000 and 2000 m, and 10–50 m in the upper 1000 m of the water column. At each grid point in both latitude and longitude, the vertical profiles in  $\Omega$  were linearly interpolated to determine the density where  $\Omega = 1$  (Fig. 6) and then the depth of the CSH and ASH (Fig. 7).

The CSH is at highest densities in the South Atlantic, where the NADW has high salinities, and in the cold, dense waters south of the PF (Fig. 6). The ASH also shows the highest densities in these regions, with a dramatic increase at the PF. The ASH generally sits at the base of the AAIW at  $\sigma_{\theta} = 27.3$ , but sits at a higher density (and is much more variable) in the South Atlantic, probably due to mixing between the higher alkalinity, denser NADW and the lower alkalinity, less dense AAIW. The lowest density as sity ASH is found off the west coast of South America due to the upwelling into the

sity ASH is found off the west coast of South America due to the upwelling into the thermocline waters and the southward flow of EqPIW, with high DIC (Bostock et al., 2010).



The depth of the ASH and CSH show similar patterns to previous global compilations (Feely et al., 2004) but have significantly more detail. Figure 7 shows the ASH and CSH maps derived from GLODAP gridded alkalinity and DIC data. This was supplemented with the temperature and salinity from CARS subsampled to the coarser (both vertical and horizontal) GLODAP grid and followed the same procedure followed to determine the depth where  $\Omega = 1$ . For CSH, the coarser grid in the GLODAP data resulted in significant masking from the lower resolution bathymetry. The gridded GLO-DAP data appears to have been interpolated without taking into account bathymetry.

- This has created patterns in the ASH and CSH that are inconsistent with known ocean
   circulation. For example, there is evidence for a shoaling of the CSH in the eastern
   Tasman Sea a flow over effect from the data in the main South Pacific basin east of
   New Zealand yet the only flow of deep waters into this basin is from the south due
   to the topographic highs such as Lord Howe Rise (Bostock et al., 2011). In contrast,
   CARS reduces distortion in the gridded fields by taking into account both bathymetry
   and landmasses (Dunn and Ridgway, 2002). Thus we are able to derive maps of ASH
   and CSH that have higher resolution and are more consistent with the known oceano-
- and CSH that have higher resolution and are more consistent with the known oceanographic circulation.

South of 45° S (approximately the location of the STF), the CSH in the Southern Ocean is fairly uniform around 3100–3400 m. There is a subtle deepening of the CSH <sup>20</sup> between the SAF and the PF throughout the Southern Ocean. This is not an artefact of the CARS data, as it is also evident in the raw data from the individual transects (e.g. Fig. 5). This deepening of the CSH is coincident with a shoaling of the  $\Omega$  calcite = 1.4 to 1.6, which suggests it is related to the physical oceanography perhaps the upwelling of PDW at the PF also results in the minor depression of the CSH.

<sup>25</sup> The old corrosive PDW causes the CSH to be considerably shallower (< 3000 m) in most of the South Pacific Basin. The influence of the PDW into the South Fiji and the New Caledonia basins to the north of New Zealand is readily apparent, while the Tasman Sea has a deeper CSH as it is fed from the Southern Ocean by CDW, with no influence of PDW (Bostock et al., 2011). The deep western boundary current, which is



predominantly made up of CDW and flows east of New Zealand around the Campbell Plateau, Chatham Rise and then north along the Kermadec ridge, is also evident with a deepening of the CSH along its flow path compared to the rest of the South Pacific Basin.

The NADW influence is clearly shown with a deeper CSH (> 3500 m) in the South Atlantic and in the western Indian Ocean, to the west of the Madagascar Ridge. The eastern Indian Ocean has the largest difference in the CSH between the interpolated GLODAP data and the estimates from the CARS climatology. The alkalinity data from GLODAP is patchy for this region and thus the calculated CSH is highly variable, which is then interpolated across the ocean. In the eastern Indian Ocean, the deep waters are made up of CDW, and therefore we would expect the depth of the CSH to be similar to the Southern Ocean.

The ASH depth estimated from the CARS dataset shows a significant shoaling between the SAF and the PF with the shallowest ASH at the PF due to the upwelling of corrosive uCDW. During January (Austral Summer), the ASH shoals to < 1000 m in the South Atlantic and Indian sectors of the Southern Ocean and < 750 m water depth in

the Pacific region of the Southern Ocean (Fig. 7). This detail is not evident in the GLO-DAP interpolations (Fig. 7; Feely et al., 2004). Similar to the GLODAP gridded data, the ASH is deeper, but highly variable in depth in the South Atlantic, probably due to

the mixing of the NADW and the AAIW, while off the west coast of South America there is considerable shoaling of the ASH to < 500 m due to the upwelling. These more detailed maps of the estimated ASH and CSH from the CARS climatology will be used for predictive benthic habitat and carbonate sediment models.</p>

While these MLR algorithms work extremely well for estimating the alkalinity, DIC,  $[CO_3^{2^-}]$ ,  $\Omega$  aragonite and  $\Omega$  calcite for the intermediate and deep waters of the Southern Hemisphere open oceans, slight improvements can be made when the South Pacific, South Atlantic and Indian basin data are run separately. Work in the coastal zone of northeast Pacific (Oregon) (Juranek et al., 2009) and the Sea of Japan (Kim et al., 2010), has shown that separate, localised, algorithms are required. Hence, although we



found our algorithm to work well in the open ocean, more testing is needed to determine if is useful in marginal seas. South of the PF our MLR overestimates the alkalinity and DIC in the upper 1000 m (Fig. 5), suggesting that waters around Antarctica may be sufficiently distinct as to benefit from a separate routine.

- <sup>5</sup> With continued uptake of anthropogenic CO<sub>2</sub> the relationship between DIC and alkalinity and hydrographic parameters will alter, as demonstrated by McNeil et al. (2001). Previous studies have used differences between MLR fits in different time periods, in a technique called extended MLR (eMLR), to determine the uptake of anthropogenic CO<sub>2</sub> over the past couple of decades (McNeil et al., 2001b; Peng et al., 2003; Friis et
- al., 2005; Sabine et al., 2008; Wanninkhof et al., 2010; Peng and Wanninkhof, 2010; Feely et al., 2012). This is an especially important problem in the Southern Ocean, where the AASW are taking up a large proportion of anthropogenic CO<sub>2</sub>. These waters then subduct to form AAIW, changing its carbonate chemistry, and storing large concentrations of CO<sub>2</sub> in AAIW (Sabine et al., 2004; Murata et al., 2007, 2008, 2010; Feely et al., 2012). The small differences in the algorithms for the 1990's and 2000's
- that we found suggest that the anthropogenic carbon bias is relatively small at present, but in the future, new data will be needed to determine how the algorithms evolve in response to anthropogenic uptake.

With the potential routine deployment of dissolved oxygen sensors on future Argo floats, algorithms like these will allow routine determination of carbonate parameters from Argo floats (Juranek et al., 2011). Giving the potential for both higher spatial and temporal resolution of carbonate saturation estimates for the intermediate and deep waters of the Southern Hemisphere oceans. This would help to determine if there are seasonal, interannual (Feely et al., 1988; Juranek, et al., 2009; McNeil et al., 2011; Alin

et al., 2012), or decadal (Kim et al., 2010) variability in intermediate and deep waters. This could be significant in areas of upwelling like the west coast of South America. If future Argo floats will also incorporate direct in-situ carbonate measurements (Byrne and Yao, 2008), these algorithms could also be a useful tool for quality control of the data.



MLR algorithms such as these, and other methods such as neural networks (Velo et al., 2013; Sasse et al., 2013), do not abrogate the need for ongoing sampling to directly measure DIC and alkalinity. Instead they give us the tools to maximise the value of direct measurements by allowing meaningful extrapolation to larger areas. Potentially they will allow identification of specific regions of interest, where processes can only be understood with dedicated sampling programmes.

## 6 Conclusions

5

20

Using the global carbonate datasets of GLODAP (1990s) and CLIVAR (2000s), we have developed MLR algorithms to accurately estimate the DIC, alkalinity, and saturation states of calcite and aragonite for intermediate and deep waters of the Southern Hemisphere open oceans. When used in conjunction with the CARS (2009) database this provides new detailed maps of the CSH and ASH, which are oceanographically

consistent. These will be used for future benthic habitat mapping and carbonate sediment models. With the deployment of oxygen sensors on Argo floats, these algorithms

15 can be used to look at seasonal and interannual changes in the carbonate saturation states in the intermediate and deep waters.

There are larger errors south of the PF and further testing is required for marginal seas. These algorithms do not abolish the need for future sampling and measurement of DIC and alkalinity, as the coefficients of the MLR algorithms will change with future anthropogenic  $CO_2$  uptake by the oceans. They, however, may help to identify specific regions and depths of interest for targeted future sampling.

Acknowledgements. The authors would like to acknowledge all the funding agencies, voyage leaders and participants and that contributed towards the global databases of WOCE/GLODAP and CLIVAR these are an invaluable resource. Funding for this work has come from the New Zealand Ministries for Primary Industries (formerly the Ministry of Fisheries) (ZBD2010/41).

25 Zealand Ministries for Primary Industries (formerly the Ministry of Fisheries) (ZBD2010/41), and Business Innovation and Employment (CO1X1226) and NIWA as part of its government funded core research.



#### References

5

10

Alin, S. R., Feely, R. A., Dickson, A. G., Hernández-Ayón, J. M., Juranek, L. W., Ohman, M. D., and Goericke, R.: Robust empirical relationships for estimating the carbonate systemin the southern California Current System and application to CalCOFI hydrographic cruise data (2005–2011), J. Geophys. Res., 117, C05033, doi:10.1029/2011JC007511, 2012.

Archer, D. E.: An atlas of the distribution of calcium carbonate in sediments of the deep sea, Global Biogeochem. Cy., 10, 159–174, 1996.

Bostock, H. C., Opdyke, B. N., and Williams, M. J. M.: Characterising the intermediate depth waters of the Pacific Ocean using  $\delta^{13}$ C and other geochemical tracers, Deep-Sea Res. I, 57, 847–859, 2010.

Bostock, H. C., Hayward, B. W., Neil, H. L., Currie, K. I., and Dunbar, G. B.: Deep-water carbonate concentrations in the southwest Pacific, Deep-Sea. Res. Deep-Sea Res., I, 58, 72–85, 2011.

Bostock, H. C., Sutton, P. J., Williams, M. J. M., and Opdyke B. N.: Reviewing the circulation and

- <sup>15</sup> mixing of Antarctic Intermediate Water in the South Pacific using evidence from geochemical tracers and Argo float trajectories, Deep-Sea Res. I, 73, 84–98, 2013.
  - Brewer, P. G., Glover, D. M., Goyet, C., and Shafer, D. K.: The pH of the North Atlantic Ocean: Improvements to the global model for sound absorption in seawater, J. Geophys. Res. 100, 8761–8776, 1995.
- Brewer, P. G., Goyet, C., and Friederich, G.: Direct observation of the oceanic CO<sub>2</sub> increase revisited, P. Natl. Acad. Sci. USA, 94, 8308–8313, 1997.
  - Byrne, R. H. and Yao, W.: Procedures for measurement of carbonate ion concentrations in seawater by direct spectrophotometric observations of Pb(II) complexation, Mar. Chem., 112, 128–135, 2008.
- 25 CARS: CSIRO Atlas of Regional Seas, available at: http://www.marine.csiro.au/~dunn/ cars2009/, 2009.

Dickson, A. G.: Reference materials for oceanic CO<sub>2</sub> measurements, Oceanography, 14, 21–22, 2001.

Dickson, A. G. and Millero, F. J.: A comparison of the equilibrium constants for the dissociation

<sup>30</sup> of carbonic acid in seawater media, Deep-Sea Res. 34, 1733–1743, 1987.



Dickson, A. G., Sabine, C. L., and Christian J. R.: Guide to Best Practices for Ocean CO<sub>2</sub> Measurements, PICES Spec. Publ., vol. 3, 191 pp., N. Pac. Mar. Sci. Organ., Sidney, B. C., Canada, 2007.

Dunn J. R. and Ridgway, K. R.: Mapping ocean properties in regions of complex topography, Deep-Sea Res. I, 49, 591–604, 2002.

Feely, R. A., Byrne, R. H., Acker, J. G., Betzer, P. R., Chen, C.-T. A., Gendron, J. F., and Lamb, M. F.: Winter-summer variations of calcite and aragonite saturation in the northeast Pacific, Mar. Chem., 25, 227–241, doi:10.1016/0304-4203(88)90052-7, 1988.

5

- Feely, R. A., Sabine, C. L., Lee, K., Millero, F. J., Lamb, M. F., Greeley, D., Bullister, J. L., Key, R.
- M., Peng, T.-H., Kozyr, A., Ono, T., and Wong, C. S.: In situ calcium carbonate dissolution in the Pacific Ocean, Global Biogeochem. Cy., 16, 1144, doi:10.1029/2002GB001866, 2002.
   Feely, R. A., Sabine, C. L., Lee, K., Berelson, W., Kleypas, J., Fabry, V. J., and Millero, F. J.: Impact of anthropogenic CO<sub>2</sub> on the CaCO<sub>3</sub> system in the oceans, Science, 305, 362–366, 2004.
- <sup>15</sup> Feely, R. A., Sabine, C. L., Byrne, R. H., Millero, F. J., Dickson, A. G., Wanninkhof, R., Murata, A., Miller, L. A., and Greeley, D.: Decadal changes in the aragonite and calcite saturation state of the Pacific Ocean, Global Biogeochem. Cy., 26, GB3001, doi:10.1029/2011GB004157, 2012.
- Friis, K., Körtzinger, A., Pätsch, J., and Wallace D. W. R.: On the temporal increase of anthropogenic CO<sub>2</sub> in the subpolar North Atlantic, Deep-Sea Res., I, 52, 681–698, doi:10.1016/j.dsr.2004.11.017, 2005.
  - Ganachaud, A., Wunch, C., Marotzke, J., and Toole, J.: Meridional overturning and large-scale circulation of the Indian Ocean, J. Geophys Res., 105, 26117–26134, 2000.

González-Dávila, M., Santana-Casiano, J. M., Fine, R. A., Happell, J., Delille, B., and Speich,

S.: Carbonate system in the water masses of the Southeast Atlantic sector of the Southern Ocean during February and March 2008, Biogeosciences, 8, 1401–1413, doi:10.5194/bg-8-1401-2011, 2011.

Guinotte, J. M., Orr, J., Cairns, S., Freiwald, A., Morgan, L., and George, R.: Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals?, Front.

<sup>30</sup> Ecol. Environ., 4, 141–146, doi:10.1890/1540-9295(2006)004[0141:WHCISC]2.0.CO;2, 2006.

Hamilton, L. J.: Structure of the Subtropical Front in the Tasman Sea, Deep-Sea Res. I, 53, 1989–2009, 2006.



- Juranek, L. W., Feely, R. A., Peterson, W. T., Alin, S. R., Hales, B., Lee, K., Sabine, C. L., and Peterson, J.: A novel method for determination of aragonite saturation state on the continental shelf of central Oregon using multi-parameter relationships with hydrographic data, Geophys. Res. Lett., 36, L24601, doi:10.1029/2009GL040778, 2009.
- Juranek, L. W., Feely, R. A., Gilbert, D., Freeland, H., and Miller, L. A.: Real-time estimation of pH and aragonite saturation state from Argo profiling floats: Prospects for an autonomous carbon observing strategy, Geophys. Res. Lett., 38, L17603, doi:10.1029/2011GL048580, 2011.

Key, R. M., Quay, P. D., Jones, G. A., McNichol, A. P., von Reden, K. F., and Schneider, R.

- J.: WOCE Radiocarbon I: Pacific Ocean Results; P6, P16, P17, Radiocarbon. 38, 425–518, 1996.
  - Key, R. M., Quay, P. D., Schlosser, P., McNichol, A. P., von Reden, K. F., Schneider, R. J., Elder, K. L., Stuiver, M., and Östlund H. G.: WOCE radiocarbon IV: Pacific Ocean results; P10, P13N, P14C, P18, P19 and S4P, Radiocarbon, 44, 239–392, 2002.
- <sup>15</sup> Key, R. M., Kozyr, A., Sabine, C. L., Lee, K., Wanninkhof, R., Bullister, J. L., Feely, R. A., Millero, F. J., Mordy, C., and Peng T.-H.: A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), Global Biogeochem. Cy., 18, GB4031, doi:10.1029/2004GB002247, 2004.

Kim, T.-W., Lee, K., Feely, R. A., Sabine, C. L., Chen, C.-T. A., Jeong, H. J., and Kim, K. Y.: Pre-

- diction of Sea of Japan (East Sea) acidification over the past 40 years using a multiparameter regression model, Global Biogeochem. Cy., 24, GB3005, doi:10.1029/2009GB003637, 2010.
  - Lamb, M. F., Sabine, C. L., Feely, R. A., Wanninkhof, R., Key, R. M., Johnson, G. C., Millero, F. J., Lee, K., Peng, T.-H., Kozyr, A., Bullister, J. L., Greeley, G., Byrne, R. H., Chipman, D.
- W., Dickson, A. G., Goyet, C., Guenther, P. R., Ishii, M., Johnson K. M., Keeling, C. D., Ono, T., Shitashima, K., Tilbrook, B., Takahashi, T., Wallace, D. W. R., Watanabe, Y. W., Winn, C., and Wong, C. S.: Consistency and synthesis of Pacific Ocean CO<sub>2</sub> survey data, Deep-Sea Res. II, 49, 21–58, 2002.
- Lee, K., Wanninkhof, R., Feely, R. A., Millero, F. J., and Peng T-.H.: Global relationships of total inorganic carbon with temperature and nitrate in surface seawater, Global Biogeochem. Cy., 14. 979–994. doi:10.1029/1998GB001087. 2000.
  - Lee, K., Tong, L. T., Millero, F. J., Sabine, C. L., Dickson, A. G., Goyet, C., Park, G. H., Wanninkhof, R., Feely, R. A., and Key, R. M.: Global relationships of total alkalinity with salinity



and temperature in surface waters of the world's oceans, Geophys. Res. Lett., 33, L19605, doi:10.1029/2006GL027207, 2006.

- Lewis, E. and Wallace, D. W. R.: Program developed for CO<sub>2</sub> system calculations, Rep. 105, 33 pp., Oak Ridge Natl. Lab., Oak Ridge, Tenn. available at: http://cdiac.esd.ornl.gov/oceans/ co2rprt.html, 1998.
- McCartney, M. S.: Subantarctic mode water, Deep-Sea Res., 24, 103–119, 1977.

5

- McCartney, M. S.: The subtropical recirculation of Mode Waters, J. Mar. Res., 40, 427–464, 1982.
- McNeil, B. I.: Diagnosing coastal ocean CO<sub>2</sub> interannual variability from a 40 year hydrographic
- time series station off the east coast of Australia, Global Biogeochem. Cy., 24, GB4034, doi:10.1029/2010GB003870, 2010.
  - McNeil, B. I. and Matear, R. J.: Southern Ocean acidification: A tipping point at 450-ppm atmospheric CO<sub>2</sub>, P. Natl. Acad. Sci. USA, 105, 18860–18864, 2008.
  - McNeil, B. I., Tilbrook, B., and Matear, R. J.: Accumulation and uptake of anthropogenic CO2
- <sup>15</sup> in the Southern Ocean, south of Australia between 1968 and 1996, J. Geophys. Res. 106, 31431–31445, doi:10.1029/2000JC000331, 2001.
  - McNeil, B. I., Sweeney, C., and Gibson, J. A. E.: Natural seasonal variability of aragonite saturation state within two Antarctic coastal ocean sites, Antarctic Sci., 23, 411–412, doi:10.1017/S0954102011000204, 2011.
- Mehrbach, C., Culberson, C. H., Hawley, J. E., and Pytkowicz R. M.: Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, Limnol. Oceanogr., 18, 897–907, doi:10.4319/lo.1973.18.6.0897, 1973.
  - Mucci, A.: The solubility of calcite and aragonite in seawater at various salinities, temperatures and one atmosphere total pressure, Am. J. Sci., 283, 780–799, 1983.
- <sup>25</sup> Millero, F. J.: Thermodynamics of the carbon dioxide system in the Oceans, Geochim. Cosmochim. Ac., 59, 661–677, doi:10.1016/0016-7037(94)00354-O, 1995.
  - Millero, F. J., Lee, K., and Roche, M.: Distribution of alkalinity in the surface waters of the major oceans, Mar. Chem., 60, 111–130, 1998.
  - Murata, A., Kumamoto, Y, Watanabe, S., and Fukasawa, M.: Decadal increases of anthro-
- <sup>30</sup> pogenic CO<sub>2</sub> in the South Pacific subtropical ocean along 32° S, J. Geophys. Res., 112, C05033, doi:10.1029/2005JC003405, 2007.



6245

- Murata, A., Kumamoto, Y., Sasaki, K., Watanabe, S., and Fukasawa, M.: Decadal increases of anthropogenic CO<sub>2</sub> in the subtropical South Atlantic Ocean along 30° S, J. Geophys. Res., 113, C06007, doi:10.1029/2007JC004424, 2008.
- Murata, A., Kumamoto, Y., Sasaki, K., Watanabe, S., and Fukasawa, M.: Decadal increases in anthropogenic CO<sub>2</sub> along 20° S in the South Indian Ocean, J. Geophys. Res., 115, C12055, doi:10.1029/2010JC006250, 2010.
  - Orr, J. C., Fabry, V. J., Aumont, O., Bopp, L., Doney, S. C., Feely, R. A., Gnanadesikan, A., Gruber, N., Ishida, A., Joos, F., Key, R. M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar, R. G., Plattner, G.-K., Rodgers, K. B., Sabine, C. L., Sarmiento, J.
- L., Schlitzer, R., Slater, R. D., Totterdell, I. J., Weirig, M.-F., Yamanaka, Y., and Yool, A.: Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, Nature, 437, 681–686, 2005.
  - Orsi, A. H. and Whitworth III, T.: Hydrographic atlas of the world ocean circulation experiment (WOCE), in: Southern Ocean, vol. 1, International WOCE project Office, edited by: Sparrow,
- M., Chapman, P., and Gould, J., International WOCE Project Office Southampton, UK, ISBN 0-904175-49-9, 2005.
  - Pearson, R. K.: Outliers in process modelling and identification, IEEE Trans. Control Syst. Tech., 10, 55–63, 2002.
  - Peng, T.-H., Wanninkhof, R., Feely, R. A.: Increase of anthropogenic CO<sub>2</sub> in the Pacific Ocean over the last two decades, Deep-Sea Res. Pt. II, 50, 3065–3082, 2003.

20

25

- Peng, T.-H., Wanninkhof, R.: Increase in anthropogenic CO<sub>2</sub> in the Atlantic Ocean in the last two decades, Deep-Sea Res. I, 57, 755–770, 2010.
- Ridgway K. R., Dunn, J. R., and Wilkin, J. L.: Ocean interpolation by four-dimensional least squares Application to the waters around Australia, J. Atmos. Ocean. Tech., 19, 1357–1375, 2002.
- Sabine, C. L., Key, R. M., Johnson, K. M., Millero, F. J., Poisson, A., Sarmiento, J. L., Wallace, W. R., and Winn C. D.: Anthropogenic CO<sub>2</sub> inventory of the Indian Ocean, Global Biogeochem. Cy., 13, 179–198, 1999.

Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wanninkhof, R.,

<sup>30</sup> Wong, C. S., Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, T.-H., Kozyr, A., Onon, T., and Rios, A. F.: The Oceanic Sink for Anthropogenic CO<sub>2</sub>, Science, 305, 367–371, 2004.





Sabine, C. L., Feely, R. A., Millero, F. J., Dickson, A. G., Langdon, C., Mecking, S., and Greeley, D.: Decadal changes in Pacific carbon, J. Geophys. Res., 113, C07021, doi:10.1029/2007JC004577, 2008.

Sabine, C. L., Hoppema, M., Key, R. M., Tilbrook, B., van Heuven, S., Lo Monaco, C., Metzl, N.,

Ishii, M., Murata, A., and Musielewicz, S.: Assessing the internal consistency of the CARINA data base in the Pacific sector of the Southern Ocean, Earth Syst. Sci. Data, 2, 555–578, 2009,

http://www.earth-syst-sci-data.net/2/555/2009/.

10

Sallée, J-.B., Speer, K., Rintoul, S., and Wijffels, S.: Southern Ocean thermocline ventilation, J. Phys. Ocean., 40, 509–529, 2010.

Sallée, J-.B., Matear, R. J., Rintoul, S. R., and Lenton, A.: Localized subduction of anthropogenic carbon dioxide in the Southern Hemisphere oceans, Nat. Geosci., 5, 579–584, doi:10.1038/NGEO1523, 2012.

Sloyan, B. M., Talley, L. D., Chereskin, T. K., Fine, R. A., and Holte, J.: Antarctic Intermediate

- <sup>15</sup> Water and Subantarctic Mode Water formation in the Southeast Pacific: The role of turbulent mixing, J. Phys. Oceanogr., 40, 1558–1574, 2010.
  - Sokolov, S. and Rintoul, S. R.: Circulation and water masses of the southwest Pacific: WOCE section P11, Papua New Guinea to Tasmania, J. Mar. Res., 58, 223–268, 2000.

Stramma, L. and England, M.: On the water masses and mean circulation of the South Atlantic

<sup>20</sup> Ocean, J. Geophys. Res., 104, 20863–20883, 1999.

Talley, L. D.: Antarctic Intermediate Water in the South Atlantic, In: The South Atlantic: Present and past circulation, edited by:Wefer, G., Berger, W. H., Siedler, G., and Webb, D. J., Springer, New York, 219–238, 1996.

Talley L. D.: Some aspects of ocean heat transport by the shallow, intermediate and deep

overturning circulations, In: Mechanisms of Global Climate Change at Millennial Time Scales, edited by: Clark, P. U., Webb, R. S., and Keigwin, L. D., Geophys. Mono. Series 112, AGU, 1–22, 1999.

Tanhua, T., Olsen, A., Hoppema, M., Jutterström, S., Schirnick, C., van Heuven, S., Velo, A., Lin, X., Kozyr, A., Alvarez, M., Bakker, D. C. E., Brown, P., Falck, E., Jeansson, E., Lo Monaco,

<sup>30</sup> C., Olafsson, J., Perez, F. F., Pierrot, D., Rios, A. F., Sabine, C. L., Schuster, U., Steinfeldt, R., Stendardo, I., Anderson, L. G., Bates, N. R., Bellerby, R. G. J., Blindheim, J., Bullister, J. L., Gruber, N., Ishii, M., Johannessen, T., Jones, E. P., Köhler, J., Körtzinger, A., Metzl, N., Murata, A., Musielewicz, S., Omar, A. M., Olsson, K. A., de la Paz, M., Pfeil, B., Rey,



F., Rhein, M., Skjelvan, I., Tilbrook, B., Wanninkhof, R., Mintrop, L., Wallace, D. W. R., and Key, R. M.: CARINA Data Synthesis Project. ORNL/CDIAC-157, NDP-091, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/otg.ndp091, 2008.

<sup>5</sup> Tanhua, T., van Heuven, S., Key, R. M., Velo, A., Olsen, A., and Schirnick, C.: Quality control procedures and methods of the CARINA database, Earth Syst. Sci. Data, 2, 35–49, doi:10.5194/essd-2-35-2010, 2010.

Tomczak, M. and Godfrey, J. S.: Regional oceanography: an introduction, Pergamon Press, 1994.

- <sup>10</sup> Velo, A., Pérez, F. F., Tanhua, T., Gilcoto, M., Ríos, A. F., and Key, R. M.: Total alkalinity estimation using MLR and neural network techniques, J. Mar. Syst., 111–112, 11–18, 2013.
  - Wallace, D. W. R.: Monitoring global ocean carbon inventories, Ocean Observing System Development Panel, Texas A&M University, College Station, TX, 54 pp., 1995.

Wanninkhof, R., Doney, S. C., Bullister, J. L., Levine, N. M., Warner, M., and Gruber, N.: Detecting anthropogenic CO<sub>2</sub> changes in the interior Atlantic Ocean between 1989 and 2005,

J. Geophys. Res., 115, C11028, doi:10.1029/2010JC006251, 2010. Warren, B. A.: Deep circulation of the world ocean, In: Evolution of Physical Oceanography,

15

20

- edited by: Warren B. A. and Wunsch, C., MIT Press, Cambridge, 6–41, 1981.
- WOA: World Ocean Atlas, available at: http://www.nodc.noaa.gov/OC5/WOA09/pr\_woa09.html, 2009.



#### Table 1. GLODAP/CLIVAR voyages used for this study.

WOCE transect number	Dates	Research Ship	Voyage Leaders and Principal Scientists responsible for carbon analyses	
Pacific				
P15S 2001 P14S 1996 P16S 2005 P18 2008 P18 1994 P06 2003	24 May–8 Jun 2001 05 Jan–10 Mar 1996 9 Jan–22 Feb 2005 15 Dec 2007–23 Feb 2008 26 Jan–27 Apr 1994 3 Aug–16 Oct, 2003	R/V Franklin R/V Discoverer R/V Revelle R/V Ronald H. Brown R/V Discoverer R/V Mirai	Wijffels, Tilbrook Bullister, Feely Sloyan, Sabine Bullister, Feely Feely Fukasawa, Murata	
Southern				
S04I 1996 S04 2008 S04 1995 SR03 2001 SR03 1995	3 May–4 Jul 1996 15 Dec 2007–23 Feb 2008 13 Dec 1994–02 Feb 1995 29 Oct–22 Nov 2001 13 Dec 1994–02 Feb 1995	R/V Nathaniel Palmer R/V Ronald H. Brown R/V Aurora Australis R/V Aurora Australis R/V Aurora Australis	Nowlin, Millero Bullister, Feely Rintoul, Tilbrook Rintoul, Tilbrook Rintoul, Tilbrook	
Indian				
106S 2008 106S 1996 108 2007 109 1995 108 1995 107 1995 105 1995 105 2002	5 Feb—8 Mar 2008 20 Feb–22 Mar 1996 4 Feb–17 Mar 2007 01 Dec 1994–19 Jan 1995 01 Dec 1994–19 Jan 1995 19 Jun–20 Jul 1995 19 Jun–20 Jul 1995 10 Mar–16 Apr 1995	R/V Revelle R/V Marion Dufresne R/V Revelle R/V Knorr R/V Knorr R/V Knorr R/V Knorr	Speer, Feely Poisson Swift, Feely McCartney, Wallace McCartney, Wallace Talley, Wallace Talley, Wallace Talley, Winn	
Atlantic				
A17 1995 A16S 2005 A10 2003 A10 1993	04 Jan–22 Mar 1994 11 Jan–26 Feb 2005 6 Nov–5 Dec 2003 27 Dec–31 Jan 1993	R/V Maurice Ewing R/V Ronald H. Brown R/V Mirai R/V Meteor	Memery, Wallace Wanninkhof Yoshikawa, Murata Siedler, Wallace	



**Table 2.** Initial quality control on the GLODAP and CLIVAR data.

Parameter	Data removed if:
Salinity	< 33.5 or > 36
Oxygen	$>$ 350 $\mu$ mol kg <sup>-1</sup>
Alkalinity	$<$ DIC or $<$ 2000 or $>$ 2600 $\mu$ mol kg <sup>-1</sup>
DIC	< 1800 or > 2500 $\mu$ mol kg <sup>-1</sup>



Discussion Pa	BGD 10, 6225–6257, 2013 Estimating carbonate in the Southern Oceans H. C. Bostock et al. Title Page						
ner   Diecue							
r – Dier	Abstract Conclusions	Introduction References					
ruccion Dan		► I					
her – D	■ Back Full Screet	Close					
	Printer-friendly Version						
Der							

**Table 3.** Coefficients and constants, RSE and  $R^2$  for the MLR algorithms.

Depth	Para- meter	Coefficients for $T$ , $S$ – 35, dissolved O respectively			RSE	$R^2$	
		α	β	Ŷ	Constant		
Intermediate	Alk	-7.418	96.957	-0.079	2412.5	9.8	0.91
(200 m to < 27.5 $\pm$ 0.05 $\sigma_{\!\theta})$	DIC	-14.866	53.682	-0.569	2410.5	7.3	0.98
Deep	Alk	-17.027	100.25	-0.663	2543.4	9.8	0.91
$(>27.5\pm0.05\sigma_{\theta})$	DIC	-23.154	13.524	-1.017	2493.6	7.3	0.98





















**Fig. 4.** P16S transect. Predicted alkalinity and DIC using the CTD data from CLIVAR transect P16 2005 using the MLR algorithms. **(A)** Alkalinity (with  $\Omega$  calcite overlain), **(B)** residuals between **(A)** and the measured bottle data (Fig. 1d), **(C)** DIC (with  $\Omega$  aragonite overlain), **(D)** residuals between **(C)** and the measured bottle data (Fig. 1e).











**Fig. 6.** Potential density of the (A) CSH (contours at  $\sigma_{\theta} = 0.02$  intervals) and (B) ASH (contours at  $\sigma_{e} = 0.2$  intervals) predicted from the CARS 2009 data (January). Potential density of (C) CSH and (D) ASH from the bottle data from GLODAP and CLIVAR.

**Printer-friendly Version** 

Interactive Discussion



Fig. 7. (A) Depth of the CSH and (B) ASH estimated from the CARS 2009 data (January). (C) Depth of the CSH and (D) ASH from the GLODAP gridded data. Contours are at 250 m intervals.

**Printer-friendly Version** 

Interactive Discussion