The Changes of the Carbonate Parameters in the Ocean: Anthropogenic and Natural Processes

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THE CHANGES IN THE CARBONATE PARAMETERS IN THE OCEAN:
ANTHROPOGENIC AND NATURAL PROCESSES

by

Mareva Chanson

A DISSERTATION

Submitted to the Faculty
of the University of Miami
in partial fulfillment of the requirements for
the degree of Doctor of Philosophy

Coral Gables, Florida

August 2009
THE CHANGES IN THE CARBONATE PARAMETERS IN THE OCEAN:
ANTHROPOGENIC AND NATURAL PROCESSES

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Since the industrial revolution, CO$_2$ has increased in the atmosphere and about 40% of the increase has been taken up by the ocean. An artifact of increasing CO$_2$ in the ocean is ocean acidification; it changes the calcium carbonate saturation state, which in turn alters the calcification rate of shelled organisms. The purpose of this dissertation is to estimate the changes in the carbonate system in the oceans, and whether these changes are due to natural (biological activity, chemical transformation or mixing of water masses) or anthropogenic (human activities) perturbations. The first hypothesis states that the presence of boric acid (B(OH)$_3$) in seawater changes the thermodynamic constants of CO$_2$, pK$_{1}^{*}$ and pK$_{2}^{*}$. Due to experimental limitations, the solubility of B(OH)$_3$ was determined in electrolyte solutions (LiCl, NaCl, KCl, RbCl and CsCl) instead of real or artificial seawater. The results can be used to estimate the B(OH)$_3$ activity coefficients $\gamma_{B}$ and solubility [B] in natural mixed electrolyte solutions. The second hypothesis states that filtering seawater sampled in the open ocean is necessary for the determination of total alkalinity (TA). Measurement of 180 samples of surface, oxygen minimum, and deep waters in the Pacific and Indian oceans revealed that the at-sea measured TA of filtered and unfiltered samples were not statistically different. Finally, a synthesis and analysis of the carbonate parameters in the Atlantic and Indian oceans is undertaken. Results from repeat hydrographic cruises in these oceans were
used for this task. Parameters TA and total CO$_2$ (TCO$_2$) are predicted using hydrographic properties and a multi-linear regression method to obtain a more homogenous dataset. The results of the predicted TA prove to be successful, which is not the case for TCO$_2$ at the surface of the ocean. Finally, it is found that the increase in anthropogenic CO$_2$ signal remineralization and mixing of water masses increase the acidity of the ocean at the surface and in deep waters, respectively. This causes the aragonite saturation horizon to shoal. Recommendations for further studies are provided in the “Summary and conclusion” chapter.
to my parents Paul and Marie-Paule,
and
to my husband Christopher
Acknowledgement

This project introduced me to the world’s foremost scientific researchers in the field of marine CO₂ chemistry, and allowed me to learn from their collective expertise. It also allowed me to cross the world’s major oceans on five separate research cruises. For this privilege, I would like to express my profound gratitude to my advisor, Dr. Frank J. Millero, for his invaluable support, supervision and constructive suggestions throughout this research.

I am also grateful to Dr. Rik Wanninkhof, Dr. Rana A. Fine and Dr. Dennis A. Hansell for their suggestions. Their assistance was invaluable. I also appreciated the kindness of Mrs. Gay Ingram, Mrs. Sandrine Appelbaum and Mrs. Lynette Washington - I enjoyed my coffee and lunch breaks with them immensely. Finally, I would like to thank the National Science Foundation and the National Oceanic and Atmospheric Administration for supporting my research.

I am as ever, especially indebted to my parents, Mr. and Mrs. Paul Chanson for their love and support throughout my life, and to my husband, Dr. Christopher P. Kuchinke, who shared his love and experience with me.
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Chapter 1: Introduction

The CO$_2$ in the atmosphere is increasing due to the burning of fossil fuels (see Figure 1.1) and deforestation. Three quarters of the increase in the anthropogenic CO$_2$ is due to fossil fuel burning and one quarter to deforestation. Since the industrial revolution, the concentration of atmospheric CO$_2$ increased by 36 % from 280 to 384 ppm in 2007 (Keeling et al., 2008). This is equivalent to 0.4 % or 1.5 ppm per year (Houghton et al., 2001). The increase is more than 2 ppm yr$^{-1}$ for the past 5 years. Approximately 40% of the CO$_2$ added to the atmosphere is taken up by the oceans (Table 1.1).

This increase of CO$_2$ in the oceans is resulting in a lowering of the pH of surface waters (Haugan and Drange, 1996). The lower pH will also lower the concentration of CO$_3^{2-}$ in seawater, which will directly impact aragonite shelled organisms such as pteropods, calcite shelled organisms (foraminifera and copepods) and corals (Kleypas et al., 2006; Riebesell et al., 2000). The lower pH may decrease the biogenic aragonite production by 14 to 30 % (Kleypas et al., 1999), and the Southern Ocean will begin to become undersaturated with respect to aragonite by the year 2050 (Orr et al., 2005). These estimates were derived from a “business as usual” scenario, which assumes no climate interventionist policy during the next century.
Figure 1.1 Global fossil fuel carbon emission estimates and atmospheric CO$_2$ increase rate (Houghton et al., 2001)

<table>
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<tr>
<th>Sources</th>
<th>1980s $^*$</th>
<th>1990s $^*$</th>
<th>2000-2007$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emissions (fossil fuel, cement)</td>
<td>5.4</td>
<td>6.3</td>
<td>7.6</td>
</tr>
<tr>
<td>Deforestation</td>
<td>1.6</td>
<td>1.6</td>
<td>1.5</td>
</tr>
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<table>
<thead>
<tr>
<th>Sinks</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
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<td>Atmosphere</td>
<td>3.1</td>
<td>3.2</td>
<td>4.1</td>
</tr>
<tr>
<td>Ocean</td>
<td>1.9</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Land</td>
<td>2.0</td>
<td>2.7</td>
<td>2.8</td>
</tr>
</tbody>
</table>

$^*$ Houghton et al., 2001
$^+$ Canadell et al., 2007
The World Ocean Circulation Experiment (WOCE) and the Joint Global Ocean Flux Study (JGOFS) Hydrographic Programs in the 1990s have been used to estimate the inventory of CO₂ into the world oceans (Sabine et al., 2004). Recently, the Climate Variability Program (CLIVAR) has conducted repeat cruises in the 2000s, and will continue in the future to examine the changes in the CO₂ taken up by the oceans. Some of the results of these recent studies are discussed in this dissertation.

Total dissolved inorganic CO₂ (TCO₂), total alkalinity (TA), pH and partial pressure of CO₂ (pCO₂) are the four parameters that are measured in order to study the carbonate system in the oceans. It is important to choose the best combination of CO₂ parameters to analyze the CO₂ system (Millero, 2006). The choice depends on what needs to be revealed, that is the changes of the CO₂ system caused by the oxidation of organic matter or dissolution of calcium carbonate (CaCO₃), the CO₂ parameter percent change and the present capabilities of measuring them. The parameters pH and TA, for example, are the best choice to unravel the changes in CO₂ due to the dissolution of CaCO₃. On the other hand, pCO₂ and TCO₂ are the best option to unveil the changes in CO₂ due to production or oxidation of organic matter. Two of them are needed to calculate the components of the CO₂ system using stoichiometric dissociation constants for carbonic acid, pK*₁ and pK*₂ (Goyet and Poisson, 1989; Roy et al., 1993; Millero et al., 2002; Mojica-Prieto and Millero, 2002; Millero et al., 2006). The recent constants of Millero et al. (2006) cover a wider salinity and temperature range (S = 1 - 50 ºC and t = 0 - 50 ºC) than the earlier studies.
Measurements of the pK*₂ in artificial seawater (ASW) (Goyet and Poisson, 1989; Hansson, 1973; Roy et al., 1993) and real seawater (SW) (Mehrbach et al., 1973; Mojica-Prieto and Millero, 2002) have been shown to be different by as much as 0.04 (Millero et al., 2006). Others have suggested that it may be related to the decrease in TA due to organic compounds in seawater (Millero et al., 2002). Mojica-Prieto and Millero (2002) suggest that interaction between boric acid (B(OH)₃) and carbonate (CO₃²⁻) are the cause of this difference.

In Chapter 2 of this dissertation the interaction of boric acid with a number of the major components of natural waters is studied. Boric acid is a major component of seawater (Millero, 2006) and the ionized form B(OH)₄⁻ contributes to the alkalinity of seawater. It is also at high concentrations in some brine lakes (Felmy and Weare, 1986). At 25°C, the pK* of B(OH)₃ is equal to 8.9 and at a pH of 8, the borate ion B(OH)₄⁻ is 10% of the total boric acid (Millero, 2006). Felmy and Weare (1986) use solubility data of boric acid (Linke, 1965) and other borate species to predict the borate mineral equilibria in natural waters. They added borate parameters to the seawater model of Harvie et al. (1984), which is based on the ionic interaction model of Pitzer (1991). The Felmy and Weare (1986) model examines the borate system in brines such as the Searles Lake evaporite deposits in California. The solubility of boric acid in this study has been measured at 25°C in LiCl, NaCl, KCl, RbCl and CsCl from ionic strengths 0 to 6 mol.kg H₂O⁻¹ (or molality). By definition, solubility is a measure of a given substance that can dissolve in a solution. By determining the solubility of boric acid in these electrolyte
solutions, the Pitzer coefficients for the interactions of non-electrolytes with electrolytes in aqueous solutions were determined. These coefficients can be used in any solution.

Chapter 3 of this dissertation focuses on the measurement of total alkalinity. Before one starts to study the CO$_2$ system, it is important to have adequate methods for the measurement of the CO$_2$ parameters. Phytoplankton and bacterial cells have been shown to affect the measured TA of unfiltered seawater collected in Young-II Bay, Korea (Kim et al., 2006). These authors suggested that TA measurements made on samples at sea should be filtered and questioned the validity of earlier measurements. Phytoplankton growth can also change TA by the addition of protons when organic matter is oxidized (Brewer and Goldman, 1976). The assimilation of nitrate or ammonia by phytoplankton generates a strong base or strong acid, respectively and that may increase or decrease TA. Although this may be true for coastal waters, Chapter 3 provides measurements that show that there is no need to filter seawater samples collected in the open ocean. The results are based on samples analyzed at sea during the CLIVAR/CO$_2$ repeat hydrography cruises in the Pacific and Indian oceans on P16N and I9N (Figure 1.2).
Chapters 4 and 5 of this dissertation explore the anthropogenic inventory of CO$_2$ in the Atlantic and Indian oceans respectively and its impact on ocean acidity and on the calcium carbonate saturation horizon. The CO$_2$ parameters pH, TA, TCO$_2$ and pCO$_2$ were measured on WOCE and CLIVAR cruises with corresponding hydrographic properties (eg., salinity, temperature, pressure, nutrients, oxygen, latitude, longitude etc.). The results are synthesized, examined for internal consistency and used to estimate the decadal changes of these parameters.

In the late 1970s, the first oceanic anthropogenic CO$_2$ inventories were derived from direct measurements (Brewer, 1978; Chen and Millero, 1979). This was done by
subtracting the added CO\textsubscript{2} due to the remineralization of organic carbon and the dissolution of CaCO\textsubscript{3}(s) in the waters

\[
\text{CO}_2^{\text{anth}} = \text{CO}_2^{\text{meas}} - \text{CO}_2^{\text{org}} - \text{CO}_2^{\text{CaCO}_3}
\]  

(1.1)

Inventory uncertainties were reduced in the late 1990s when the quality of the measurements was improved (Gruber 1998; Goyet et al., 1999; Sabine et al., 2004; Touratier and Goyet, 2004b; Touratier et al., 2007). This led to improvements in estimating the anthropogenic CO\textsubscript{2} by Gruber et al., (1996) and Touratier and Goyet, (2004a). These workers estimated the preformed inorganic carbon CO\textsubscript{2}\textsuperscript{0} in the water masses from the pre-industrial era and solved some of the problems due to mixing of different water masses. Gruber et al. (1996) estimated CO\textsubscript{2}\textsuperscript{anth} using

\[
\Delta\text{CO}_2^{\text{anth}} = \Delta C^* - \Delta C_{\text{desiq}}
\]  

(1.2)

where $\Delta C^*$ is a quasi conservative tracer reflecting the uptake of anthropogenic CO\textsubscript{2} and $\Delta C_{\text{desiq}}$ is the air-sea disequilibirum when a water parcel loses contact with the atmosphere. Touratier and Goyet (2004b) estimated the CO\textsubscript{2}\textsuperscript{anth} using

\[
\text{CO}_2^{\text{anth}} = (\text{TrOCA} - \text{TrOCA}^\circ)/2
\]  

(1.3)

with

\[
\text{TrOCA} = O_2 + 1.2 \text{ CO}_2 -0.6 \text{ TA}
\]  

(1.4)
where TrOCA is a Tracer using Oxygen, total dissolved inorganic CO$_2$ and TA, and TrOCA$^\circ$ is similar to TrOCA but without any anthropogenic contribution. The anthropogenic CO$_2$ inventory of the Atlantic Ocean (80°N – 50°S) was estimated to be 40 Pg C in the 1980s and increased to up to 45 Pg C in the 1990s (Touratier and Goyet, 2004b).

The so called ΔC* method of Gruber et al., (1996) estimated an anthropogenic CO$_2$ inventory of 20 ± 4 Pg C in the North Atlantic between 10°N and 80°N. This method was widely used, sometimes in modified form, for different oceans (Lee et al., 2003; Sabine et al., 1999). The estimates for the world’s oceans are tabulated in Table 1.2 (Sabine et al., 2004). For the period 1800 to 1994, 118 ± 19 Pg of carbon were uptaken by the global oceans (Sabine et al., 2004). The MIX model is an alternative method that was developed by Goyet et al. (1999).

Atlantic Ocean transect A16 at meridian 20°W (Figure 1.2) has the most complete dataset from South to North on a decadal time scale in the Atlantic basin. Scientific cruises took place in 1989, 1991 and 1993 as part of the WOCE program and in 2003 and 2005 as part of the CLIVAR/CO$_2$ studies. Indian Ocean transect I9N at meridian 90°E (also Figure 1.2) was surveyed in 1995 and 2007. The thermocline of this ocean is very dynamic because of the monsoon seasons and directional shift of the winds and ocean currents. Indeed, the Indian Ocean is also the smallest ocean in volume with connections to the Atlantic, Southern and Pacific oceans, the Arabian Sea and the Bay of Bengal. The
conservative and non-conservative properties of the water masses in the Indian Ocean could therefore change because of the convergence in the South Indian Ocean, the fresh water input from the Bay of Bengal, and mixing by the Indonesian Through Flow from the Pacific Ocean.

Table 1.2 Estimated anthropogenic CO$_2$ budget since 1800 (Sabine et al., 2004).

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PgC</td>
<td>PgC</td>
</tr>
<tr>
<td><em>Constrained sources and sinks</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) Emissions (fossil fuel, cement)</td>
<td>244 ± 20</td>
<td>117 ± 5</td>
</tr>
<tr>
<td>(2) Storage in the atmosphere</td>
<td>-165 ± 4</td>
<td>-65 ± 1</td>
</tr>
<tr>
<td>(3) Uptake and storage in the ocean</td>
<td>-118 ± 19</td>
<td>-37 ± 8</td>
</tr>
<tr>
<td><em>Inferred net terrestrial balance</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net terrestrial balance = -(1) – (2) – (3)</td>
<td>39 ± 28</td>
<td>-15 ± 9</td>
</tr>
<tr>
<td><em>Terrestrial balance</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5) Emissions from land-use change</td>
<td>100 ± 180</td>
<td>24 ± 12</td>
</tr>
<tr>
<td>(6) Terrestrial biosphere sink = (4) – (5)</td>
<td>-61 ± 141</td>
<td>-39 ± 18</td>
</tr>
</tbody>
</table>

In summary, Chapter 2 discusses the solubility of boric acid in electrolyte solutions at 25 °C. The results of this study have been published in the Journal of Solution Chemistry in 2006. Chapter 3 examines the effect of filtration on total alkalinity measurement in the open ocean, with results published in Limnology Oceanography: Methods in 2007. Chapter 4 is a synthesis and analysis of the carbonate parameters in the
Atlantic Ocean based on a transect along the 20°W meridian. Finally, Chapter 5 is an analysis of the change of the carbonate parameters due to changes of the distribution of water masses in the Indian Ocean thermocline and intermediate waters. The findings are summarized in the Conclusion chapter of this thesis along with ideas and recommendations for future CO₂ work.
Chapter 2: The solubility of boric acid in electrolyte solutions†

2.1 Background information

Boric acid is a major component of seawater (Millero, 2006) and forms ortho borate that contributes to its alkalinity. It is also at high concentrations in some brine lakes (Felmy and Weare, 1986). At 25 °C, the pK* of B(OH)₃ is equal to 8.9 and at a pH of 8, the borate ion is 10% of the total boric acid (Millero, 2006). Felmy and Weare (1986) used solubility data of boric acid (Linke, 1965) and other borate species to predict the borate mineral equilibria in natural waters. The borate parameters are added to the seawater model of Harvie, et al. (1984) that is based on the ionic interaction model of Pitzer (1991). The Felmy and Weare (1986) model was used to examine the borate system in brines such as the Searles Lake evaporite deposits in California.

The solubility of boric acid has been measured in salt solutions at few temperatures (Linke, 1965). In this chapter, the solubility of boric acid was measured at 25 °C in LiCl, NaCl, KCl, RbCl and CsCl as a function of ionic strength (I = 0 to 6 mol kg⁻¹). These results and literature data (Linke, 1965) were then fit to the Pitzer equation (Pitzer, 1991) for the interactions of non-electrolytes with electrolytes in

† This chapter has been previously published as: Chanson, M and F.J. Millero, The solubility of boric acid in electrolyte solutions, J.Sol. Chem., 35,5,689-703, 2006.
aqueous solutions. This equation accounts for the interaction of boric acid (B) with the cations (c) and anions (a) in the solution

\[
\ln \left\{ \frac{[B]^0}{[B]} \right\} = \ln \gamma_B = (2v_c \lambda_{Bc} + 2v_a \lambda_{Ba}) m + v_c v_a \zeta_{B-a-c} m^2 \tag{2.1}
\]

where \([B]^0\) is the concentration of boric acid (B) in water and \([B]\) in solution; \(\gamma_B\) is the activity coefficient; \(v_i\) is the number of ions (i) in the electrolyte; parameters \(\lambda_{Bc}\) and \(\lambda_{Ba}\) are related to the interaction of boric acid with cation c and anion a; parameter \(\zeta_{B-a-c}\) is related to the interaction of boric acid with both cation and anion and \(m\) is the molality of the electrolyte. The resulting salting coefficients were then examined by considering the interactions of boric acid with various cations and anions with

\[
k_S = 2 v_c \lambda_{Bc} + 2 v_a \lambda_{Ba} \tag{2.2}
\]

### 2.2 Experimental methods

The salts used in this study were reagent grade or higher (Omnipur EMD). The solutions were prepared by weight with ion exchanged water (18 MΩ) from a Millipore Super-Q system. The solution concentrations were verified from densities measured with a Mettler densimeter. The densimeter was calibrated using water and seawater of known salinity (Millero and Poisson, 1981). The densities for the salt solutions were taken from the literature (Vaslow, 1966; Perron et al., 1974). The densities of the solutions of boric
acid and the salts were also measured. The mixtures were kept in a water bath at 25 °C for 2 days before being filtered through a 0.45 µm pore size Baxter filter. Solutions of about 1.0 and 2.0 mol kg\(^{-1}\) KOH (J.T. Baker Dilut it) were prepared and standardized with 0.2 mol kg\(^{-1}\) HCl (J.T. Baker). The molality of the HCl solution was determined from density measurements (Hershey et al., 1984). Several batches of KOH were prepared in this manner with molalities of 1.00 ± 0.016 mol kg\(^{-1}\) and 1.98 ± 0.032 mol kg\(^{-1}\).

The concentration of boric acid in the solutions was determined by titration with KOH. The pH of the solutions was determined using an Orion combination electrode. The combination electrode was calibrated by titrating NaCl solutions (0 to 6.0 mol kg\(^{-1}\)) with 0.2 mol kg\(^{-1}\) HCl. The combination electrode had an average slope of -59.15 ± 0.03 mV pH\(^{-1}\) from I = 0.1 to 6 mol kg\(^{-1}\). The titrations were made in a 50 cm\(^3\) water jacketed cell at 25 °C. The KOH was delivered with a Dosimat system. The equivalence point was determined using the Gran method (Gran, 1952) that linearizes the acidic and basic part of the titration curve. The Gran functions are as follows:

\[
F_{\text{acidic}} = V_{\text{KOH}} 10^{\text{emf/slope}} \\
F_{\text{basic}} = [V_{\text{KOH}} + V_{\text{B}}] 10^{\text{emf/slope}}
\]

Where \(V_{\text{KOH}}\) and \(V_{\text{B}}\) are the volumes of KOH and boric acid added and quantity emf/slope is the pH of the solution. The equivalence point can be found by determining
the intersection of the fitted Gran functions. Three titrations were made for every mixed solution studied. The resultant solubilities agreed to within 3 %.

2.3 Results and calculations

The solubility of boric acid in LiCl, NaCl, KCl, RbCl and CsCl as a function of molality are given in Table 2.1 and depicted as a function of molality in Figure 2.1. The obtained value of the solubility of boric acid in water $[B]^0$ is 0.905 mol kg$^{-1}$. This is in good agreement with the value in Linke (1965) of 0.912 ± 0.016 mol kg$^{-1}$. The results here were fitted to the second degree equation

$$\ln \{[B]^0/[B]\} = \ln \gamma_B = a \, m + b \, m^2 \quad (2.5)$$

The coefficients $a$ and $b$ for the salts are given in Table 2.2.

The literature measurements in the different salt solutions were determined using measurements made on a molarity (M) concentration scale. These measurements were converted to molality using density data found in the literature (Vaslow, 1966). The densities ($\rho$) were determined from tabulated partial molal volume data using

$$\rho = \rho^0 + c \, \{(M - \rho^0 \rho^v)/1000\} - c^{1.5} \, \{S_v \rho^0/1000\} \quad (2.6)$$
where \( \rho^0 \) is the density of pure water, \( M \) is the molecular weight of the salt, \( \phi_{V}^0 \) is the apparent molal volume at infinite dilution and \( S_V \) is the experimental slope (Millero, 1972b). The molality of the salt solutions, \( m \), can then be determined from

\[
m = c \frac{1000}{(1000 \, \rho - c \, M)}
\]  
(2.7)

The effect of adding boric acid to the solutions was determined by assuming that the apparent molal volume of the mixture is equal to the contributions of boric acid and the salt \( MX \) (Ward and Millero, 1974) using

\[
\Phi = (\phi_{V(B)} \, m_B + \phi_{V(MX)} \, m_{MX})/(m_B + m_{MX})
\]  
(2.8)

and

\[
\Phi = 1000 \, (\rho^0 - \rho)/(\rho^0 \, \rho m) + M/\rho
\]  
(2.9)

The densities can be estimated by rearranging Equation (2.9) and solving for \( \rho \)

\[
\rho = \rho^0 \, (1000 + m \, M) / (\Phi - 1000)
\]  
(2.10)

The resulting molal solubilities of boric acid from the literature were then fit to Equation (2.5) and the results are given in Table 2.2.
Table 2.1 Solubility of boric acid $[B]$ in LiCl, NaCl, KCl, RbCl, CsCl and NaCl-MgCl$_2$ mixtures at 25 °C and molality $m$.

<table>
<thead>
<tr>
<th>[B]$^a$</th>
<th>$m^a$</th>
<th>$\ln(\gamma_B)$</th>
<th>[B]$^a$</th>
<th>$m^a$</th>
<th>$\ln(\gamma_B)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>KCl</td>
<td>LiCl</td>
<td>KCl</td>
<td>LiCl</td>
<td>KCl</td>
</tr>
<tr>
<td>0.905</td>
<td>0.000</td>
<td>0.000</td>
<td>0.905</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>0.840</td>
<td>0.501</td>
<td>0.079</td>
<td>0.915</td>
<td>0.134</td>
<td>-0.006</td>
</tr>
<tr>
<td>0.774</td>
<td>1.000</td>
<td>0.161</td>
<td>0.921</td>
<td>0.267</td>
<td>-0.013</td>
</tr>
<tr>
<td>0.712</td>
<td>1.501</td>
<td>0.245</td>
<td>0.932</td>
<td>0.534</td>
<td>-0.025</td>
</tr>
<tr>
<td>0.658</td>
<td>2.001</td>
<td>0.323</td>
<td>0.939</td>
<td>0.693</td>
<td>-0.032</td>
</tr>
<tr>
<td>0.608</td>
<td>2.500</td>
<td>0.402</td>
<td>0.955</td>
<td>1.007</td>
<td>-0.050</td>
</tr>
<tr>
<td>0.564</td>
<td>3.001</td>
<td>0.477</td>
<td>0.970</td>
<td>1.303</td>
<td>-0.065</td>
</tr>
<tr>
<td>0.528</td>
<td>3.500</td>
<td>0.542</td>
<td>1.005</td>
<td>2.001</td>
<td>-0.100</td>
</tr>
<tr>
<td>0.500</td>
<td>4.002</td>
<td>0.599</td>
<td>1.024</td>
<td>2.321</td>
<td>-0.119</td>
</tr>
<tr>
<td>0.467</td>
<td>4.572</td>
<td>0.666</td>
<td>1.037</td>
<td>2.590</td>
<td>-0.131</td>
</tr>
<tr>
<td>0.415</td>
<td>5.765</td>
<td>0.785</td>
<td>1.066</td>
<td>3.241</td>
<td>-0.160</td>
</tr>
<tr>
<td>0.405</td>
<td>6.220</td>
<td>0.808</td>
<td>1.101</td>
<td>3.963</td>
<td>-0.191</td>
</tr>
<tr>
<td>NaCl</td>
<td>NaCl-MgCl$_2$$^b$</td>
<td>NaCl</td>
<td>NaCl-MgCl$_2$$^b$</td>
<td>NaCl</td>
<td>NaCl-MgCl$_2$$^b$</td>
</tr>
<tr>
<td>0.905</td>
<td>0.000</td>
<td>0.000</td>
<td>0.905</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>0.894</td>
<td>0.343</td>
<td>0.017</td>
<td>0.905</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>0.871</td>
<td>1.031</td>
<td>0.044</td>
<td>0.963</td>
<td>1.001</td>
<td>-0.058</td>
</tr>
<tr>
<td>0.861</td>
<td>1.376</td>
<td>0.055</td>
<td>1.019</td>
<td>2.001</td>
<td>-0.114</td>
</tr>
<tr>
<td>0.850</td>
<td>1.717</td>
<td>0.068</td>
<td>1.082</td>
<td>2.999</td>
<td>-0.174</td>
</tr>
<tr>
<td>0.839</td>
<td>2.082</td>
<td>0.081</td>
<td>1.169</td>
<td>3.999</td>
<td>-0.252</td>
</tr>
<tr>
<td>0.826</td>
<td>2.764</td>
<td>0.096</td>
<td>1.261</td>
<td>4.997</td>
<td>-0.327</td>
</tr>
<tr>
<td>0.820</td>
<td>3.140</td>
<td>0.104</td>
<td>1.376</td>
<td>6.001</td>
<td>-0.414</td>
</tr>
<tr>
<td>0.811</td>
<td>4.146</td>
<td>0.114</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.810</td>
<td>4.480</td>
<td>0.116</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.811</td>
<td>4.982</td>
<td>0.115</td>
<td>0.905</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>0.816</td>
<td>5.467</td>
<td>0.109</td>
<td>0.971</td>
<td>0.997</td>
<td>-0.066</td>
</tr>
<tr>
<td>0.815</td>
<td>5.472</td>
<td>0.110</td>
<td>1.031</td>
<td>2.000</td>
<td>-0.125</td>
</tr>
<tr>
<td>0.822</td>
<td>5.927</td>
<td>0.101</td>
<td>1.087</td>
<td>3.002</td>
<td>-0.179</td>
</tr>
<tr>
<td>0.825</td>
<td>6.092</td>
<td>0.097</td>
<td>1.164</td>
<td>3.996</td>
<td>-0.247</td>
</tr>
<tr>
<td></td>
<td>1.234</td>
<td>4.995</td>
<td>-0.306</td>
<td>1.326</td>
<td>5.996</td>
</tr>
</tbody>
</table>

$^a$ Units in µmol kg$^{-1}$

$^b$ 0.427 m NaCl and 0.055 m MgCl$_2$

$^c$ Measured

$^d$ Calculated from Equation (2.27)
The solubility of boric acid at 25 °C in LiCl, NaCl, KCl, RbCl and CsCl as a function of molality. Boric acid is less soluble in LiCl and NaCl than in KCl, RbCl and CsCl because Li$^+$ and Na$^+$ are structure-makers. These cations build a structure around the ions leaving less room for boric acid to be soluble. Conversely, K$^+$, Rb$^+$ and Cs$^+$ are structure-breakers. These cations allow more boric acid to be soluble.

The effect of temperature on the solubility of boric acid in some electrolytes has been measured (Linke, 1965). The results for these salts are shown in Figure 2.1 and have been fitted to

\[ a = a_0 + a_1 (25 - t) \]  

(2.11)
where $a_0$ and $a_1$ are adjustable coefficients and $t$ is the temperature in degrees Celsius.

The coefficients $a_0$ and $a_1$ are given in Table 2.2.

**Table 2.2 Coefficients and standard error for the fit to Equation (2.5) of solubility of boric acid**

<table>
<thead>
<tr>
<th>Salt</th>
<th>Maximum m</th>
<th>$a$</th>
<th>$b$</th>
<th>S.D</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>1.546$^a$</td>
<td>0.240$^a$</td>
<td>-0.032$^a$</td>
<td>0.003</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td></td>
<td>16.031</td>
<td>0.193</td>
<td>-0.009</td>
<td>0.045</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>LiCl</td>
<td>6.22</td>
<td>0.178</td>
<td>-0.008</td>
<td>0.009</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>4.124</td>
<td>0.167$^b$</td>
<td>0.000</td>
<td>0.005</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>NaCl</td>
<td>6.092</td>
<td>0.047</td>
<td>-0.005</td>
<td>0.002</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>3.493</td>
<td>0.062$^c$</td>
<td>-0.010</td>
<td>0.000</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>KCl</td>
<td>4.822</td>
<td>-0.050</td>
<td>0.000</td>
<td>0.002</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>3.133</td>
<td>-0.051$^d$</td>
<td>0.001</td>
<td>0.001</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>RbCl</td>
<td>6.001</td>
<td>-0.053</td>
<td>-0.003</td>
<td>0.003</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>2.613$^a$</td>
<td>-0.085$^a$</td>
<td>0.004$^a$</td>
<td>0.000</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td></td>
<td>1.299</td>
<td>-0.018</td>
<td>-0.018</td>
<td>0.002</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>CsCl</td>
<td>5.996</td>
<td>-0.063</td>
<td>0.000</td>
<td>0.004</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>2.400$^a$</td>
<td>-0.074$^a$</td>
<td>0.000$^a$</td>
<td>0.001</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>KI</td>
<td>2.708$^a$</td>
<td>-0.008$^a$</td>
<td>0.004$^a$</td>
<td>0.000</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>2.073$^a$</td>
<td>0.382$^a$</td>
<td>-0.016$^a$</td>
<td>0.002</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>2.450$^a$</td>
<td>0.329$^a$</td>
<td>-0.010$^a$</td>
<td>0.001</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>BaCl$_2$</td>
<td>0.815$^b$</td>
<td>0.180$^b$</td>
<td>-0.052$^a$</td>
<td>0.000</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>27.198</td>
<td>0.136</td>
<td>-0.003</td>
<td>0.049</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>NaN$_3$</td>
<td>0.941</td>
<td>-0.042</td>
<td>-0.008</td>
<td>0.001</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>KNO$_3$</td>
<td>0.791</td>
<td>-0.120</td>
<td>-0.012</td>
<td>0.002</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0.563</td>
<td>-0.303</td>
<td>-0.065</td>
<td>0.002</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>0.459</td>
<td>-0.510</td>
<td>-0.043</td>
<td>0.001</td>
<td>(Linke, 1965)</td>
</tr>
<tr>
<td>KF</td>
<td>0.330$^c$</td>
<td>-0.980$^c$</td>
<td>-0.989$^c$</td>
<td>0.081</td>
<td>(Linke, 1965)</td>
</tr>
</tbody>
</table>

$^a$ Values at 18°C; units in mol kg$^{-1}$ for this column  
$^b$ $a_0 = 0.167, a_1 = 0.002$  
$^c$ $a_0 = 0.062, a_1 = -0.005$  
$^d$ $a_0 = -0.051, a_1 = -0.002$  
$^e$ Values at 30 °C
Figure 2.2 The salting coefficients of boric acid in HCl (●), LiCl (▼), NaCl (■), KCl (♦) and RbCl (▲) as a function of temperature (°C). The values at 25 °C in LiCl, NaCl, KCl and RbCl are from this study. The other values are taken from Linke, 1965.

2.4 Discussion

The activity coefficients of boric acid in the solutions can be calculated from the measured solubility data and fitted to the Pitzer’s equation (2.1). The coefficients are related to the Pitzer parameters by

\[ 2 \upsilon_c \lambda_B + 2 \upsilon_a \lambda_{Ba} = a \]  

(2.12)
\[ \zeta_{B-a-c} = b \quad \text{for 1-1 electrolyte} \quad (2.13) \]
\[ \zeta_{B-a-c} = b/2 \quad \text{for 1-2 electrolyte} \quad (2.14) \]

The salting coefficients \( k_S = a \) for the various solutions. The values of \( \lambda_{Bc} \) are determined by assuming that \( 2 \lambda_{BCl} = 0 \) (Pitzer, 1991; Millero, 2000) and are tabulated in Table 2.3. The values of \( \lambda_{Ba} \) are determined from the known values of \( \lambda_{Bc} \). For example, the value of \( \lambda_{BSO_4} \) is determined from

\[ \lambda_{BSO_4} = (-a(Na_2SO_4) - 4 \lambda_{BNa})/2 \quad (2.15) \]

When the value of an anion (\( SO_4^{2-} \)) can be determined from a number of salts (\( Na_2SO_4, K_2SO_4 \), etc.) an average value of \( \lambda_{BSO_4} \) is used and the values of \( \zeta_{B-a-c} \) are determined from the individual salts (\( B-Na-SO_4, B-K-SO_4 \) etc.). The solubility data compiled in Linke (1965) may be less reliable than the ones measured in this study. However, they must be used if a more comprehensive, although necessarily approximate, view of salting effects is to be obtained. The values of \( \lambda_{Bc}, \lambda_{Ba} \) and \( \zeta_{B-a-c} \) determined in this manner are tabulated in Table 2.3. The value and sign of the salting coefficient \( k_s = a \) are a function of the salt solutions studied (Table 2-2). It is positive (salting out) in HCl, LiCl and NaCl, but negative (salting in) in KCl, RbCl and CsCl. The \( H^+, Li^+ \) and \( Na^+ \) ions are structure-makers, meaning they have the net effect of building or ‘making’ more structure around the ion. This leads to salting out of boric acid in these electrolyte solutions. Conversely, \( K^+, Rb^+ \) and \( Cs^+ \) are structure-breaking ions, meaning they have a net effect of breaking
down the structure of water, leading to ‘salting in’ of boric acid in these electrolyte solutions. The division of ions in these two classes has been made by examining the viscosity and entropy of the ions (Millero, 1972b). The effect of the structure-makers or structure-breakers is also related to the common ion because the salting coefficient is a function of the cation boric acid interaction $\lambda_{Bc}$ and the anion (common ion) boric acid interaction $\lambda_{Ba}$. That is, boric acid is more soluble in sulfate salt solutions than in nitrate solutions. Similarly, it is more soluble in fluoride than in chloride or iodide salt solutions ($\text{SO}_4 > \text{NO}_3$ and $\text{F} > \text{Cl} > \text{I}$).

The sign of $k_S$ is related to the influence of the salt on the structure of water according to McDevit-Long theory (McDevit and Long, 1952). In effect, if the ion-water interactions compress the solution, it is difficult to introduce the non-electrolyte into the solution (salting out). On the other hand, if the ion-water interactions are weak and the solution becomes less structured, the non-electrolyte has a greater chance of induction into the solution (salting in). The McDevit-Long model relates the value of the salting coefficient as follows

$$k_S = V_2^0 (V_3 - V_3^0) / (2.303 \beta RT)$$

(2.16)

where $V_2^0$ and $V_3^0$ are the infinite dilution molal volumes of the non-electrolyte 2 and electrolyte 3, $V_3$ is the molar volume of the pure liquid electrolyte, $\beta$ is the compressibility of the solvent, $R$ is the gas constant and $T$ is the temperature in degrees Kelvin. The overall sign of $k_S$ depends on the magnitude of the electrostatic (salting out)
and dispersion (salting in) terms. The ion-water interaction model divides the partial molal volume of ions in solution $V_{ion}^0$ into the sum of the intrinsic partial molal volume $V_{int}^0$ that is equal to the size of the ion $V_{cryst}^0$ plus the packaging effects, and the electrostriction partial molal volume $V_{elect}^0$ that is the decrease in volume due to the ion-water interaction

$$V_{ion}^0 = V_{int}^0 + V_{elect}^0$$  \hfill (2.17)

The partial molal volume $V_{cryst}^0 = (4\pi r^3)/3 = 2.52 \text{ r}^3$ where $r$ is the crystal radius expressed in Ångström units. The intrinsic volume $V_{int}^0 = 1.8 \text{ V}_{cryst}^0 = 4.48 \text{ r}^3$. The values of $\lambda_{Bi}$ for various ions as a function of the intrinsic partial molal volumes (Millero, 1969; Millero, 1972b) are shown in Figure 2.3. The relationship between the salting coefficient $k_S$ and the partial molal volumes of the salts are shown in Figure 2.4.

These results suggest that the values can be separated into two groups: the structure-makers with $H^+$, $Li^+$ and $Na^+$ and the structure-breakers with $K^+$, $Rb^+$ and $Cs^+$. In the first group, the electrostatic partial molal volume is greater for $H^+$ than it is for $Li^+$ and $Na^+$ respectively.

The relationship between $k_S$ or $\lambda$ and the partial molal volumes is not only linear, as predicted by the McDevit-Long theory, but also parallel (Figure 2.4) suggesting that the Pitzer parameters are additives. Therefore, the salting coefficients and the $\zeta$ terms of the missing salts can be calculated using this relationship. For example, the $k_s$ value for $Rb_2SO_4$ can be calculated in two ways.
Table 2.3 Pitzer Parameters $\lambda_{(B-i)}$ and $\zeta_{B-c-a}$ for the Solubility of Boric Acid

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\lambda_{(B-i)}$</th>
<th>c-a</th>
<th>$\zeta_{B-c-a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>0.109</td>
<td>H-Cl</td>
<td>-0.021</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>0.087</td>
<td>Li-Cl</td>
<td>-0.004</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.028</td>
<td>Na-Cl</td>
<td>-0.008</td>
</tr>
<tr>
<td>K$^+$</td>
<td>-0.026</td>
<td>K-Cl</td>
<td>0.001</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>-0.026</td>
<td>Rb-Cl</td>
<td>-0.006</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>-0.035</td>
<td>Cs-Cl</td>
<td>0.000</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.191</td>
<td>Mg-Cl</td>
<td>-0.016$^a$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.165</td>
<td>Ca-Cl</td>
<td>-0.010$^b$</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>0.141</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>0.090</td>
<td>Ba-Cl</td>
<td>-0.052$^a$</td>
</tr>
<tr>
<td>F$^-$</td>
<td>-0.465$^c$</td>
<td>K-F</td>
<td>-0.989$^c$</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br$^-$</td>
<td>0.007$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I$^-$</td>
<td>0.022</td>
<td>K-I</td>
<td>0.004$^e$</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>-0.041$^e$</td>
<td>H-NO$_3$</td>
<td>-0.003</td>
</tr>
<tr>
<td>Na-NO$_3$</td>
<td></td>
<td></td>
<td>-0.008</td>
</tr>
<tr>
<td>K-NO$_3$</td>
<td></td>
<td></td>
<td>-0.012</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>-0.205$^f$</td>
<td>Na-SO$_4$</td>
<td>-0.065</td>
</tr>
<tr>
<td>K-SO$_4$</td>
<td></td>
<td></td>
<td>-0.043</td>
</tr>
</tbody>
</table>

$^a$Values at 18 °C  
$^b$Calculated from $k_3$(SrCl$_2$) in Table 2.4  
$^c$Values at 30 °C  
$^d$Calculated from $k_3$(KBr) in Table 2.4  
$^e$-0.029 from H$^+$, -0.045 from Na$^+$, and -0.035 from K$^+$  
$^f$-0.098 from Na$^+$ and -0.115 from K$^+$
Firstly,

\[ k_s(Rb_2SO_4) = 2k_s(RbCl) + k_s(Na_2SO_4) - 2k_s(NaCl) \] (2.18)

and the second method is to use \( \lambda_{Bi} \) from Equation (2.2) such that
\[ k_s(\text{Rb}_2\text{SO}_4) = 4 \lambda_{\text{B-Rb}} + 2 \lambda_{\text{B-SO}_4} \]  

(2.19)

The \( \zeta \) terms can be then be calculated using the following relationship

\[ \zeta_{\text{B-Rb-SO}_4} = 2 \zeta_{\text{B-Rb-Cl}} + \zeta_{\text{B-Na-SO}_4} - 2 \zeta_{\text{B-Na-Cl}} \]  

(2.20)

Figure 2.4 The Additivity Characteristic of the Salting Coefficients shown by the Linearity and Parallelism of these Values as a Function of the Partial Molal Volumes of the Salts \( V^0_{\text{salt}} \).
In the second group, the electrostatic partial molal volume becomes more positive and could be referred to as a dispersion term. Because the slope of the first group is greater than the near negligible slope of the second group, the electrostatic partial molal volumes have less influence on the solubility of boric acid in structure breaking solutions than in structure making solutions. The salting coefficients of the alkaline-earth ions (Mg$^{2+}$, Ca$^{2+}$ and Ba$^{2+}$) are greater than those of the alkaline ions (H$^+$, Li$^+$ and Na$^+$) suggesting that boric acid is less soluble in alkaline-earth chloride solutions than it is in alkali-chloride solutions.

When the value of a salt (Rb$_2$SO$_4$) can be determined from a number of salts (Na$_2$SO$_4$, K$_2$SO$_4$, etc.) an average value is used. The Pitzer parameters and the salting coefficients along with the partial molal volumes of the salts are summarized in Table 2.4. Since the literature (Linke, 1965) doesn’t provide solubility data in bromide and strontium salt solutions, the salting coefficient for KBr was estimated from fitting the values of KCl and KI with $V^0_{\text{salt}}$ giving

$$k_S(^{\text{KBr}}) = 0.004 \ V^0_{\text{salt}} - 0.136 \quad (2.21)$$

The $k_S$ value of KF was not taken into account in this fit because the fluoride crystal is smaller in size (6.3 cm$^3$ mol$^{-1}$) than the chloride (14.9 cm$^3$ mol$^{-1}$), bromide (18.7 cm$^3$ mol$^{-1}$) and iodide (25.4 cm$^3$ mol$^{-1}$) crystals (Millero, 1972b). The $\lambda$$_{BF}$ and $\zeta_{B-K-F}$ values are also very large and negative, indicative of strong dissociation. Aqueous boric acid
may not be the only species in KF, but additional borate species with fluoride may have formed.

The other $k_S$ and $\zeta_{B-c-F}$ values were therefore not calculated. The ionic value $\lambda_{BB}$ was calculated using $k_S(KBr)$. The $k_S$ values for the other Br salt solutions were calculated using Equations (2.18) and (2.2). The $\zeta$ terms for the Br salts solutions cannot be estimated because no solubility measurements were available in these electrolyte solutions. The ionic value $\lambda_{BS}$ was calculated by fitting $\lambda_B$ of $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, and $\text{Ba}^{2+}$ with the intrinsic partial molal volumes giving

$$\lambda_{BS} = -0.010 \, V_0^{\text{int}} + 0.206$$

(2.22)

Then, the $k_S$ values for $\text{SrCl}_2$, $\text{SrI}_2$, $\text{Sr(NO}_3)_2$, and $\text{SrSO}_4$ were calculated from $\lambda_{BS}$ in Equation (2.2) and were also estimated from fitting the values of $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, and $\text{Ba}^{2+}$ in common anion solutions with $V_0^{\text{salt}}$ giving

- for $\text{SrCl}_2$: $k_S = -0.037 \, V_0^{\text{salt}} + 1.519$  
  (2.23)

- for $\text{SrI}_2$: $k_S = -0.037 \, V_0^{\text{salt}} + 2.385$  
  (2.24)

- for $\text{Sr(NO}_3)_2$: $k_S = -0.037 \, V_0^{\text{salt}} + 1.815$  
  (2.25)

- for $\text{SrSO}_4$: $k_S = -0.037 \, V_0^{\text{salt}} + 0.808$  
  (2.26)
Table 2.4 The Partial Molal Volume of the Salts and the Best Current Estimated Salting Coefficients and Pitzer Parameter $\zeta_{B-c}$.

<table>
<thead>
<tr>
<th>Salt</th>
<th>$V^0_{salt}$</th>
<th>$k_s^a$</th>
<th>$k_s^b$</th>
<th>Cation</th>
<th>Anion</th>
<th>$\zeta_{B-c-d}^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>14.9</td>
<td>0.217</td>
<td>0.217</td>
<td>H</td>
<td>Cl</td>
<td>-0.021</td>
</tr>
<tr>
<td>LiCl</td>
<td>15.4</td>
<td>0.173</td>
<td>0.173</td>
<td>Li</td>
<td>Cl</td>
<td>-0.004</td>
</tr>
<tr>
<td>NaCl</td>
<td>17.0</td>
<td>0.055</td>
<td>0.055</td>
<td>Na</td>
<td>Cl</td>
<td>-0.008</td>
</tr>
<tr>
<td>KCl</td>
<td>20.8</td>
<td>-0.051</td>
<td>-0.051</td>
<td>K</td>
<td>Cl</td>
<td>0.001</td>
</tr>
<tr>
<td>RbCl</td>
<td>23.1</td>
<td>-0.051</td>
<td>-0.052</td>
<td>Rb</td>
<td>Cl</td>
<td>-0.006</td>
</tr>
<tr>
<td>CsCl</td>
<td>27.1</td>
<td>-0.069</td>
<td>-0.069</td>
<td>Cs</td>
<td>Cl</td>
<td>0.000</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>30.5</td>
<td>0.382</td>
<td>0.382</td>
<td>Mg</td>
<td>Cl</td>
<td>-0.016</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>32.2</td>
<td>0.329</td>
<td>0.329</td>
<td>Ca</td>
<td>Cl</td>
<td>0.010</td>
</tr>
<tr>
<td>SrCl$_2$</td>
<td>33.4</td>
<td>0.283</td>
<td>0.283</td>
<td>Sr</td>
<td>Cl</td>
<td></td>
</tr>
<tr>
<td>BaCl$_2$</td>
<td>36.0</td>
<td>0.180</td>
<td>0.180</td>
<td>Ba</td>
<td>Cl</td>
<td>-0.052</td>
</tr>
<tr>
<td>HBr</td>
<td>18.7</td>
<td>0.230</td>
<td>0.230</td>
<td>H</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>LiBr</td>
<td>19.2</td>
<td>0.186</td>
<td>0.186</td>
<td>Li</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>NaBr</td>
<td>20.8</td>
<td>0.068</td>
<td>0.068</td>
<td>Na</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>KBr</td>
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<td>-0.038</td>
<td>-0.038</td>
<td>K</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>RbBr</td>
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<td>-0.039</td>
<td>-0.039</td>
<td>Rb</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>CsBr</td>
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<td>-0.056</td>
<td>-0.056</td>
<td>Cs</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>MgBr$_2$</td>
<td>38.1</td>
<td>0.409</td>
<td>0.409</td>
<td>Mg</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>CaBr$_2$</td>
<td>39.8</td>
<td>0.356</td>
<td>0.356</td>
<td>Ca</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>SrBr$_2$</td>
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<td>0.310</td>
<td>Sr</td>
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<td></td>
</tr>
<tr>
<td>BaBr$_2$</td>
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<td>0.207</td>
<td>Ba</td>
<td>Br</td>
<td></td>
</tr>
<tr>
<td>HI</td>
<td>25.4</td>
<td>0.260</td>
<td>0.260</td>
<td>H</td>
<td>I</td>
<td>-0.018</td>
</tr>
<tr>
<td>LiI</td>
<td>25.9</td>
<td>0.216</td>
<td>0.216</td>
<td>Li</td>
<td>I</td>
<td>-0.001</td>
</tr>
<tr>
<td>NaI</td>
<td>27.5</td>
<td>0.098</td>
<td>0.098</td>
<td>Na</td>
<td>I</td>
<td>-0.005</td>
</tr>
<tr>
<td>KI</td>
<td>31.3</td>
<td>-0.008</td>
<td>-0.008</td>
<td>K</td>
<td>I</td>
<td>0.004</td>
</tr>
<tr>
<td>RbI</td>
<td>33.6</td>
<td>-0.009</td>
<td>-0.009</td>
<td>Rb</td>
<td>I</td>
<td>-0.003</td>
</tr>
<tr>
<td>CsI</td>
<td>37.6</td>
<td>-0.026</td>
<td>-0.026</td>
<td>Cs</td>
<td>I</td>
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</tr>
<tr>
<td>MgI$_2$</td>
<td>51.5</td>
<td>0.468</td>
<td>0.468</td>
<td>Mg</td>
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</tr>
<tr>
<td>CaI$_2$</td>
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<td>0.415</td>
<td>Ca</td>
<td>I</td>
<td>-0.004</td>
</tr>
<tr>
<td>SrI$_2$</td>
<td>54.4</td>
<td>0.369</td>
<td>0.369</td>
<td>Sr</td>
<td>I</td>
<td></td>
</tr>
<tr>
<td>BaI$_2$</td>
<td>57.0</td>
<td>0.266</td>
<td>0.266</td>
<td>Ba</td>
<td>I</td>
<td>-0.046</td>
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<tr>
<td>HNO$_3$</td>
<td>21.1</td>
<td>0.136</td>
<td>0.135</td>
<td>H</td>
<td>NO$_3$</td>
<td>-0.003</td>
</tr>
<tr>
<td>LiNO$_3$</td>
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<td>0.094</td>
<td>0.091</td>
<td>Li</td>
<td>NO$_3$</td>
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</tr>
<tr>
<td>NaNO$_3$</td>
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<td>-0.027</td>
<td>Na</td>
<td>NO$_3$</td>
<td>-0.008</td>
</tr>
<tr>
<td>KNO$_3$</td>
<td>27.0</td>
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<td>-0.133</td>
<td>K</td>
<td>NO$_3$</td>
<td>-0.012</td>
</tr>
<tr>
<td>RbNO$_3$</td>
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<td>-0.134</td>
<td>Rb</td>
<td>NO$_3$</td>
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<td>CsNO$_3$</td>
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<td>-0.151</td>
<td>Cs</td>
<td>NO$_3$</td>
<td>0.002</td>
</tr>
<tr>
<td>Salt</td>
<td>$V^0_{\text{salt}}$</td>
<td>$k^b_s$</td>
<td>$k^c_s$</td>
<td>Cation</td>
<td>Anion</td>
<td>$\zeta_{B-c-a}^{d}$</td>
</tr>
<tr>
<td>------------</td>
<td>---------------------</td>
<td>---------</td>
<td>---------</td>
<td>--------</td>
<td>-----------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Mg(NO$_3$)$_2$</td>
<td>42.9</td>
<td>0.217</td>
<td>0.217</td>
<td>Mg</td>
<td>NO$_3$</td>
<td>-0.013</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$</td>
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<td>0.164</td>
<td>0.164</td>
<td>Ca</td>
<td>NO$_3$</td>
<td>-0.007</td>
</tr>
<tr>
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<td>0.118</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ba(NO$_3$)$_2$</td>
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<td>0.015</td>
<td>Ba</td>
<td>NO$_3$</td>
<td>-0.049</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>21.7</td>
<td>0.024</td>
<td>0.024</td>
<td>H</td>
<td>SO$_4$</td>
<td>-0.089</td>
</tr>
<tr>
<td>Li$_2$SO$_4$</td>
<td>22.7</td>
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<td>-0.065</td>
<td>Li</td>
<td>SO$_4$</td>
<td>-0.055</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>25.9</td>
<td>-0.303</td>
<td>-0.301</td>
<td>Na</td>
<td>SO$_4$</td>
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</tr>
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<td>-0.513</td>
<td>K</td>
<td>SO$_4$</td>
<td>-0.043</td>
</tr>
<tr>
<td>Rb$_2$SO$_4$</td>
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<td>-0.515</td>
<td>Rb</td>
<td>SO$_4$</td>
<td>-0.059</td>
</tr>
<tr>
<td>Cs$_2$SO$_4$</td>
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<td>-0.549</td>
<td>Cs</td>
<td>SO$_4$</td>
<td>-0.047</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>22.4</td>
<td>-0.029</td>
<td>-0.029</td>
<td>Mg</td>
<td>SO$_4$</td>
<td>-0.117</td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>24.1</td>
<td>-0.082</td>
<td>-0.082</td>
<td>Ca</td>
<td>SO$_4$</td>
<td>-0.111</td>
</tr>
<tr>
<td>SrSO$_4$</td>
<td>25.3</td>
<td>-0.128$^i$</td>
<td>-0.128$^i$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaSO$_4$</td>
<td>27.9</td>
<td>-0.230</td>
<td>-0.231</td>
<td>Ba</td>
<td>SO$_4$</td>
<td>-0.153</td>
</tr>
</tbody>
</table>

$^a$ Calculated from $V^0_{\text{cryst}}$ (Millero, 1972b; Millero, 1969)

$^b$ The underlined values of this column are calculated from Equation (2.18)

$^c$ The underlined values of this column are calculated from Equation (2.2)

$^d$ The underlined values of this column are calculated from Equation (2.20)

$^e$ $k^c_s = -0.037 \times V^0_{\text{salt}} - 1.519$ using $k^c_s$ values of MgCl$_2$, CaCl$_2$ and BaCl$_2$

$^f$ $k^c_s = 0.004 \times V^0_{\text{salt}} - 0.106$ using $k^c_s$ values of KCl and KI

$^g$ $k^c_s = -0.037 \times V^0_{\text{salt}} - 2.385$ using $k^c_s$ values of MgI$_2$, CaI$_2$ and BaI$_2$

$^h$ $k^c_s = -0.037 \times V^0_{\text{salt}} - 1.815$ using $k^c_s$ values of Mg(NO$_3$)$_2$, Ca(NO$_3$)$_2$ and Ba(NO$_3$)$_2$

$^i$ $k^c_s = -0.037 \times V^0_{\text{salt}} - 0.808$ using $k^c_s$ values of MgSO$_4$, CaSO$_4$ and BaSO$_4$

From these calculated values in Table 2.4, one can see that boric acid is soluble in this order $SO_4 > NO_3$ and $F > Cl > Br > I$ in common cation solutions. In common anion salt solutions, the order becomes $Cs > Rb > K > Na > Li > H$ and $Ba > Sr > Ca > Mg$. These $\lambda_{Bi}$ and $\zeta_{B-c-a}$ values can also be used to estimate the activity coefficients $\gamma_B$ and the solubility [B] of B(OH)$_3$ in mixed solutions (seawater and brines) using the more general Pitzer equation (Pitzer, 1991)
\[
\ln \{[B]^0/[B]\} = \ln \gamma_B = 2 \sum C \lambda_{BC} \cdot m_c + 2 \sum A \lambda_{BA} \cdot m_a + \sum C \sum A \zeta_{BC-CA} \cdot m_c \cdot m_a
\]  
(2.27)

For example, the solubility of boric acid (0.866 mol kg\(^{-1}\)) determined from Equation (2.27) in 0.427 mol kg\(^{-1}\) NaCl and 0.055 mol kg\(^{-1}\) MgCl\(_2\), which are the molalities in artificial seawater (Millero 2006), is in good agreement with the measured value (0.864 mol kg\(^{-1}\)).

### 2.5 Chapter summary

In summary, the solubility of boric acid in electrolyte solutions measured in this study was in good agreement with those found in the literature (Linke, 1965). Temperature appears to have little effect on the solubility in LiCl, NaCl, and KCl solutions. Thus, the salting coefficients \(k_S\) and the parameters \(\lambda_{Bi}\) and \(\zeta_{B-C-A}\) derived in this study can be used over a limited temperature range (5 to 35 °C). When direct measurements were not available the estimated salting coefficients \(k_S\) and the triplet interaction term \(\zeta_{B-C-A}\) should give reasonable estimates of the solubility of boric acids in salts with no experimental measurements. The activity coefficients of boric acid in mixed electrolyte solutions can also be estimated from the Pitzer parameters determined in this study.
Chapter 3: Effect of filtration on the total alkalinity of open-ocean seawater*

3.1 Background information

Total alkalinity (TA) is a parameter that is often measured along with pH, total inorganic CO\(_2\) (TCO\(_2\)) and partial pressure of CO\(_2\) (pCO\(_2\)) for the understanding of the oceanic CO\(_2\) system. Measuring any two of these four parameters allows one to calculate the other two. The total alkalinity of seawater is the amount of acid that needs to be added (per kg of seawater) to reach that point when the right hand side of Equation (3.1) is zero (Dickson, 1981):

\[
TA = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] \\
+ 2[\text{PO}_4^{3-}] + [\text{SiO(OH)}_3^-] + [\text{NH}_3] + [\text{HS}^-] - [\text{H}^+]_F - [\text{HSO}_4^-] \\
- [\text{HF}] - [\text{H}_3\text{PO}_4] \tag{3.1}
\]

The brackets represent the concentrations in micromoles per kilogram (µmol kg\(^{-1}\)) and [H\(^+\)]\(_F\) is the concentration of free hydrogen ion. In seawater, NH\(_3\) and HS\(^-\) are usually negligible and often omitted from the equation. The major bases in seawater are HCO\(_3^-\),

* This chapter has been previously published as: Chanson, M. and F.J. Millero, Effect of filtration on total
CO$_3^{2-}$ and B(OH)$_4^-$ and all make major contributions to alkalinity. In deep waters, the TA increases due to the dissolution of CaCO$_3$ (Chen, 1978). In surface seawater, the change in salinity and temperature manifested by evaporation or fresh water input contribute to TA variations (Millero et al., 1998; Lee et al., 2000). Changes in alkalinity can also be affected by the growth of phytoplankton (Brewer and Goldman, 1976). The assimilation of nitrate or ammonia by phytoplankton generates a strong base or strong acid respectively and therefore increases or decreases TA. Phytoplankton and bacterial cells can affect the measured alkalinity of unfiltered seawater samples like those collected in Young-II bay, Korea (Kim et al., 2006). Kim et al. (2006) in particular suggested that the alkalinity measurements made at sea should be made on filtered seawater. Although this may be true for coastal waters, this chapter provides measurements that show that there is no need to filter seawater samples collected in the open ocean. The results are based on samples analyzed at sea during the CLIVAR/CO$_2$ repeat hydrography on P16N and I9N cruises in the Pacific and Indian Oceans.

### 3.2 Materials and procedures

The cruises were part of the Repeat Hydrography CLIVAR/CO$_2$ program. The P16N cruise was divided in a leg from Tahiti to Hawaii (February 13 - March 3, 2006) and a leg from Hawaii to Kodiak, Alaska (March 10 - March 30, 2006). The I9N cruise started in Fremantle, Australia on March 22 and ended in Phuket, Thailand on May 01.

Both cruise tracks are illustrated in Figure 3.1. Filtered samples were taken at different depths and stations. Unfiltered samples were also collected at the same stations and depths for comparison. A Welch vacuum pump model 2546B-01 was used and the samples were filtered through 0.45 µm membrane filters immediately after collecting them from the Niskin bottles. After filtration, total alkalinity was determined according to the method described elsewhere (Millero et al., 1993). The maximum salinity change due to filtration was 0.008, equivalent to a maximum change in TA of 0.5 µmol kg\(^{-1}\).

Figure 3.1 The P16N 2006 and I9N 2007 cruise tracks in the Pacific Ocean from Feb 13 to Mar 30, 2006 and in the Indian Ocean from Mar 22 to May 01, 2007. Each dot represents a station where total alkalinity was measured on both unfiltered and filtered seawater samples.
Two titration systems were used at sea and were checked for accuracy using several batches of Certified Reference Material (CRM batch 73 and 78 during the Pacific and Indian Ocean cruises respectively). The mean TA difference between the measured values and the certified values was $-1.2 \pm 4.3$ $\mu$mol kg$^{-1}$ ($n = 125$) in the Pacific Ocean and $0.8 \pm 3.3$ $\mu$mol kg$^{-1}$ ($n = 168$) in the Indian Ocean. The precision was checked by making duplicate measurements of the same Niskin bottles on the same system A or B or by using the two systems A and B. The true standard deviation from a set of duplicate measurements was calculated as described in Dickson et al. (2007). All the filtered and unfiltered samples were measured on the same titration system. Table 3.1 gives the assigned values of the CRM, which is also used by the groups who measured TCO$_2$.

Table 3.1 Certified values of the CRM batch 73 and 78 provided by Professor Andrew Dickson at SIO, California.

<table>
<thead>
<tr>
<th></th>
<th>Batch 73 - P16N 2006</th>
<th>Batch 78 - I9N 2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity</td>
<td>33.523</td>
<td>33.285</td>
</tr>
<tr>
<td>Total Alkalinity ($\mu$mol kg$^{-1}$)</td>
<td>2253.50 ± 0.84</td>
<td>2185.57 ± 0.45</td>
</tr>
<tr>
<td>Total Dissolved Inorganic Carbon ($\mu$mol kg$^{-1}$)</td>
<td>2057.30 ± 0.45</td>
<td>1991.93 ± 0.58</td>
</tr>
<tr>
<td>Phosphate ($\mu$mol kg$^{-1}$)</td>
<td>0.35</td>
<td>0.37</td>
</tr>
<tr>
<td>Silicate ($\mu$mol kg$^{-1}$)</td>
<td>1.1</td>
<td>2.0</td>
</tr>
<tr>
<td>Nitrite ($\mu$mol kg$^{-1}$)</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Nitrate ($\mu$mol kg$^{-1}$)</td>
<td>1.5</td>
<td>0.52</td>
</tr>
</tbody>
</table>
An integrated program controls the titration, data collection, and the calculation of the carbonate parameters (TA, pH and TCO₂) (Millero et al., 1993). The program is patterned after those developed by Dickson (1981, 2007) and Johansson and Wedborg (1982). The program uses a Levenberg-Marquardt non-linear least-squares algorithm to calculate $E^0$, pH, TA, TCO₂ and pK*₁ from the potentiometric titration data. A comparison of measured values of TA, TCO₂, pH and pK*₁ made on CRM during the cruise are given in Table 3.2.

The precision in the measured values of TA, TCO₂ and pH are reasonable. The average measured value for TA is in good agreement with the assigned value. The measured values of TCO₂ are higher than the assigned value, in agreement with the findings of Millero et al. (1993). Measurements made on Cell A (I9N) changed throughout the first part of the Indian cruise. This is thought to be related to problems in the assigned volume of the cell. The large offset was used to correct all of the earlier measurements of TA and TCO₂ on the cruise. Although the potentiometric values of pH are precise, both cells show an offset from the assigned value of 0.014 to 0.015. This same trend was also found in earlier studies and probably is related to the non-Nernst behavior of the electrodes. By calibrating the cells with CRM of known pH it is possible to obtain reliable values for all the titrated samples. This adjustment has been made to all the potentiometric values of pH. All of the titrations of CRM yield values of pK*₁ that
are in excellent agreement (± 0.004, n = 101) with the carbonate equations of Millero et al. (2006). It is interesting to note that the values of pK*₁ for all the titrations (n = 2200) determined on the cruise also agree with the equations of Millero et al. (2006) to within ± 0.004. This is important because it gives support to the use of the seawater pH scale determined by titration and used to determine the carbonate constants. The calculation of carbonate parameters using input of pH-TA or pH-TCO₂ require reliable constants on the same pH scale.

Reproducibility of the measurements is checked by comparing the results of both systems on seawater sampled from the same Niskin bottle. The results of measurements for the same samples on cells A and B are given in Table 3.3. The measurements of TA and TCO₂ with two cells on the same sample normally agree to within ± 2 µmol kg⁻¹ and the values of pH agreed to within ± 0.006. The true standard deviation from a set of duplicate measurements was calculated as described in Dickson et al. (2007). Duplicate measurements were also made on the sample system. The reproducibility of both systems is in good agreement (within ± 2σ = ± 3 µmol kg⁻¹ for TA; ± 4 µmol kg⁻¹ for TCO₂ and ± 0.008 for pH). This a good measure of the precision of the two cells throughout the cruise.
Table 3.2 Comparison of the measured TA (µmol kg\(^{-1}\)), TCO\(_2\) (µmol kg\(^{-1}\)), pH and pK\(_*1\) with the values of CRM using Cell A and B during the cruise also given.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CRM</th>
<th>Average</th>
<th>Stdev</th>
<th>Number</th>
<th>Meas-CRM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P16N 2006</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TA</td>
<td>2253.5</td>
<td>2253.6</td>
<td>4.1</td>
<td>53</td>
<td>0.3</td>
</tr>
<tr>
<td>TCO(_2)</td>
<td>2057.3</td>
<td>2068.0</td>
<td>2.8</td>
<td>53</td>
<td>10.7</td>
</tr>
<tr>
<td>pH</td>
<td>7.842</td>
<td>7.826</td>
<td>0.005</td>
<td>53</td>
<td>-0.012</td>
</tr>
<tr>
<td>pK(_*1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cell A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TA</td>
<td>2253.5</td>
<td>2257.2</td>
<td>2.0</td>
<td>60</td>
<td>3.7</td>
</tr>
<tr>
<td>TCO(_2)</td>
<td>2057.3</td>
<td>2071.4</td>
<td>2.2</td>
<td>60</td>
<td>14.1</td>
</tr>
<tr>
<td>pH</td>
<td>7.842</td>
<td>7.826</td>
<td>0.005</td>
<td>60</td>
<td>0.012</td>
</tr>
<tr>
<td>pK(_*1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cell B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TA</td>
<td>2185.57</td>
<td>2184.3</td>
<td>4.7</td>
<td>96</td>
<td>-1.3</td>
</tr>
<tr>
<td>TCO(_2)</td>
<td>1991.93</td>
<td>1998.6</td>
<td>5.7</td>
<td>95</td>
<td>6.7</td>
</tr>
<tr>
<td>pH</td>
<td>7.870(^a)</td>
<td>7.855</td>
<td>0.006</td>
<td>94</td>
<td>-0.015</td>
</tr>
<tr>
<td>pK(_*1)</td>
<td>5.849(^b)</td>
<td>5.845</td>
<td>0.004</td>
<td>93</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I9N 2007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TA</td>
<td>2185.57</td>
<td>2184.9</td>
<td>3.6</td>
<td>107</td>
<td>0.33</td>
</tr>
<tr>
<td>TCO(_2)</td>
<td>1991.93</td>
<td>1996.4</td>
<td>4.0</td>
<td>102</td>
<td>4.5</td>
</tr>
<tr>
<td>pH</td>
<td>7.870</td>
<td>7.856</td>
<td>0.005</td>
<td>104</td>
<td>0.014</td>
</tr>
<tr>
<td>pK(_*1)</td>
<td>5.849</td>
<td>5.849</td>
<td>0.003</td>
<td>102</td>
<td>0.004</td>
</tr>
</tbody>
</table>

\(^a\) This value of pH is from the mean value determined on the cruise. It agrees with the value that is obtained from an input of TA and TCO\(_2\) assigned by the CRM.

\(^b\) Calculated from the pK\(_*1\) equations of Millero, et al. (2006). It is interesting to note that the values of pK\(_*1\) for all the titrations agree with the equations of Millero, et al. (2006).
Table 3.3 Comparison of duplicate measurements of TA, TCO$_2$ and pH.

<table>
<thead>
<tr>
<th></th>
<th>Cell A-Cell B</th>
<th></th>
<th>Cell A</th>
<th></th>
<th>Cell B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P16N  I9N P16N I9N P16N I9N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>TA (µmol kg$^{-1}$)</strong></td>
<td>Mean</td>
<td>0.3</td>
<td>-1.0</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>Stdev</td>
<td>2.3</td>
<td>2.6</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>62</td>
<td>65</td>
<td>59</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>0.4</td>
<td>0.7</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td><strong>TCO$_2$ (µmol kg$^{-1}$)</strong></td>
<td>Stdev</td>
<td>3.9</td>
<td>3.2</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>62</td>
<td>67</td>
<td>59</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>-0.001</td>
<td>-0.002</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>Stdev</td>
<td>0.008</td>
<td>0.006</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>62</td>
<td>57</td>
<td>59</td>
<td>84</td>
</tr>
</tbody>
</table>

3.3 Assessment and discussion

The differences in alkalinity between unfiltered and filtered samples are shown in Figure 3.2 and Figure 3.3 as a function of latitude (left panels) and depth (right panels) and yield a mean value of $-0.10 \pm 1.1 \, \mu\text{mol kg}^{-1}$ in the Pacific and $0.13 \pm 1.25 \, \mu\text{mol kg}^{-1}$ in the Indian Ocean. The results indicate that, statistically, there is no difference in the measured TA at sea between the unfiltered and filtered seawater samples. This also proves that there was no need to check if water depth or latitude were factors that contributed to any measured TA changes.
The difference between the unfiltered and filtered TA is greater than 5 $\mu$mol kg$^{-1}$ and increase when the particulate organic carbon (POC) values are greater than 200 $\mu$mol L$^{-1}$ (Kim et al., 2006). Since oceanic POC values are typically around 5 $\mu$mol L$^{-1}$ (Bacon et al., 1996; Gardner et al., 2003), the change in TA due to POC concentration is insignificant in the open ocean. Moreover, all the TA measurements made during the iron enrichment experiments inside and outside the patch agree to within 5 $\mu$mol kg$^{-1}$ (Coale et al., 2004; Hiscock and Millero, 2005). TA changes observed during earlier iron enrichment experiments (IronEx) are compared with those observed during Southern Ocean Iron Experiment (SOFeX) (Hiscock and Millero, 2005). TA changed by $-2 \pm 2$ $\mu$mol kg$^{-1}$ during IronEx I, $-1 \pm 3$ $\mu$mol kg$^{-1}$ during IronEx II, and $0 \pm 5$ $\mu$mol kg$^{-1}$ in the North and South patch during SOFeX. The SOFeX TA changes occurred with increasing POC of $8 \pm 0.8$ and $11 \pm 3$ $\mu$mol L$^{-1}$ in the North and South patch respectively. The maximum POC values recorded were around 15 $\mu$mol L$^{-1}$ (Coale et al., 2004). These results demonstrate that the reported TA values were within experimental errors and did not change during the iron experiments. Therefore, even in High Nutrient Low Chlorophyll (HNLC) areas such as the Southern Ocean, filtering seawater samples for alkalinity measurements would not be necessary.

The findings of this chapter demonstrate that filtration of open-ocean seawater is not necessary when measuring TA. This means that one does not have to take the time to filter samples before measuring the TA, and more importantly, that the unfiltered measurements made on seawater over the last 20 years are valid in this sense.
Figure 3.2 The differences in the unfiltered and filtered samples of seawater ($n = 60$) collected in the North Pacific during the P16N 2006 cruise as a function of latitude (left) and depth (right). The vertical solid line represents the mean difference (mean = -0.10 µmol kg$^{-1}$) and the vertical dashed lines represent two standard deviations from the mean (one standard deviation = 0.95 µmol kg$^{-1}$).
Figure 3.3 The differences in the unfiltered and filtered samples of seawater \((n = 120)\) collected in the Indian Ocean during the I9N 2007 cruise as a function of latitude (left) and depth (right). The vertical solid line represents the mean difference \((\text{mean} = -0.13 \ \mu\text{mol kg}^{-1})\) and the vertical dashed lines represent two standard deviations from the mean \((\text{one standard deviation} = 1.25 \ \mu\text{mol kg}^{-1})\).
Chapter 4: Synthesis and analysis of the inorganic carbon parameters in the Atlantic Ocean based on decadal occupations of the meridional section A16

4.1 Background information

The objective of the CO₂ component of the CLIVAR/Repeat Hydrography program is to monitor the changing patterns of CO₂, and to improve forecasting skills for ocean and global climate. In this chapter, the CO₂ on section A16 along the meridian 20°W in the Atlantic Ocean is examined. This transect has the most complete dataset from south to north on a decadal time scale in the Atlantic basin. Scientific cruises took place between 1989 and 1993 as part of the WOCE program and in 2003 and 2005 as part of the CLIVAR/CO₂ studies. On these cruises, the CO₂ parameters pH, TA, TCO₂, and pCO₂ were measured along with hydrographic properties. The results have been synthesized, examined for internal consistency, and used to estimate the decadal changes of these parameters. The anthropogenic uptake of CO₂ in the Atlantic Ocean is examined along with the impact on ocean acidity on the calcium carbonate saturation horizon. Since the first estimated oceanic anthropogenic CO₂ from direct measurements (Brewer, 1978; Chen and Millero, 1979), several investigators have improved the quantifications
by reducing the uncertainties (Gruber, 1998; Goyet et al., 1999; Sabine et al., 2004; Touratier and Goyet, 2004a; Touratier et al., 2007).

In this work, the anthropogenic CO$_2$, CO$_2^{\text{anth}}$ was calculated using the TrOCA method (Touratier and Goyet, 2004b; Touratier, 2007). The biological increase in CO$_2$, CO$_2^{\text{bio}}$, due to the oxidation of organic matter and dissolution of CaCO$_3$ is also determined using the methods developed by Chen and Millero (1979) and used to examine the anthropogenic uptake of CO$_2$ in the oceans (Brewer, 1978; Chen and Millero, 1979). The CO$_2^{\text{bio}}$ was also determined from MLR calculations performed on TCO$_2$ with apparent oxygen utilization (AOU) and TA as dependent variables. This chapter examines the changes of the carbonate system on a decadal and seasonal time scale. The observed changes in TCO$_2$ are used to quantify the contributions of mixing, anthropogenic, or biological CO$_2$ and the effect on the calcium carbonate saturation depths.

4.2 Data and calculations

4.2.1 Quality control of the cruises data sets

The CO$_2$ system parameters, transient tracers and hydrographic data were measured along the meridian 20°W in the Atlantic Ocean from 1989 to 2005 (Figure 4.1).
Table 4.1 identifies the cruises during this period and lists the total number of measurements taken for the various parameters of the carbonate system. All data are available at

http://whpo.ucsd.edu,

http://cdiac.esd.orl.gov/oceans/glodap/GlopDV.htm,

http://cdiac.ornl.gov/oceans, and


Oxygen and nutrient values of the Ocean-Atmosphere Carbon Exchange Study (OACES) 1991 are in µmol kg⁻¹. A value of 7.5 µmol kg⁻¹ has been added to the 1993 oxygen concentrations as recommended by Castle et al. (1998).

Samples of TA, pH and TCO₂ were collected and measurements were made according to the procedures outlined in the Handbook of Methods for CO₂ Analysis (Dickson et al., 2007). TA, pH and TCO₂ were measured by potentiometry (Millero et al., 1993a), pH by spectrophotometry (Clayton, 1995) and TCO₂ by coulometry (Johnson et al., 1985; Johnson et al., 1987; Johnson et al., 1993). When a CO₂ parameter was not available, it was calculated using two of the measured values using the carbonic acid constants of Millero et al. (2006). The values obtained for TA, TCO₂ and pH were compared to the CRM throughout the cruises to examine the accuracy of our measurements. Tris buffers (Ramette et al., 1977) were also used to examine the precision of pH measurements. The pH of the CRMs and Tris buffers were measured on the seawater scale at 25 °C in the laboratory prior to going to sea.
Table 4.2 gives a summary of the CRMs and Tris measurements. The values of TA agree to $\pm 3.0 \mu$mol kg$^{-1}$; those of TCO$_2$ agree to $3.1 \mu$mol kg$^{-1}$; and those of pH agree to $\pm 0.0024$ with the CRMs and $0.0007$ with Tris.

Figure 4.1 Cruise tracks for A16 transect during the WOCE (black dots) and CLIVAR (grey open circles) programs from 1989 to 2005. The WOCE89 cruise surveyed from 60°S to 32°S, the OACE91 from 42°S to 5°S, the OACE93 and A16N2003 from 60°N to 5°S, and the A16S2005 from 63°S to 5°S.
### Table 4.1 Cruise Data Information

<table>
<thead>
<tr>
<th>Section</th>
<th>Total number of measurements</th>
<th>Stations</th>
<th>TCO$_2$ (µmol kg$^{-1}$)</th>
<th>pCO$_2$ (µatm)</th>
<th>TA (µmol kg$^{-1}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A16S (WOCE89) Jan - Mar, 1989</td>
<td>45</td>
<td>1710</td>
<td>1491</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A16S (OACES91_1) Jul - Sept, 1991</td>
<td>18</td>
<td>335</td>
<td></td>
<td>320</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A16N (OACES93) Jul - Aug, 1993</td>
<td>83</td>
<td>1724</td>
<td></td>
<td>1645</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A16N Jun - Aug, 2003</td>
<td>150</td>
<td>2426</td>
<td>1457</td>
<td>2317</td>
<td>2229</td>
<td></td>
</tr>
<tr>
<td>A16S Jan - Feb, 2005</td>
<td>121</td>
<td>2447</td>
<td>843</td>
<td>2368</td>
<td>2466</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4.2 Summary of Certified Reference Material Measurements during A16N-2003 and A16S-2005.

<table>
<thead>
<tr>
<th>Cert. Value</th>
<th>TA (µmol kg$^{-1}$)</th>
<th>TCO$_2$ (µmol kg$^{-1}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRM 59</td>
<td>2221.0 ± 0.6</td>
<td>2007.1 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>CRM 66</td>
<td>2193.3 ± 0.9</td>
<td>1969.6 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>CRM 59</td>
<td>2222.7 ± 3.6</td>
<td>a</td>
<td>7.895</td>
</tr>
<tr>
<td>CRM 66</td>
<td>2193.0 ± 2.7</td>
<td>1973 ± 3</td>
<td>7.904</td>
</tr>
<tr>
<td>Tris</td>
<td>8.090 ± 0.001</td>
<td>n = 255</td>
<td></td>
</tr>
</tbody>
</table>

*a For A16N the gas calibration loops for TCO$_2$ malfunctioned and the CRMs were used as the absolute calibrant.
Duplicate measurements at the surface, at about 1000 m, and at the bottom were made throughout the study. They usually consisted of measuring two samples from the same Niskin bottle on two different TA or TCO$_2$ systems. Duplicate pH measurements were made on the same instrument. The overall mean differences for the duplicate measurements were 1.7 ± 1.4 $\mu$mol kg$^{-1}$ for TA, 1.1 ± 0.8 $\mu$mol kg$^{-1}$ for the TCO$_2$ values and 0.0003 ± 0.004 for pH. A summary of these measurements are given in Table 4.3.

The internal consistency of the data was checked using the 1991-1993 data sets (Lee et al., 1997; Wanninkhof, et al, 2003) and the 2003-2005 data sets (Millero et al., 2004; Millero et al., 2005). By having two of the four carbonate parameters, one can calculate the other two using the carbonic acid constants of Millero et al. (2006). The agreement was checked by looking at the difference between the calculated and the measured parameters. A summary of the internal consistency is given in Table 4.4. The work of Lee et al. (1997) indicates that the measurements were internally consistent to ± 0.006 in pH, ± 3 $\mu$mol kg$^{-1}$ in TCO$_2$, and ± 3 $\mu$mol kg$^{-1}$ in TA during the cruise A16N 1993. No adjustments were recommended for the 1991 and 1993 cruises (Wanninkhof, et al, 2003).

Once the quality of the data was evaluated, the relationships of TCO$_2$ and TA with other hydrographic parameters using multi linear regressions were examined. The concentration of the anthropogenic, biological, and mixing CO$_2$ in the ocean and the changes in the saturation depth with respect to calcium carbonate were also estimated.
Table 4.3 Summary of duplicate TA, TCO₂ and pH measurements during A16N 2003 and A16S 2005.

<table>
<thead>
<tr>
<th></th>
<th>ΔTA (µmol kg⁻¹)</th>
<th>ΔTCO₂ (µmol kg⁻¹)</th>
<th>ΔpH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A16N</td>
<td>1.0 ± 0.1</td>
<td>1.1 ± 0.8</td>
<td>0.0003 ± 0.0043</td>
</tr>
<tr>
<td></td>
<td>n = 159</td>
<td>n = 222</td>
<td>n = 143</td>
</tr>
<tr>
<td>A16S</td>
<td>2.8 ± 1.9</td>
<td>1.1 ± 0.8</td>
<td>0.0003 ± 0.0037</td>
</tr>
<tr>
<td></td>
<td>n = 152</td>
<td>n = 356</td>
<td>n = 246</td>
</tr>
<tr>
<td>A16S</td>
<td>1.3 ± 1.1</td>
<td>0.9 ± 0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n = 62</td>
<td>n = 64</td>
<td></td>
</tr>
<tr>
<td>Overall</td>
<td>1.7 ± 1.4</td>
<td>1.0 ± 0.8</td>
<td>0.0003 ± 0.004</td>
</tr>
<tr>
<td></td>
<td>n = 373</td>
<td>n = 642</td>
<td>n = 389</td>
</tr>
</tbody>
</table>

*Measurements of 2 samples from the same Niskin bottle made on the same instrument

Table 4.4 Summary of internal consistency on the Atlantic carbonate parameters. Δ is the difference between the measured and calculated carbonate parameter from that in the parenthesis.

<table>
<thead>
<tr>
<th></th>
<th>A16S 1991⁹</th>
<th>A16N 1993⁹</th>
<th>A16N 2003</th>
<th>A16S 2005</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔTCO₂ (pH, TA)</td>
<td>-3.7 ± 3.6</td>
<td>2.1 ± 5.8</td>
<td>3.1 ± 6.2</td>
<td></td>
</tr>
<tr>
<td>ΔTA (pH, TCO₂)</td>
<td>3.8 ± 4.2</td>
<td>2.2 ± 6.1</td>
<td>3.2 ± 6.4</td>
<td></td>
</tr>
<tr>
<td>ΔTCO₂ (TA, fCO₂)</td>
<td>3.3 ± 11.6</td>
<td>-0.9 ± 4.5</td>
<td>-1 ± 5.1</td>
<td>1.9 ± 4.4</td>
</tr>
<tr>
<td>ΔTA (fCO₂, TCO₂)</td>
<td>-3.7 ± 13.5</td>
<td>1.0 ± 5.1</td>
<td>1.4 ± 4.4</td>
<td>-2 ± 4.9</td>
</tr>
<tr>
<td>ΔpH (TA, TCO₂)</td>
<td>0.004 ± 0.013</td>
<td>0.012 ± 0.014</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ΔpH (fCO₂, TCO₂)</td>
<td>0.004 ± 0.009</td>
<td>0.004 ± 0.007</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

⁹ Source (Wanninkhof et al., 2003)
4.2.2 Multi linear regressions

Fitted surface values of TCO\textsubscript{2} and TA were previously estimated from sea surface temperature (SST), salinity (S) and nitrate (NO\textsubscript{3}\textsuperscript{-}) (Millero et al., 1998; Lee et al., 2000). These relationships differ depending on the zone (upwelling, marginal seas) and temperature range (e.g. 20 to 29 °C). The multi linear regression technique is also a tool to quantify the changes in TCO\textsubscript{2} over the last decade in the Pacific Ocean (Sabine et al., 2008). Surface TCO\textsubscript{2} and TA are fitted to within 8 µmol kg\textsuperscript{-1} in the Southern Indian Ocean to estimate the air-sea CO\textsubscript{2} flux (McNeil et al., 2007). A global surface total alkalinity relationship with only salinity and temperature resulted in an area-weighed uncertainty of ± 8.1 µmol kg\textsuperscript{-1} (Lee et al., 2006). Anthropogenic CO\textsubscript{2} uptake in the Indian and Pacific oceans was quantified by comparing direct TCO\textsubscript{2} measurements from 1978 and 1995 using fitted equations (Peng et al., 1998; Peng, 2003). Other types of multi-linear regressions were also carried out on a regional scale to check the offsets in TCO\textsubscript{2} and TA, and to check the measurements made on overlapping cruises (Wanninkhof et al, 2003). In this work, MLR techniques are applied to the measured values of TA and TCO\textsubscript{2} using hydrographic variables in equations of the form

\[
e^Y = a_i + a_{\theta} T^\theta + a_{\text{Lat}} \text{Lat} + a_{\text{P}} \text{P} + a_{\text{S}} S + a_{\text{Si}} S_i + a_{\text{NO3}} NO_3^- + a_{\text{AOU}} AOU + R_i
\]  

\( (4.1) \)
with $Y_i$ representing either the predicted TA or TCO$_2$ of the year $i$. The $a_i$ coefficients are determined by fitting the measured values of $Y$ with the different dependent variable $X$. The neutral density surface ($\gamma^p$, kg m$^{-3}$), latitude (Lat, deg), pressure (P, db), potential temperature ($\theta$, °C), silicate (Si, µmol kg$^{-1}$) and nitrate (NO$_3$, µmol kg$^{-1}$) were selected as dependent variables. Neutral density surface, $\gamma^p$, was chosen in lieu of potential density for reasons described in Appendix 2. Since the OACES 91 cruise did not include phosphate measurements, phosphate concentrations were omitted in the fits. By choosing latitude as a dependent variable, it is unnecessary to separate the Atlantic Ocean into separate regions. The water column is divided into the top 200 db (mixed layer) and below 200 db. Samples with salinity less than 34 collected on A16S 2005 from surface Antarctic Intermediate Waters (AAIW) south of 50º S are not used. Since the differences in the MLRs for the 1989-1993 and 2003-2005 datasets are examined, they are referred to as extended MLR ($\Delta$eMLR = eMLR$_1$ – eMLR$_0$). In this chapter, subscript 1 and 0 represent the data from the years 2003-2005 and 1989-1993 respectively.
Table 4.5 Extended multi linear regressions of TA and TCO₂ for the years 1989-1993 (eY₀) and 2003-2005 (eY₁) in the top 200 db and below 200db with salinity greater than 34. RMSE is the root mean square error and R² is the coefficient of determination. δeY and δΔeY are the predicted accuracy of eY₁ and ΔY respectively.

<table>
<thead>
<tr>
<th></th>
<th>TA₁&lt;sup&gt;200&lt;/sup&gt;</th>
<th>TA₀&lt;sup&gt;200&lt;/sup&gt;</th>
<th>TA₁&lt;sup&gt;200&lt;/sup&gt;</th>
<th>TA₀&lt;sup&gt;200&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>278.0 ± 14.8</td>
<td>228.9 ± 17.1</td>
<td>577.8 ± 24.4</td>
<td>578.0 ± 42.8</td>
</tr>
<tr>
<td>a₀</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a₁</td>
<td>-0.17 ± 0.01</td>
<td>-0.15 ± 0.01</td>
<td>-0.02 ± 0.006</td>
<td>-0.04 ± 0.009</td>
</tr>
<tr>
<td>a₂</td>
<td>-0.070 ± 0.004</td>
<td>-0.057 ± 0.006</td>
<td>0.003 ± 0.000</td>
<td>0.005 ± 0.000</td>
</tr>
<tr>
<td>a₃</td>
<td>-1.34 ± 0.06</td>
<td>-1.37 ± 0.07</td>
<td>-0.71 ± 0.07</td>
<td>-0.31 ± 0.13</td>
</tr>
<tr>
<td>a₄</td>
<td>58.80 ± 0.45</td>
<td>60.26 ± 0.52</td>
<td>49.55 ± 0.71</td>
<td>49.61 ± 1.28</td>
</tr>
<tr>
<td>a₅</td>
<td>0.43 ± 0.02</td>
<td>0.69 ± 0.06</td>
<td>0.50 ± 0.01</td>
<td>0.49 ± 0.01</td>
</tr>
<tr>
<td>a₆</td>
<td></td>
<td></td>
<td>-0.09 ± 0.03</td>
<td>-0.25 ± 0.05</td>
</tr>
<tr>
<td>a₇</td>
<td>-0.06 ± 0.00</td>
<td>-0.10 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMSE</td>
<td>6.5</td>
<td>5.8</td>
<td>6.2</td>
<td>6.9</td>
</tr>
<tr>
<td>R²</td>
<td>0.98</td>
<td>0.98</td>
<td>0.92</td>
<td>0.88</td>
</tr>
<tr>
<td>δeY</td>
<td>± 0.2</td>
<td>± 0.3</td>
<td>± 0.2</td>
<td>± 0.2</td>
</tr>
<tr>
<td>δΔeY</td>
<td>± 0.3</td>
<td>± 0.3</td>
<td>± 0.4</td>
<td>± 0.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>TCO₂₁&lt;sup&gt;200&lt;/sup&gt;</th>
<th>TCO₂₀&lt;sup&gt;200&lt;/sup&gt;</th>
<th>TCO₂₁&lt;sup&gt;200&lt;/sup&gt;</th>
<th>TCO₂₀&lt;sup&gt;200&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>451.7 ± 18.1</td>
<td>592.3 ± 25.0</td>
<td>381.8 ± 16.6</td>
<td>244.6 ± 38.5</td>
</tr>
<tr>
<td>a₀</td>
<td>12.77 ± 1.80</td>
<td>8.78 ± 3.14</td>
<td>12.00 ± 0.26</td>
<td>17.29 ± 0.60</td>
</tr>
<tr>
<td>a₁</td>
<td>-1.33 ± 0.63</td>
<td>-3.68 ± 1.06</td>
<td>0.06 ± 0.24</td>
<td>0.52 ± 0.49</td>
</tr>
<tr>
<td>a₂</td>
<td>36.63 ± 1.87</td>
<td>36.62 ± 3.12</td>
<td>38.68 ± 0.38</td>
<td>38.32 ± 0.88</td>
</tr>
<tr>
<td>a₃</td>
<td>0.25 ± 0.04</td>
<td>0.47 ± 0.12</td>
<td>0.40 ± 0.00</td>
<td>0.36 ± 0.10</td>
</tr>
<tr>
<td>a₄</td>
<td>4.14 ± 0.16</td>
<td>2.30 ± 0.24</td>
<td>4.77 ± 0.02</td>
<td>4.85 ± 0.05</td>
</tr>
<tr>
<td>a₅</td>
<td>0.17 ± 0.02</td>
<td>0.40 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMSE</td>
<td>9.1</td>
<td>9.6</td>
<td>5.4</td>
<td>7.1</td>
</tr>
<tr>
<td>R²</td>
<td>0.97</td>
<td>0.97</td>
<td>0.98</td>
<td>0.96</td>
</tr>
<tr>
<td>δeY</td>
<td>± 0.3</td>
<td>± 0.3</td>
<td>± 0.4</td>
<td>± 0.4</td>
</tr>
<tr>
<td>δΔeY</td>
<td>± 0.4</td>
<td>± 0.4</td>
<td>± 0.4</td>
<td>± 0.4</td>
</tr>
</tbody>
</table>

This revised version of the traditional MLR technique was introduced by Friis et al. (2005) where instead of applying the data of time 1 into the MLR derived from data of time 0, the extended MLR would be
\[ \Delta eY = (a_1 - a_0) + (a_{1n} - a_{0n})y^n + (a_{1\text{Lat}} - a_{0\text{Lat}})\text{Lat} + \ldots + (R_1 - R_0) \]  

(4.2)

which would be applied to the newer dataset (time 1). Equation (4.2) assumes that the dependent variables do not change over time. This is not totally true with potential temperature (Levitus et al., 2000; Johnson and Doney, 2006; Ivchenko et al., 2006; Cunningham and Alderson, 2007), salinity (Levitus et al., 2000; Cunningham and Alderson, 2007), oxygen (Keeling and Garcia, 2002; Deutsch et al., 2006) and nutrients (Gruber and Sarmiento, 1997). Therefore, it would be more accurate to subtract eMLR_0 from eMLR_1 without assuming no change in the dependent variables over time, such that

\[ \Delta eY = a_1 - a_0 + a_{1n}y_1^n - a_{0n}y_0^n + a_{1\text{Lat}} - a_{0\text{Lat}} + \ldots + R_1 - R_0 \]  

(4.3)

In this case, the gridded independent variables are used in lieu of the real values.

The eMLR residuals of eTCO_2^{>200} show a scatter in the mixed layer, above 200 db (Figure 4.3), which indicates that TCO_2 is affected by seasonal variations at the surface from both physical and biological processes. Because of that, the root mean square error (RMSE) of the eTCO_2^{<200} fits are large and greater than 9 \( \mu \text{mol kg}^{-1} \) (Table 4.5). On the contrary, the RMSE of the eTA^{<200} fits are reasonable and equal to the eTA^{>200} fits (Table 4.5) and the residuals are constant in the whole water column (Figure 4.2).
Figure 4.2 Residuals of the MLR $TA_1$ for the 2003-2005 data (a) and $TA_0$ for the 1989-1993 data (b).
Figure 4.3 Residuals of the MLR TCO$_{2-1}$ for the 2003-2005 data (a) and TCO$_{2-0}$ for the 1989-1993 data (b).

The precision of the eMLRs, $\delta Y$ are estimated by using each independent variable measurement error $\delta X_i$ ($\delta X_i^n = 0.0002$ kg m$^{-3}$, $\delta$Lat = 0.02 deg, $\delta$P = 0.05 db, $\delta$θ = 0.005 °C, $\delta$S = 0.001, $\delta$Si = 0.4 $\mu$mol kg$^{-1}$, $\delta$NO$_3$ = 0.08 $\mu$mol kg$^{-1}$ and $\delta$AOU = 0.2 $\mu$mol kg$^{-1}$) in the general error propagation formula for a linear function.
\[
\delta^2 eY = a^2_{i,n} \delta^2 \gamma^n_i + a^2_{i,\text{Lat}} \delta^2 \text{Lat} + a^2_{i,p} \delta^2 P + a^2_{i,\theta} \delta^2 \theta + a^2_{i,S} \delta^2 S \\
+ a^2_{iSi} \delta^2 \text{Si} + a^2_{i\text{NO}_3} \delta^2 \text{NO}_3^- + a^2_{i\text{AOU}} \delta^2 \text{AOU}
\]  

(4.4)

The results of the MLRs are given in Table 4.5 with different combinations of dependent variables along with the RMSE, the coefficient of determination, \(R^2\), the predicted accuracy of the MLR, \(\delta eY\), and the predicted accuracy of the extended MLR, \(\delta \Delta eY\). Assuming the variable measurement errors are the same at time 1 and 0, the predicted accuracy of the MLR difference, \(\delta \Delta eY = \delta (eY_1 - eY_0)\), is given by

\[
\delta^2 eY = (a^2_{1,n} + a^2_{0,n}) \delta^2 \gamma^n_1 + (a^2_{1,\text{Lat}} + a^2_{0,\text{Lat}}) \delta^2 \text{Lat} + (a^2_{1,p} + a^2_{0,p}) \delta^2 P \\
+ (a^2_{1,\theta} + a^2_{0,\theta}) \delta^2 \theta + (a^2_{1S} + a^2_{0S}) \delta^2 S + (a^2_{1Si} + a^2_{0Si}) \delta^2 \text{Si} \\
+ (a^2_{1\text{NO}_3} + a^2_{0\text{NO}_3}) \delta^2 \text{NO}_3^- + (a^2_{1\text{AOU}} + a^2_{0\text{AOU}}) \delta^2 \text{AOU}
\]  

(4.5)

which is also equivalent to

\[
\delta^2 \Delta eY = \delta^2 eY_1 + \delta^2 eY_0
\]  

(4.6)

The expected predicted accuracies for TA and TCO\(_2\) and their changes range from \(\pm 0.2\) to \(\pm 0.4\) \(\mu\text{mol kg}^{-1}\) (Table 4.5). These predicted accuracies are smaller than those reported in other articles (McNeil et al., 2001; Friis et al., 2005; Levine et al., 2008) where TA, which has the highest measurement errors amongst the other independent parameter (\(\sim \pm 4\) \(\mu\text{mol kg}^{-1}\)), was used in the regressions.
4.2.3 Quantification of the biological CO\textsubscript{2}, CO\textsubscript{2}\textsuperscript{bio} 

The decomposition of organic matter and the dissolution of CaCO\textsubscript{3} result in the production of CO\textsubscript{2}. The concentration of CO\textsubscript{2} due to these processes, CO\textsubscript{2}\textsuperscript{bio}, can be calculated as a function of AOU and total alkalinity following the equation of Chen and Millero (1979):

\[
CO\textsubscript{2}\textsuperscript{bio} = 0.83 \text{ AOU} + 0.5 \Delta \text{NTA}^o
\]

(4.7)

where \(\Delta \text{NTA}^o\) represents the difference between the measured normalized total alkalinity (TA*35/S) at any depth and the value at the surface and is assumed not be a function of changes in the anthropogenic CO\textsubscript{2}.

The precision for CO\textsubscript{2}\textsuperscript{bio} can be estimated using the error propagation of a non linear equation and is

\[
\delta^2 \text{CO}_{2}\textsuperscript{bio} = \left[ \frac{\partial \text{CO}_{2}\textsuperscript{bio}}{\partial \text{AOU}} \delta \text{AOU} \right]^2 + \left[ \frac{\partial \text{CO}_{2}\textsuperscript{bio}}{\partial \Delta \text{NTA}^o} \delta \Delta \text{NTA}^o \right]^2
\]

(4.8)

The error associated with \(\Delta \text{NTA}^o\) is
\[ \delta^2 \Delta NTA^o = \delta^2 NTA_{surf} + \delta^2 NTA_{depth} \] (4.9)

or equivalent to

\[ \delta^2 \Delta NTA^o = 2 \delta^2 NTA \] (4.10)

\[ \delta^2 NTA = \left[ \frac{\partial NTA}{\partial TA} \right]^2 + \left[ \frac{\partial NTA}{\partial S} \right]^2 \delta S \] (4.11)

\[ \delta^2 NTA = \left[ \frac{35}{S} \delta TA \right]^2 + \left[ \frac{35 \ TA}{S^2} \delta S \right]^2 \] (4.12)

Therefore, Equation (4.8) becomes

\[ \delta^2 CO_{2}^{\text{bio}} = \{0.83 \ \delta AOU\}^2 + \{0.5\}^2 4 \left( \left[ \frac{35}{S} \ \delta TA \right]^2 + \left[ \frac{35 \ TA}{S^2} \ \delta S \right]^2 \right)^2 \] (4.13)
and $\delta^2 \text{CO}_2^{\text{bio}}$ is a function of $S$ and $\text{TA}$. Based on the error estimates, $\delta \text{AOU} = 0.2 \mu\text{mol kg}^{-1}$, $\delta \text{TA} = 2 \mu\text{mol kg}^{-1}$ at time 1, $\delta \text{TA} = 4 \mu\text{mol kg}^{-1}$ at time 0 and $\delta S = 0.001$, one can approximate some terms in Equation (4.13). The term $\left(0.83 \delta \text{AOU}\right)^2$ becomes negligible with a value of $0.03 \mu\text{mol kg}^{-1}$. Based on the salinity and TA ranges, and $\delta S$, the term $\left[\frac{35 \text{TA}}{S^2} \delta S\right]^2$ also becomes negligible with a mean value of $0.04 \mu\text{mol kg}^{-1}$.

Finally, based on the salinity range, the term $\frac{35}{S} \approx 1 \mu\text{mol kg}^{-1}$. Hence the estimated error of $\text{CO}_2^{\text{bio}}$ becomes

$$\delta^2 \text{CO}_2^{\text{bio}} \approx 0.5^2 \times 4 \times \delta^4 \text{TA} \tag{4.14}$$

which is equivalent to

$$\delta \text{CO}_2^{\text{bio}} \approx \delta \text{TA} \tag{4.15}$$

This final equation shows that the error in calculating $\text{CO}_2^{\text{bio}}$ is very sensitive to error in the TA measurements. At time 1, i.e in the early 2000s, $\delta \text{CO}_2^{\text{bio}} \approx 4 \mu\text{mol kg}^{-1}$, whereas at
time 0, i.e. in the 1990s, $\delta\text{CO}_2^{\text{bio}} \approx 16 \mu\text{mol kg}^{-1}$. The estimated error of the difference in biological CO$_2$ would be around 16 $\mu\text{mol kg}^{-1}$.

### 4.2.4 Quantification of anthropogenic CO$_2$, CO$_2^{\text{anth}}$

Touratier and Goyet (2004a) developed a new method to estimate the anthropogenic CO$_2$ in the ocean by introducing the new tracer TrOCA expressed by

\[
\text{TrOCA}_{2004} = O_2 + \frac{165}{131.5} (\text{TCO}_2 - 0.5\text{TA}) \tag{4.16}
\]

\[
\text{TrOCA}_{2004} = O_2 + 1.2\text{TCO}_2 - 0.6\text{TA} \tag{4.17}
\]

The stochiometric coefficients in Equation (4.16) taken from the values of $O_2$ and TCO$_2$ for phosphate are taken from Körtinzger et al. (2001). The tracer TrOCA appears to be conservative in intermediate, deep and bottom waters, but neither in surface waters nor the entire water column of the Greenland and Norwegian seas. A property is considered conservative in a mixture of water masses when its value remains on a straight mixing line. Any deviation from the conservative line indicates a local transformation (e.g. chemical or biological processes) or an interaction with the surrounding environment (e.g. atmosphere or sediments). Thus, the TrOCA tracer is only conservative in anthropogenic CO$_2$ free waters and is referred to as TrOCA$^o$.
To calculate $\text{TrOCA}^°$, the authors use data for $\text{TCO}_2$, $\text{TA}$ and $\text{O}_2$ sampled and measured in the bottom South Atlantic Ocean waters characterized by $\delta \theta \leq 2.5 \, ^\circ \text{C}$ and located between latitudes 20°S and 40°S (Touratier and Goyet, 2004a). Since the increase of atmospheric $\text{CO}_2$ has no effect on the total alkalinity (Chen and Millero, 1979; Goyet et al., 1999) and human activities are believed to have little effect on the large-scale distribution of oxygen in the anthropogenic free waters, $\text{TA}$ and $\text{O}_2$ are assumed to be equal to $\text{TA}^°$ and $\text{O}_2^°$, respectively (Touratier and Goyet, 2004a). The authors applied this method in the Atlantic Ocean where they used data sampled after 1989 and fitted $\text{TrOCA}^°$ and $\theta$ to an exponential equation

$$\text{TrOCA}_{2004}^° = (1505.04 \pm 0.46) e^{(\theta/89.04 \pm 1.50)}$$

(4.19)

From Equation (4.19), $\text{TrOCA}_{2004}^°$ can be calculated for the whole basin using the appropriate potential temperature, $\theta$. The anthropogenic $\text{CO}_2$, $\text{CO}^{\text{anth}}_2$, can be estimated from

$$C_{\text{TrOCA}}^{\text{TrOCA}} = \text{TCO}_2 - \text{TCO}_2^° = \frac{\text{TrOCA} - \text{TrOCA}^°}{1.2}$$

(4.20)
More recently (Touratier et al., 2007), the TrOCA° tracer has been updated to the following form

$$\text{TrOCA}_{2007}^\circ = e^{(b-\theta d/TA^2)}$$  \hspace{1cm} (4.21)

TrOCA$_{2007}^\circ$ has been determined in two steps. In the first step, older waters have been selected where $\Delta^{14}$C is lower than $-175\%$ corresponding to a water age of $\sim$1400 years (Key, 1991; Matsumoto and Key, 2004; Butzin et al., 2005). These old waters, consequently free of anthropogenic CO$_2$, are in the 1000-2000 db pressure range in the Pacific Ocean and in the deep waters of the Indian Ocean (http://cdiac.esd.orl.gov/oceans/glodap/GlopDV.htm). The $\theta$, TCO$_2$ and TA properties associated to these waters were used to compute TrOCA as in Equation (4.17). The second step consisted of calculating the anthropogenic CO$_2$ when pCFC$_{11}$ values were maximum in the atmosphere, hence in the surface waters of the ocean. The pCFC$_{11}$ peak was during the years 1992-1995 (Touratier et al., 2007). The anthropogenic CO$_2$ was calculated by subtracting the computed TCO$_2$ values of the pre-industrial period from the period 1992-1995. Finally, TrOCA$_{2007}^\circ$ obtained in Equation (4.21) was derived by rearranging Equation (4.12) and using the TrOCA values calculated in the first step and the anthropogenic CO$_2$ calculated from the second step. The anthropogenic CO$_2$ signal derived from the 2007 updated version of the TrOCA method is therefore
\[
C_{\text{TrOCA}2007} = \frac{O_2 + f(TCO_2 - 0.5TA) - e(b - c - d/TA^2)}{1.279}
\] (4.22)

with the optimal set of parameters

\[
\begin{aligned}
b &= 7.511 \pm 5.2 \times 10^{-3} \\
c &= -1.087 \times 10^{-2} \pm 2.5 \times 10^{-5} \\
d &= -7.81 \times 10^5 \pm 2.9 \times 10^4 \\
f &= 1.279 \pm 7.3 \times 10^{-3}
\end{aligned}
\] (4.23)

The accuracy of \(C_{\text{TrOCA}2007}\) is \(\pm 6.25 \mu\text{mol kg}^{-1}\), which is almost two times less accurate than \(C_{\text{TrOCA}2004}\) at \(\pm 3.57 \mu\text{mol kg}^{-1}\) (Touratier and Goyet, 2004b). Touratier et al. (2007) show a thorough error propagation of the method and demonstrate that the most sensitive parameter ‘f’ generates an uncertainty in \(C_{\text{TrOCA}2007}\) of 3.31 \(\mu\text{mol kg}^{-1}\).

### 4.2.5 Quantification of mixing \(CO_2, CO_2^{\text{mix}}\)

Although sections 4.2.3 and 4.2.4 gave a detailed calculation of the biological and anthropogenic \(CO_2\), respectively, mixing \(CO_2\) is calculated using the conservation of mass. Assuming that \(TCO_2\) is the sum of all the forms of \(CO_2\) with

\[
TCO_2 = CO_2^{\text{anth}} + CO_2^{\text{bio}} + CO_2^{\text{mix}}
\] (4.24)
\[ \text{CO}_{2}^{\text{mix}} = \text{TCO}_2 - \text{CO}_2^{\text{anth}} - \text{CO}_2^{\text{bio}} \]  

(4.25)

Because all the CO\(_2\) forms are independent from each other, one can assume that Equation (4.25) is linear. Therefore, the error in CO\(_2^{\text{mix}}\) can be estimated by applying the error propagation to a linear function such that

\[ \delta^2 \text{CO}_2^{\text{mix}} = \delta^2 \text{TCO}_2 + \delta^2 \text{CO}_2^{\text{anth}} + \delta^2 \text{CO}_2^{\text{bio}} \]  

(4.26)

At time 1, i.e. in the early 2000s, the \(\delta \text{CO}_2^{\text{mix}}\) is 4.5 \(\mu\)mol kg\(^{-1}\) using \(\delta \text{C}^{\text{TROCA}}_{2004}\) but is 6.8 \(\mu\)mol kg\(^{-1}\) using \(\delta \text{C}^{\text{TROCA}}_{2007}\). Similarly, at time 0, i.e. in the 1990s, the \(\delta \text{CO}_2\) is 5.6 \(\mu\)mol kg\(^{-1}\) using \(\delta \text{C}^{\text{TROCA}}_{2004}\) but is 7.6 \(\mu\)mol kg\(^{-1}\) using \(\delta \text{C}^{\text{TROCA}}_{2007}\). The estimated error of the difference in \(\text{CO}_2^{\text{mix}}\) becomes 7.2 and 10.2 \(\mu\)mol kg\(^{-1}\) using \(\delta \text{C}^{\text{TROCA}}_{2004}\) but is 7.6 \(\mu\)mol kg\(^{-1}\) using \(\delta \text{C}^{\text{TROCA}}_{2007}\), respectively.

### 4.2.6 Saturation state of seawater with respect to calcium carbonate

The saturation state (\(\Omega\)) of seawater with respect to calcium carbonate is determined from

\[ \Omega = [\text{Ca}^{2+}][\text{CO}_3^{2-}] / K^*_{sp} \]  

(4.27)
where $K_{sp}^*$ is the solubility product at \textit{in situ} conditions of aragonite or calcite determined at one atmosphere by Mucci (1983). The measurements of Ingle (1975) were used to estimate the effect of pressure on the solubility product. The concentrations of calcium were estimated from Culkin and Cox (1966)

$$[\text{Ca}^{2+}] = 2.934 \times 10^{-4} \text{S}$$

(4.28)

and the concentrations of \([\text{CO}_3^{2-}]\) given in \(\mu\text{mol kg}^{-1}\) are determined from measured values of TA and TCO$_2$ using the carbonic acid dissociation constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987). Supersaturated surface waters have $\Omega > 1$ and undersaturated deep waters have $\Omega < 1$. The probable errors estimated for $\Omega$ are $\pm 0.07$ in $\Omega_{\text{ara}}$ at 2500 db and $\pm 0.11$ in $\Omega_{\text{cal}}$ at 4500 db (Chung et al., 2003). This is equivalent to $\pm 300$ db for $\Omega_{\text{ara}} = 1$ at 2500 db and $\pm 470$ db for $\Omega_{\text{cal}} = 1$ at 4500 db.

### 4.3 Results and discussion

The results have been examined in the mixed layer (0 – 200 db, except for the changes in TCO$_2$ determined by eMLR and anthropogenic CO$_2$ determined by the TrOCA methods) and the deep waters (200 – 7000 db). The changes in the CO$_2$ were determined from gridded data. Since the stations were not sampled at the same longitude,
the distance between stations were first calculated. The grids were 20 db by 25 km for the top 200 db, and 50 db by 25 km below 200 db. All graphs were produced with the distance between stations on the x-axis, but the corresponding latitude was also reported for a better visual interpretation of the data. Depending on the month of the year the scientific cruise took place, the differences on the A16 line will show a seasonal change in the top 1000 db of the water column between the Equator and 30°S. The results in the deeper waters represent decadal changes. All of the changes are shown in Figure 4.4 to Figure 4.15 and are discussed in the next section. The changes in the gridded measurements are denoted as $\Delta Y$ and the results from the eMLR equations are denoted as $\Delta eY$, which are calculated using Equation (4.3) instead of Equation (4.2) as in Friis et al. (2005).

4.3.1 Changes in the four carbonate parameters

The values of $\Delta$NTA (measured) and $\Delta$eNTA are shown in Figure 4.4. In surface waters, the changes in salinity due to evaporation or input of fresh water contributes to changes in TA (Millero et al., 1998; Lee et al., 2000). The TA can decrease if CaCO$_3$ shells are formed in surface waters. In deep waters (below 1000 db) where salinity does not vary as at the surface, TA increases when CaCO$_3$ dissolves (Chen 1978). The normalized TA ($NTA = TA \times 35/S$) removes much of the seasonal differences in the mixed layer. Within experimental error or within 95% confidence interval ($2 \times \pm 3$
$\mu$mol kg$^{-1}$ for the measured TA and $2 \times \pm 6.5$ $\mu$mol kg$^{-1}$ for the eMLR) the NTA of Atlantic waters show no apparent seasonal or decadal change.

The values of $\Delta$TCO$_2$ (measured) and $\Delta$eTCO$_2$ (calculated from Table 4.5) are shown in Figure 4.5. The changes in the TCO$_2$ system (and pCO$_2$) in deep waters are due to changes in the oxidation of organic carbon over time. In surface waters, the changes in TCO$_2$ are due to losses during photosynthesis and increases due to changes in the oxidation of organic matter. The measured surface values of TCO$_2$ increased by 20 $\mu$mol kg$^{-1}$ in the tropics and gyres, but decreased by 20 $\mu$mol kg$^{-1}$ in the equatorial waters. The changes given for eTCO$_2$ are the same in the gyres and in the tropical waters. These changes could be attributed to changes in seasonality (summer 2005 compared to winter 1991) for the South Atlantic (between the Equator and 30°S) or higher productivity along the whole transect in these waters in 2003 and 2005 compared to 1989, 1991 and 1993.

The changes in pCO$_2$ and pH shown in Figure 4.6 are determined from calculated $in situ$ conditions and values of TA and TCO$_2$, since pH measurements were limited on the 2003 and 2005 cruises and nonexistent on the earlier cruises. Overall, $\Delta$pCO$_2$ shows an increase of about 25 $\mu$atm. Exceptions are observed in the AAIW ($27.1 < \gamma^0 < 27.5$ kg m$^{-3}$) and the surface of the subtropical South Atlantic Ocean with $\Delta$pCO$_2 \approx 75$ $\mu$atm. The subsurface waters around the Equator also display interesting features.
Figure 4.4 Changes between the early 2000s and 1990s of measured NTA (a) and eNTA (b). Values are given in \( \mu \text{mol kg}^{-1} \). From bottom to surface, the black contours represent neutral density surfaces \( \gamma^n \) at 28.0, 27.5, 27.1, 26.5, 25.5, 24.5 and 23.5 kg m\(^{-3}\).
Figure 4.5 Changes between the early 2000s and 1990s of measured TCO$_2$(a) and eTCO$_2$ (b). Values are given in $\mu$mol kg$^{-1}$. From bottom to surface, the black contours represent neutral density surfaces $\gamma^n$ at 28.0, 27.5, 27.1, 26.5, 25.5, 24.5 and 23.5 kg m$^{-3}$.

The center part of the figure shows a decrease in pCO$_2$ of ~ 100 $\mu$atm and is limited by + 75 $\mu$atm in the south and + 150 $\mu$atm in the north. The increase in pCO$_2$ in surface waters can be caused by oxidation of organic matter, by dissolution of CaCO$_3$ and by increases
in CO$_2$ in the atmosphere from fossil fuel burning. On the contrary, decrease in pCO$_2$ in surface waters can be caused by photosynthesis, by formation of CaCO$_3$ and by solar heating. Once below the mixed layer, pCO$_2$ is more likely to increase by oxidation of organic material and/or by formation of CaCO$_3$. The changes in pH displayed in Figure 4.6 are a mirror image of ΔpCO$_2$. The decrease in pH or ocean acidification has a negative impact on calcifying organisms such as pteropods and reefs (Riebesell et al., 2000; Orr et al., 2005; Kleypas et al., 2006) by changing the carbonate composition of seawater. Dissolved CO$_2^{\text{anth}}$ in the ocean has reduced the pH by approximately 0.1 units since the industrial era began (Haugan and Drange, 1996) and is predicted to further drop by 0.3 to 0.4 units by 2100 (Houghton et al., 2001; Orr et al., 2005). Results from this study show that pH increased by 0.05 units at the surface around the Equator where primary productivity has more likely increased, but pH has decreased by around 0.05 units in the upper and intermediate Atlantic Ocean. It also has decreased to a maximum of 0.12 units in the tropical mode waters (Figure 4.6). This decrease in pH is also characteristic of upwelling waters. The observed decrease in pH could have different sources. One source could be the dissolution of CO$_2^{\text{anth}}$; another source could be the increase in TCO$_2$ due to the oxidation of organic material; and finally, mixing of water bodies could also cause a decrease in pH. One consequence of these changes in pH is the alteration of the carbonate composition of seawater.
Figure 4.6 Changes between the early 2000s and 1990s of *in situ* $pCO_2$ (a) in µatm and *in situ* pH (b) on the seawater scale. From bottom to surface, the black contours represent neutral density surfaces $\gamma^0$ at 28.0, 27.5, 27.1, 26.5, 25.5, 24.5 and 23.5.
4.3.2 Changes in biological activity

The changes in AOU are shown in Figure 4.7a. Below 200 db, AOU has increased by 20 \( \mu \text{mol kg}^{-1} \) in intermediate and deep waters \((27.1 < \theta_n < 28.0)\). At the surface, above 200 db, AOU has decreased to a maximum of 20 \( \mu \text{mol kg}^{-1} \) except in the North Atlantic gyre and the surface north of 40 \(^\circ\)S \(+20 \ \mu \text{mol kg}^{-1}\). The surface tropical waters display the highest increase of AOU (~70 \( \mu \text{mol kg}^{-1} \)) whereas the north equatorial waters \((5-10 \ ^{\circ} \text{N})\) show the lowest decrease in AOU (~40 \( \mu \text{mol kg}^{-1} \)).

The changes in CO\(_2\)\(^{\text{bio}}\) are shown in Figure 4.7b and reveal the same trend as AOU with a higher concentration in the surface waters around the Equator except between 5-10 \(^\circ\)N. The gyres indicate a decrease of biological CO\(_2\) suggesting that the increase observed for TCO\(_2\) is from another source, anthropogenic or mixing. The A16S 1991 cruise was in July-August, which is the boreal summer, while A16S 2005 was in February, which is the boreal winter (Figure 4.1). In the thermocline of the inter-tropical waters, TCO\(_2\) and AOU increased by 20 and 30 \( \mu \text{mol kg}^{-1} \) respectively, while pH decreased by 0.15 units. These changes can be attributed to an increase in the oxidation of plant material falling from the surface or from the remineralized CO\(_2\) from up-welled water. The changes in TCO\(_2\) are also related to changes in water temperature resulting from solar radiation. Although CO\(_2\) is less soluble in warmer water, the biological activity appears to produce more CO\(_2\). Antoine et al. (2005) shows a decadal increase of ~22% in chlorophyll at the surface of the intertropical regions of the Atlantic Ocean by analyzing the ocean color.
time series (1979-2002) retrieved from two satellite sensors: the Coastal Zone Color Scanner (CZCS) and the Sea-viewing Wide Field-of-view Sensor (SeaWiFS). The major chlorophyll increases are located off Europe, around the Equator (10 °S – 10 °N) and at the subtropical convergence (40 °S). The major chlorophyll decreases are located in the Sargasso Sea, the South Atlantic gyre, and above the Equator (10 °N). The relative difference between the average CZCS (1979-1983) and SeaWiFS (1998-2003) chlorophyll concentration showed decadal increases, but more importantly, an increase in the significant seasonal peaks in the equatorial and tropical regions. These are the same areas where strong seasonal changes in TCO$_2$, pH, pCO$_2$, and AOU were observed.
Figure 4.7 Changes between the early 2000s and 1990s of measured (a) AOU and (b) biological CO₂ calculated using Equation (4.7). Values are given in µmol kg⁻¹. From bottom to surface, the black contours represent neutral density surfaces $\gamma^n$ at 28.0, 27.5, 27.1, 26.5, 25.5, 24.5 and 23.5 kg m⁻³.
4.3.3 Anthropogenic CO$_2$, CO$_{anth}$

4.3.3.1 Comparison between the 2004 and 2007 TrOCA methods

The anthropogenic CO$_2$ signal (Figure 4.8) was calculated using the 2003 (A16N) and 2005 (A16S) data and the 2004 and 2007 TrOCA methods. Concentrations range from 5 to 60+ $\mu$mol kg$^{-1}$ depending on the TrOCA method used. Overall, the 2007 TrOCA method yields a higher signal.

Since no comparison has been made between the two TrOCA versions for the Atlantic Ocean data (1980s and 1990s), the following compares the anthropogenic CO$_2$ calculated using the TrOCA methods of 2004 and 2007, C$_{\text{TrOCA}}^{\text{2004}}$ and C$_{\text{TrOCA}}^{\text{2007}}$ respectively, for the A16 line (Figure 4.9). The difference in the methods would only be significant outside the 95% confidence interval or above $2 \times 7.2$ $\mu$mol kg$^{-1}$, which is estimated by quadratic error addition of the C$_{\text{TrOCA}}^{\text{2004}}$ and C$_{\text{TrOCA}}^{\text{2007}}$ errors. Above 200 db, the TrOCA methods of 2004 and 2007 are not conservative and should not be applied (Touratier and Goyet, 2004a). A property is considered conservative in a mixture of water masses when its value remains on a straight mixing line. Any deviation from the conservative line indicates a local transformation (e.g. chemical or biological processes) or an interaction with the surrounding environment (e.g. atmosphere or sediments). Between 200 and 3000 db, the average difference decreases from 20 $\mu$mol kg$^{-1}$ to around 10 $\mu$mol kg$^{-1}$ meaning the 2007 TrOCA version gives higher values than the original one. The
calculated \( \text{CTrOCA}_{2004} \) values of this study are in good agreement with those of Gruber et al. (1998), Lee et al. (2003) and Touratier and Goyet (2004b) but these values were proven to be overestimated in relatively young waters and underestimated in older waters (Hall et al., 2004; Matsumoto and Gruber, 2005). Figure 4.10 is a contour plot of the difference in the calculated anthropogenic CO\(_2\) and shows that the difference is significant in the Labrador Sea Water (LSW) and in the gyres above 1200 db. Therefore, because \( \text{CTrOCA}_{2004} \) values are biased in relatively young waters, the bias in \( \text{CTrOCA}_{2007} \) would be stronger. Below 3000 db these two oceans are anthropogenic-CO\(_2\) free showing a non-significant average difference of 5 \( \mu \)mol kg\(^{-1}\) in the deep and bottom waters even though waters with very low or zero CFC signal still contain a significant amount of anthropogenic CO\(_2\) (Körtzinger et al., 1999; Wallace, 2001; Matsumoto and Gruber, 2005; Tanhua et al., 2006).
Figure 4.8 Anthropogenic CO$_2$ concentration calculated with the 2004 (a) and 2007 (b) TrOCA methods and below 200 db. The 2003 and 2005 datasets of A16N and A16S, respectively were used for the calculation. Areas in white have values less than 5 µmol kg$^{-1}$. Black contours are the neutral density surfaces, $\gamma^N$. 
Figure 4.9 Difference of anthropogenic CO$_2$ concentration, in $\mu$mol kg$^{-1}$, calculated as $C_{\text{TrOCA}}^{2007}$ minus $C_{\text{TrOCA}}^{2004}$. CO$_2$ differences are considered significant if greater than 15 $\mu$mol kg$^{-1}$. The data collected during the 2003 and 2005 A16 cruise were used for the computation of anthropogenic CO$_2$. 
Figure 4.10 Section of the difference in $\mu$mol kg$^{-1}$ between the anthropogenic CO$_2$, calculated as $C^{\text{TrOCA}}_{\text{2007}}$ minus $C^{\text{TrOCA}}_{\text{2004}}$. CO$_2$ differences are considered significant if greater than 15 $\mu$mol kg$^{-1}$. The data used are those from the A16N (2003) and A16S (2005) cruises. Overlays are the neutral density surfaces, $\gamma^p$. 
4.3.3.2 *Column inventory of the change in anthropogenic CO₂*

In this section \( \Delta C_{\text{TrOCA}2004} \) is defined as the changes of anthropogenic CO₂ calculated using the 2004 TrOCA method at time 1 (2003-2005) minus that at time 0 (1989, 1991 and 1993). Similarly, \( \Delta C_{\text{TrOCA}2007} \) is defined as the anthropogenic CO₂ calculated using the 2007 TrOCA method at time 1 − time 0. The changes in anthropogenic CO₂ are shown for one of the methods, \( \Delta C_{\text{TrOCA}2004} \), in Figure 4.11. This shows an increase of about 5 to 10 \( \mu \text{mol kg}^{-1} \) above the thermocline and the LSW. The results show a negative change in anthropogenic CO₂ in the upwelling water masses, around the Equator. This implies that the anthropogenic CO₂ signal at time 0 (1989, 1991 and 1993) was higher than that at time 1 (2003 and 2005). It could also mean that more water has up-welled during the period 1989-2005. This suggests that the increase in TCO₂ observed around the Equator is due to both the oxidation of organic material and to the water up-welled off the coast of West Africa. This is confirmed by the increase of AOU observed in this region as discussed in the previous section (Figure 4.7).

The increase of CO₂\text{anth} around 2500 db in the LSW was more likely due to mixing. The LSW has been shown to have deepened and thickened in this region (Johnson et al., 2005). The LSW originates in the Labrador Sea and travels east crossing the Atlantic ridge (Talley and McCartney, 1982; Schmitz and McCartney, 1993; Rhein et al., 2002). By becoming significantly cooler, denser, deeper and thicker (Levitus et al., 2000; Yashayaev et al., 2004; Johnson et al., 2005), the Labrador Sea is a location where CO₂\text{anth} dissolves, sinks and circulates along the isopycnals.
Figure 4.11 Change of anthropogenic CO$_2$ concentration calculated with the C$_{2004}^{\text{TROCA}}$ method over the period 1989-2005 in the South Atlantic and 1993-2003 in the North Atlantic. Values are given in µmol kg$^{-1}$ and black contours are the neutral density surfaces, $\gamma^\rho$.

The column inventory of the change in anthropogenic CO$_2$ calculated from $\Delta C_{2004}^{\text{TROCA}}$ and $\Delta C_{2007}^{\text{TROCA}}$ was calculated for this A16 transect (Figure 4.12). The column inventory values of $\Delta C_{2007}^{\text{TROCA}}$ yield about twice that of $\Delta C_{2004}^{\text{TROCA}}$. Quay et al. (2003) reported an anthropogenic CO$_2$ accumulation rate of $0.63 \pm 0.16$ mol C m$^{-2}$ yr$^{-1}$ in the North Atlantic over the 22 year period 1981-2003. Therefore, for the shorter time period
data set 1993-2003 A16N, the anthropogenic CO₂ column inventory maximum change could lie between 0.47 and 0.79 mol C m⁻² yr⁻¹ based on the above Quay et al. (2003) accumulation rate. This updated range bounds the values of ΔCₐᵣ₀₀₄ (0.5 mol C m⁻² yr⁻¹) but not those of ΔCₐᵣ₀₀₇ (1.0 mol C m⁻² yr⁻¹). In the Pacific Ocean, Sabine et al. (2008) also reported a rate of 0.75 mol C m⁻² yr⁻¹ in the South Pacific and 0.35 mol C m⁻² yr⁻¹ in the North Pacific. Once more, the 2004 TrOCA method yields more reasonable values than the 2007 one.

TCO₂ is a combination of different forms of CO₂: biological, anthropogenic and mixing. To understand the form of CO₂ that has contributed to the change in TCO₂ in the different waters over the period 1989-2005, the column inventory change of all the CO₂ forms was estimated and plotted as a function of latitude. Since TrOCA is conservative only below 200 db, the column inventory of the changes in the different forms of CO₂ was calculated for data below 200 db (Figure 4.13). The CO₂ concentration due to mixing was estimated by subtracting the biological and anthropogenic sources from the total measured CO₂. This graph indicates a contribution to the total change in TCO₂ due to mixing of water masses south of the South Atlantic gyre, mainly in the AAIW (26.5 < γⁿ < 27.5 kg m⁻³). It also indicates a similar scenario in the NADW. In the South Atlantic gyre, although 0.16 mol C m⁻² of anthropogenic CO₂ has been added to the water column, the biological and mixing CO₂ decrease (0.2 mol C m⁻² yr⁻¹) resulted in an overall decrease of TCO₂. In the tropics, the process of biological CO₂ change was largely predominant with a rate of ~0.6 mol C m⁻² yr⁻¹. In the North Atlantic gyre, the
increase of TCO$_2$ was due to anthropogenic CO$_2$ (0.05 mol C m$^{-2}$ yr$^{-1}$). The increase of TCO$_2$ in the NADW was revealed to be largely sourced from both anthropogenic and mixing processes.

Figure 4.12 Column inventory of the change in anthropogenic CO$_2$ concentrations (2003/05 – 1989/91/93), $\Delta C^{\text{TROCA}}_{2007}$ (solid line) and $\Delta C^{\text{TROCA}}_{2004}$ (dotted line), below 200 db and in the Atlantic Ocean.
Figure 4.13 Column inventory of the changes in mol C m$^{-2}$ yr$^{-1}$ of TCO$_2$ (black), CO$_2$$^{\text{anth}}$ (red), CO$_2$$^{\text{bio}}$ (green) and CO$_2$$^{\text{mix}}$ (blue) over the period 1989-2005 and in the Atlantic Ocean.

4.3.4 Changes in the aragonite and calcite saturation state horizon

The aragonite and calcite saturation states were calculated according to Equation (4.27) for the four CO$_2$ forms (total, anthropogenic, biological, and mixing) using the program CO2SYS. TA and in situ conditions of salinity, temperature and pressure were also input. This was undertaken to estimate the changes in the aragonite and calcite saturation state due to anthropogenic, biological or mixing sources. The results are
represented in Figure 4.14 for aragonite and Figure 4.15 for calcite. Each plot has overlays of $\Omega_1 = 1$ in the bottom waters and $\Omega_3 = 3$ in the surface waters, which are indicated by solid lines for the 1989-1993 data set and dotted lines for the 2003-2005 data sets. The calcite saturation horizon ($\Omega_{\text{cal}} = 1$) lies at 3000 db at 50°S and gradually deepens between 4500 and 5000 db at 45°N. There is no significant change in the calcite 100% and 300% saturation depths.

The results show that the area of water having an aragonite saturation degree greater than 3 usually occurs at the surface. The results also show that the aragonite saturation degree has decreased, particularly in the North Atlantic, which is known to be more productive than the South Atlantic. Shallower mixed layer depth could have caused this change as shown in the change in aragonite saturation state due to $\text{CO}_2^{\text{mix}}$ in Figure 4.15d. The southern cruises, which took place in winter (1989-1991) and summer (2005), revealed a shoaling of $\Omega_{\text{cal}} = 3$, south of 40°S due to ventilation.

The aragonite 100% saturation horizon lies at around 2600 db from 60°N to 35°S and at around 1000 db in the South Atlantic from 35°S to 60°S. Near the Equator, aragonite saturated mode waters are surrounded by undersaturated waters between 500 and 1000 db and between 20°S and 20°N. The characteristics of these mode waters were previously reported by Chung et al. (2004) where they suggested that the mixing of AAIW and North Atlantic Counter Current Water (NACCW) was not the cause of the formation of isolated layers of aragonite undersaturated water. Chung et al. (2004) attributed the formation of this pocket in the eastern side of the Atlantic, and off the west coast of Africa, to be characterized by upwelling of undersaturated waters moving
towards the west. Moreover, in this region, the change in AOU also shows biological processes that are the main reason why seawater is undersaturated with aragonite (Chung et al., 2004). Because this region is a zone of upwelling, CO$_2^{\text{anth}}$ cannot be the main reason why aragonite is undersaturated here.

The aragonite 100 % horizon $\Omega_1$ has shoaled by approximately 260 – 330 db north of 40 °N. In contrast, Chung, et al. (2003) did not see any changes in the North Atlantic when comparing the 1993 A16N data to pre-industrial values. Both mixing and anthropogenic CO$_2$ have actually caused the shoaling of aragonite saturation depth in the NADW and LSW. Indeed, Johnson et al. (2005) showed that the LSW has deepened, thickened, and cooled. Although temperature has a small effect on the solubility of CaCO$_3$, the deepening and thickening of the LSW could have moved some undersaturated water from the western Atlantic. Chung et al. (2003) reported a shoaling of 100 to 150 db of the 100% aragonite saturation horizon in the western Atlantic as opposed to no change in the eastern Atlantic.

In the South Atlantic, $\Omega_1$ has shoaled by approximately 200 – 260 db south of 20°S., which is double the upward migration of 100 – 150 db reported by Chung et al. (2003). In these waters, the changes in $\Omega_1$ are predominantly due to CO$_2^{\text{bio}}$ where pCO$_2$ has increased by 50 – 100 µatm at 1000 db ($\gamma_0 = 27.5$ kg m$^{-3}$). The shoaling of the horizon in the high latitudes of the South Atlantic corresponds to a shoaling rate of 15 db yr$^{-1}$. At this rate, by 2050 the top 350 db of this same body of water would be undersaturated with respect to aragonite.
Figure 4.14 Sections of the aragonite saturation horizon change due to total CO$_2$ (a), biological CO$_2$ (b), anthropogenic CO$_2$ (c), and mixing CO$_2$ (d). Below 200 db, the contour lines represent $\Omega_{ar}=1$ for the 1989-1993 dataset (solid) and for the 2003-2005 dataset (dotted). Above 200 db, the contour lines represent $\Omega_{ar}=3$ for the 1989-1993 dataset (solid) and for the 2003-2005 dataset (dotted).
Figure 4.15 Sections of the aragonite saturation horizon change due to total CO$_2$ (a), biological CO$_2$ (b), anthropogenic CO$_2$ (c) and mixing CO$_2$ (d). Below 200 db, the contour lines represent $\Omega_{ar}$=1 for the 1989-1993 dataset (solid) and for the 2003-2005 dataset (dotted). Above 200 db, the contour lines represent $\Omega_{ar}$=3 for the 1989-1993 dataset (solid) and for the 2003-2005 dataset (dotted).

Our results reveal that the aragonite saturation state in the surface waters of the South Atlantic decreased at a high rate and are in good agreement with those predicted by Orr et al. (2005) in the high latitudes, who projected that the Southern Ocean surface waters will become undersaturated with respect to aragonite.
4.4 Chapter summary

A comparison of the data collected during the CLIVAR 2003-05 cruises with the WOCE and OACES 1989-91-93 cruises revealed interesting results. As expected, there were no significant changes in alkalinity in the Atlantic Ocean. The ocean has become more acidic because overall, the total inorganic CO$_2$ has increased in the whole basin. Overall, pH has decreased by ~0.03 units with a maximum of -0.12 in tropical waters. The acidification in the tropical waters was caused by an increase in the oxidation of organic matter from upwelled waters off the west coast of Africa. The acidification in the deep waters has caused the shoaling of the aragonite saturation horizon in both the North Atlantic (~200 db) and in the South Atlantic (~50 db). The anthropogenic CO$_2$, the biological CO$_2$ due to the decomposition of organic material and the dissolution of CaCO$_3$, and the CO$_2$ due to mixing of water masses were also estimated. The shoaling of aragonite was quantified using these calculated sources of CO$_2$ contribution. The results of this study show that after oxidation, mixing in addition to anthropogenic CO$_2$ contributed to this shoaling.
Chapter 5: Changes in the carbonate system in the Indian Ocean based on two occupations of the meridional section I9N

5.1 Background information

The 2007 I9N CLIVAR cruise along the 90 °E meridian was part of a systematic and global reoccupation of WOCE/JGOFS hydrographic sections. The I9N transect was first occupied in 1995. The goals of these programs are to quantify changes in storage of CO₂ and other hydrographic parameters, to provide data for model calibration and validation, and to study heat exchange, water mass and ventilation processes.

The I9N transect (Figure 5.1) shows four distinct water masses that were surveyed: the Indian Central Water (ICW), the Antarctic Intermediate Water (AAIW), the Indonesian Through Flow (ITF), and the Bay of Bengal (BB).

The ICW is centered at \( \gamma^o = 26.8 \text{ kg m}^{-3} \) (Fine, 1993) which is located in the upper thermocline between 100 and 400 db. The strongest component of the ICW is in the southeast Indian Ocean and weakens towards the west (Fine, 1993). It then returns north of the ITF after being entrained by the Somali Current (SC) in the western Indian Ocean and is transported eastward by the South Equatorial Counter Current (SECC) (Gordon et al., 1997).
Figure 5.1 Ship tracks and station positions during the 1995 (solid blue circles) and the 2007 (open red circles) I9N cruises. The Broken Plateau is located at site 'A' and the Ninetyeast Ridge at site 'C'. The western Australia Basin is located between sites 'A' and 'B', the northern Australia Basin between sites 'B' and 'C', the eastern Bay of Bengal between sites 'C' and 'E' and the western Bay of Bengal between sites 'D' and 'E'.

The Somali Current changes direction depending on the Monsoon season. It flows southwestward during the Northeast Monsoon (boreal winter, December-February) but northeastward during the Southwest Monsoon (boreal summer, June-August). Between these two major monsoon seasons, there is a spring inter-monsoon transition that is occurring during the boreal Spring (March-May) when the Northeast Monsoon declines, to be once again overtaken by the Southwest Monsoon. Figure 5.2 shows the currents in the Indian Ocean during the Northeast and Southwest Monsoons. During the
1995 WOCE cruise, the I9N transect was surveyed in January when the SC was flowing southwestward. During the 2007 CLIVAR cruise, the transect was surveyed in April when there was a weakening or reversing of the SC flow from southwestward to northeastward. This shift of SC flow direction yields to a northward migration of the Equatorial Counter Current from 2°S (SECC) during the Northeast Monsoon to 2°N (NECC) during the Southwest Monsoon (Figure 5.2). One could therefore assume that any parameter changes observed between the 2007 and 1995 I9 cruises are largely due to the different monsoons.

The ITF is centered at 9°S ± 3° above the thermocline (~400 db); it transports relatively warmer and fresher waters from the Pacific to the Indian Ocean. These waters are also relatively higher in nutrients and AOU.

The AAIW is limited by neutral density surfaces of 27.10 and 27.66 (Fine, 1993; You, 1998), has low salinity (34 - 34.5), low temperature (4 - 10°C), and is located at around 1000 db. The most recently ventilated AAIW enters in the southwest Indian Ocean and is limited to the north by the ITF in the eastern Indian Ocean (Fine et al., 2008).
Figure 5.2 From Schott and McCreary, 2001: A schematic representation of identified current branches during the Southwest Monsoon (top) and Northeast Monsoon (bottom), including some choke point transport numbers ($Sv=106m^3s^{-1}$). Current branches indicated are the South Equatorial Current (SEC), South Equatorial Countercurrent (SECC), Northeast and Southeast Madagascar Current (NEMC and SEMC), East African Coast Current (EACC), Somali Current (SC), Southern Gyre (SG) and Great Whirl (GW) and associated upwelling wedges, Socotra Eddy (SE), Ras al Hadd Jet (RHJ) and upwelling wedges off Oman, West Indian Coast Current (WICC), Laccadive High and Low (LH and LL), East Indian Coast Current (EICC), Southwest and Northeast Monsoon Current (SMC and NMC), South Java Current (JC) and Leeuwin Current (LC).
Bounded by the latitude 7ºN in the south and by the coastlines in the north, the Bay of Bengal is similar to an estuary. It is stratified with salinity ranging from about 31 to 35.5. Based on data collected during the WOCE I9N 1995 cruise, Gordon et al. (2002) observed a nutrient and carbon-rich, but oxygen-poor benthic layer in the bottom 100 db of the western Bay of Bengal. Furthermore, they suggested the biogeochemical anomalies in the western region are the product of the decomposition of organic matter coming from the Ganges Fan. In contrast, the benthic layer of the eastern Bay of Bengal is nutrient and carbon poor (Gordon et al., 2002). Now the Ninetyeast ridge divides the western and eastern regions of the Bay of Bengal. Therefore, because of the differences in nutrient levels between regions, and the existence of the ridge, the bottom water circulation in the eastern Bay of Bengal is assumed to be counterclockwise (Gordon et al., 2002). At the surface of the BB, the EICC changes direction between the two monsoon seasons (Figure 5.2). EICC flows northeastward during the Northeast Monsoon such as during the 1995 cruise. Reversely, EICC flows southwestward during the Southwest Monsoon season such as during the 2007 cruise.

In addition to the physical dynamics studies of the Indian Ocean and associated regional climate studies, there have been various CO₂ studies. For example, some articles cover the distribution of TCO₂ and TA (Goyet et al., 1998; Johnson et al., 1998; Roche and Millero, 1998; Sabine et al., 2000) while some estimate the anthropogenic CO₂ (Goyet et al., 1999; Sabine et al., 1999; Coatanoan et al., 2001; Touratier et al., 2007). The intention of this study is to analyze and identify the sources of the change in the carbonate parameters in the Indian Ocean along the I9N transect.
5.2 Methods

5.2.1 Quality control of the cruise data sets

The data used for this study were collected along the I9N transects during the WOCE expedition in 1995 and the CLIVAR Repeat Hydrography Program in 2007 (Figure 5.1). These data are available on the World Wide Web at http://whpo.ucsd.edu. The transect I9N is located along 95ºE (between 30ºS and 4ºS) and in the Bay of Bengal. The WOCE cruise started on January 24 1995 at Fremantle, Australia and finished in Colombo, Sri Lanka on March 5 1995. The CLIVAR cruise started in Fremantle, Australia on March 22 2007 and finished in Phuket, Thailand on May 1 2007. The 1995 cruise occurred during the boreal winter and Northeast monsoon while the 2007 cruise occurred during the boreal spring and the inter-monsoon season. The 2007 I9N stations were spaced 30 nautical miles apart, except near the equator (between 3ºS and 3ºN) where the resolution was 20 nautical miles. A total of 130 stations were sampled during 1995 I9N cruise and 111 stations during the 2007 I9N cruise. A 36 Niskin-bottles rosette was used in both cruises. Table 5.1 lists the total number of measurements taken for the four main CO\textsubscript{2} parameters, TCO\textsubscript{2}, TA, pH, and pCO\textsubscript{2} where both cruises overlapped. A summary of the CRM measurements for the I9N 2007 cruise is available in Table 3.2 and summary of the duplicate measurements is in Table 3.3. The values of pCO\textsubscript{2} and pH have been calculated for the in situ conditions of temperature and pressure and using the values of TCO\textsubscript{2}, TA, and the thermodynamic constants of Millero et al. (2007). From these data, the mixing, biological, and anthropogenic CO\textsubscript{2} are calculated following the
methods described in the previous chapter.

Table 5.1 Overlapping cruise Data Information

<table>
<thead>
<tr>
<th>Section</th>
<th>Total number of carbon system measurements</th>
<th>Stations</th>
<th>TCO$_2$ (µmol kg$^{-1}$)</th>
<th>pCO$_2$ (µatm)</th>
<th>TA (µmol kg$^{-1}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>I9N 1995</td>
<td></td>
<td>66</td>
<td>1316</td>
<td>-</td>
<td>1331</td>
<td>-</td>
</tr>
<tr>
<td>Jan 24 – Mar 05, 1995</td>
<td></td>
<td>68</td>
<td>1565</td>
<td>-</td>
<td>1518</td>
<td>1401</td>
</tr>
</tbody>
</table>

5.2.2 Multi linear regressions for total alkalinity and total dissolved inorganic CO$_2$

Similar to the regressions performed in the previous chapter for the Atlantic Ocean data, TA and TCO$_2$ were estimated using hydrographic parameters. In this chapter, eMLR (extended multi linear regressions) were performed in two neutral density surface groups, $\gamma^0 = 24$ to 27 kg m$^{-3}$, and $\gamma^0 > 27$ kg m$^{-3}$. The neutral density surface $\gamma^0 = 27$ lies between 400 db in the ITF and 700 db south of 20$^\circ$S, while the surface waters south of 25$^\circ$S have a neutral density surface of $\gamma^0 \geq 24$. North of 25$^\circ$S, $\gamma^0 = 24$ lies at 125 db. The number of independent variables (4 to 6) varies within the neutral density range, and varies for the predicted variables TA and TCO$_2$ (Table 5.2). The chosen independent variables are those corresponding to the smallest standard error in each of their respective coefficients $a_i$ and the lowest RMSE in the final fit. The residuals are shown in Figure
5.3 for the predicted TA values and in Figure 5.4 for the predicted TCO$_2$ values. Once the fits are determined, the change in TA and TCO$_2$ by the extended MLR technique are calculated following Equation (4.3).

The predicted accuracy of the MLRs, $\delta Y$, is estimated by using the general error propagation given in the previous chapter (Equation (4.5)). Each independent variable’s measurement error $\delta X (\delta Y) = 0.0002$ kg m$^{-3}$, $\delta$Lat = 0.02°, $\delta$P = 0.05 db, $\delta$θ = 0.005 °C, $\delta$S = 0.001, $\delta$Si = 0.4 µmol kg$^{-1}$, $\delta$NO$_3$ = 0.08 µmol kg$^{-1}$, $\delta$PO$_4$ = 0.08 µmol kg$^{-1}$, $\delta$AOU = 0.2 µmol kg$^{-1}$) and the error of each coefficient derived from each MLR (Table 5.2) are used in Equation (4.5).
Table 5.2 Extended multi linear regressions of TA and TCO$_2$ for the years 1995 (subscript 0) and 2007 (subscript 1). RMSE is the root mean square error and $R^2$ is the coefficient of determination. $\delta eY$ and $\delta \Delta eY$ are the predicted accuracy of $eY_i$ and $\Delta eY$ respectively.

<table>
<thead>
<tr>
<th></th>
<th>TA$_1^{24-27}$</th>
<th>TA$_0^{24-27}$</th>
<th>TA$_1^{27}$</th>
<th>TA$_0^{27}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>287.12 ± 21.10</td>
<td>256.37 ± 34.64</td>
<td>2314.40 ± 2.75</td>
<td>2320.32 ± 3.15</td>
</tr>
<tr>
<td>$a_{yn}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$a_{lat}$</td>
<td>-0.31 ± 0.03</td>
<td>-0.45 ± 0.05</td>
<td>0.37 ± 0.01</td>
<td>0.38 ± 0.01</td>
</tr>
<tr>
<td>$a_p$</td>
<td>0.007 ± 0.002</td>
<td>-</td>
<td>-0.006 ± 0.000</td>
<td>-0.006 ± 0.000</td>
</tr>
<tr>
<td>$a_0$</td>
<td>-1.07 ± 0.10</td>
<td>-1.23 ± 0.10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$a_s$</td>
<td>58.09 ± 0.59</td>
<td>58.84 ± 0.97</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$a_{Si}$</td>
<td>0.95 ± 0.03</td>
<td>0.87 ± 0.05</td>
<td>1.17 ± 0.01</td>
<td>1.16 ± 0.01</td>
</tr>
<tr>
<td>$a_{NO3}$</td>
<td>-0.55 ± 0.06</td>
<td>-0.35 ± 0.10</td>
<td>-1.21 ± 0.09</td>
<td>-1.25 ± 0.10</td>
</tr>
<tr>
<td>$a_{PO4}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$a_{AOU}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RMSE</td>
<td>2.7</td>
<td>4.0</td>
<td>3.7</td>
<td>3.9</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.98</td>
<td>0.96</td>
<td>0.99</td>
<td>0.98</td>
</tr>
<tr>
<td>$\delta eY$</td>
<td>± 0.4</td>
<td>± 0.4</td>
<td>± 0.5</td>
<td>± 0.5</td>
</tr>
<tr>
<td>$\delta \Delta eY$</td>
<td>± 0.6</td>
<td>± 0.7</td>
<td>± 0.7</td>
<td>± 0.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>TCO$<em>2$$</em>{1}^{24-27}$</th>
<th>TCO$<em>2$$</em>{0}^{24-27}$</th>
<th>TCO$<em>2$$</em>{1}^{27}$</th>
<th>TCO$<em>2$$</em>{0}^{27}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>390.95 ± 36.6</td>
<td>117.8 ± 51.88</td>
<td>2272.95 ± 5.33</td>
<td>2308.25 ± 6.41</td>
</tr>
<tr>
<td>$a_{yn}$</td>
<td>58.31 ± 1.213</td>
<td>66.53 ± 1.72</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$a_{lat}$</td>
<td>-0.012 ± 0.003</td>
<td>-0.017 ± 0.005</td>
<td>0.57 ± 0.02</td>
<td>0.47 ± 0.02</td>
</tr>
<tr>
<td>$a_p$</td>
<td>-0.012 ± 0.003</td>
<td>-0.017 ± 0.005</td>
<td>-0.003 ± 0.000</td>
<td>-0.003 ± 0.000</td>
</tr>
<tr>
<td>$a_0$</td>
<td>8.88 ± 0.33</td>
<td>11.25 ± 0.48</td>
<td>-14.87 ± 0.17</td>
<td>-16.82 ± 0.21</td>
</tr>
<tr>
<td>$a_s$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$a_{Si}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$a_{NO3}$</td>
<td>-</td>
<td>-</td>
<td>-3.02 ± 0.24</td>
<td>-5.22 ± 0.31</td>
</tr>
<tr>
<td>$a_{PO4}$</td>
<td>75.53 ± 2.65</td>
<td>95.23 ± 0.82</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$a_{AOU}$</td>
<td>0.11 ± 0.02</td>
<td>-</td>
<td>0.99 ± 0.02</td>
<td>1.22 ± 0.03</td>
</tr>
<tr>
<td>RMSE</td>
<td>3.87</td>
<td>5.8</td>
<td>3.55</td>
<td>3.47</td>
</tr>
<tr>
<td>$R^2$</td>
<td>1.0</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>$\delta eY$</td>
<td>± 6.0</td>
<td>± 7.6</td>
<td>± 0.3</td>
<td>± 0.5</td>
</tr>
<tr>
<td>$\delta \Delta eY$</td>
<td>± 9.7</td>
<td></td>
<td>± 0.6</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.3 MLR TA$_1$ residuals for the 2007 data (a) and MLR TA$_0$ residuals for the 1995 data (b).
Because phosphate is an independent variable for determination of $\text{TCO}_{21}^{24-27}$, an extra component $a_{\text{P}O_4^2-}^2$ is added to the right hand side of Equation (4.5) for the error analysis of $\text{TCO}_{2i}^{24-27}$. Therefore the predicted accuracies in MLR TA and MLR TCO$_2$ vary by neutral density range (Table 5.2). The uncertainty in the amount of change of variable $Y$, $\delta eY$, is estimated by quadratic error addition of the error in $Y_1$, $\delta Y_1$, and $Y_0$, $\delta Y_0$.
following Equations (4.5) and (4.6). Here we substitute for \( Y \) the terms (MLR TA\(_1\) – MLR TA\(_0\)) and (MLR TCO\(_{21}\) – MLR TCO\(_{20}\)).

The expected predicted accuracy for TA is about \(~0.4\mu\text{mol kg}^{-1}\) for the whole water column (Table 4.5). Below \( \gamma^p = 27\text{ kg m}^{-3} \), the predicted accuracies for TCO\(_2\) are \(\pm 0.3\) and \(\pm 0.5\mu\text{mol kg}^{-1}\) for the 2007 and 1995 data set, respectively. Above \( \gamma^p = 27\text{ kg m}^{-3} \) they are \(\pm 6.0\) and \(\pm 7.6\mu\text{mol kg}^{-1}\), respectively. In this case phosphate is the most sensitive variable, such that its associated coefficient \(a_{\text{PO}_4^{-}}\) produces an accuracy of \(\pm 6.0\) and \(\pm 7.6\mu\text{mol kg}^{-1}\) for TCO\(_{21}^{24-27}\) and TCO\(_{20}^{24-27}\) respectively. If the measurement error (i.e., random error) of phosphate improves from 0.08 to 0.01 \(\mu\text{mol kg}^{-1}\), the predicted accuracy would change to \(\pm 0.8\) and \(\pm 1.0\mu\text{mol kg}^{-1}\). To conclude here, the predicted error in the change in MLR TCO\(_2\) at the surface of the Indian Ocean is high, as found for the Atlantic Ocean. Therefore no further analysis of MLR TCO\(_2\) is feasible in this area of surface and near-surface water (24 < \(\gamma^p\) < 27 kg m\(^{-3}\)).

### 5.3 Results and discussion

#### 5.3.1 Changes in the four carbonate parameters

In this section the normalized TA is defined a TA\(_{\times35/S}\). The extended normalized NTA, eNTA, is defined as the MLR TA\(_{\times35/S}\). The values of \(\Delta\text{NTA}^{\text{measured}}\) and \(\Delta\text{eNTA}\) are shown in Figure 5.5. In surface waters, the changes in salinity due to evaporation or input of fresh water contribute to changes in TA (Millero et al., 1998; Lee et al., 2000). The TA can decrease if CaCO\(_3\) shells are formed in surface
waters. In deep waters (below 1000 db), where salinity does not vary as much as at the surface, TA increases when CaCO₃ dissolves (Chen 1978). The NTA removes much of the seasonal differences in the mixed layer. Within experimental error or within 95% confidence interval (2 × ± 4 µmol kg⁻¹ for the measured TA and 2 × ± 3.6 µmol kg⁻¹ for the eMLR), the NTA of Indian Ocean waters show significant changes (~ - 15 µmol kg⁻¹) in intermediate waters (27.1 < ρ < 27.6 kg m⁻³) and along the 25.8 ρ surface. Therefore, the changes observed in intermediate waters could be due to the dissolution of CaCO₃, whereas those at the surface could be due to the changes in the mixed layer depth.

Sections of ΔTCO₂ (measured) and ΔeTCO₂ (calculated from Table 4.5) are shown in Figure 5.6. Most of the changes occurred in the thermocline (~ + 30 µmol kg⁻¹ along the 25.8 neutral density surface) and intermediate waters (~ + 7 µmol kg⁻¹). The changes in the TCO₂ (and pCO₂) in deep waters are due to changes in the oxidation of organic carbon over time. In surface waters, the changes in TCO₂ are due to losses occurring during photosynthesis and increases due to changes in the oxidation of organic matter. The changes given for eΔTCO₂ are similar to those given for the measured ΔTCO₂ and are about 20 µmol kg⁻¹. These changes are due to changes in the seasons. TCO₂ and pCO₂ vary daily and seasonally. The 1995 cruise occurred during the boreal winter and Northeast monsoon while the 2007 cruise occurred during the boreal spring and the inter-monsoon season.
Figure 5.5 Changes between 2007 and 1995 in the measured NTA (a) and predicted eNTA (b) from the eMLR. Values are in $\mu$mol kg$^{-1}$. Data above the neutral density surface $\gamma^0 = 24$ kg m$^{-3}$ and those less than 2× standard error of measurement ($\pm 4$ $\mu$mol kg$^{-1}$) or within the 95% confidence interval are blanked.
Figure 5.6 Changes between 2007 and 1995 in the measured TCO$_2$(a) and predicted eTCO$_2$(b) from the eMLR. Values are in $\mu$mol kg$^{-1}$. Data above the neutral density surface $\gamma'' = 24$ kg m$^{-3}$ and within the 95% confidence interval are blanked. Those values are within 2$\times$ standard error of measurement ($\pm$ 2 $\mu$mol kg$^{-1}$) and eMLR ($\pm$ 3.6 $\mu$mol kg$^{-1}$).

The pCO$_2$ and pH quantities (there were no pH measurements on the 1995 cruise) shown in Figure 5.7 are determined using the program CO2SYS with TA and TCO$_2$ inputs as well as the hydrographic in situ conditions. Overall, the change in pCO$_2$,
ΔpCO₂, shows an increase of about 25 µatm. Exceptions are observed in the Bay of Bengal and the ITF with ΔpCO₂ ≈ 75 µatm. The increase in pCO₂ in surface waters can be caused by oxidation of organic matter, by dissolution of CaCO₃, by increase of water temperature and by increases in CO₂ in the atmosphere from fossil fuel burning. It is possible that these processes have been/are occurring in the Bay of Bengal and in the ITF, which it is a very old water mass (~1500 yrs (Stuiver et al., 1983)). A decrease in pCO₂ in surface waters can be caused by photosynthesis, by dissolution of CaCO₃ and by a decrease in temperature. The study of Nan et al. 2009 reveals that the SST anomalies over the subtropics and middle latitudes of the SIO seem to be followed by the SST anomalies in the equatorial Indian Ocean and Bay of Bengal. By anomalies, the authors showed that SST increase during the boreal spring (e.g. during 19N 2007 cruise) with increasing Southern Annular Mode (SAM) index. Moreover, the 1995 cruise was after a period of relatively low SAM, while the 2007 cruise followed a period of high SAM (Roemmich et al., 2007). Therefore, the increase observed in surface pCO₂ was partially due to increase in surface temperature. In deeper waters, the increase in pCO₂ due to increase in oxidation of organic matter is discussed in the following section (4.3.2).

The changes in pH are shown in Figure 5.7. The decrease in pH or ocean acidification has a negative impact on calcifying organisms such as pteropods and corals by changing the carbonate composition of seawater (Riebesell et al., 2000; Orr et al., 2005; Kleypas et al., 2006). Dissolved CO₂$_{\text{anth}}$ in the ocean has reduced the pH by approximately 0.1 units since the industrial era began (Haugan and Drange, 1996) and is predicted to drop another 0.3 to 0.4 units by 2100 (Houghton et al., 2001; Orr et al.,
Results from this study show that, in the Bay of Bengal, pH decreased by 0.05 – 0.10 units in the top 2000 db and by 0.00 – 0.05 units below 2000 db, respectively. The observed decrease in pH could be from different sources. One source could be the dissolution of $\text{CO}_2^{\text{anth}}$, another could be the increase in TCO$_2$ due to the oxidation of organic material, and finally, mixing of water masses could also cause a decrease in pH. One consequence of these changes in pH is the alteration of the carbonate composition of seawater.
Figure 5.7 Changes between 2007 and 1995 in *in situ* pCO$_2$ (a) in $\mu$atm and *in situ* pH (b) on the seawater scale.
5.3.2 Changes in biological activity

The biological CO$_2$, CO$_{2}^{\text{bio}}$, has been calculated using Equation (4.7). The changes in CO$_{2}^{\text{bio}}$ that occurred over the period 1995-2007 along 19N are shown in Figure 5.8b, along with the changes in AOU (Figure 5.8a). At the surface of the Indian Ocean, AOU has mainly increased in the Bay of Bengal ($\sim +35$ $\mu$mol kg$^{-1}$), in the upper waters and southern part of the ITF ($\sim +30$ $\mu$mol kg$^{-1}$) and in the ICW ($\sim +20$ $\mu$mol kg$^{-1}$). The waters between the equator and 5°S, and between $\gamma^p = 24$ and $\gamma^p = 25.8$ kg m$^{-3}$, show a decrease in AOU of about 40 $\mu$mol kg$^{-1}$ indicating a lower respiration rate or a shorter residence time of the water. This argument is supported by the fact that TCO$_2$ has been consumed in this area (Figure 5.6) and that chlorophyll concentration has increased, over a decade, by about 20% at the surface of the inter-tropical regions of the Indian Ocean (Antoine et al., 2005). Antoine et al. (2005) analyzed the ocean color time series (1979-2002) retrieved from two satellite sensors: CZCS and SeaWiFS. Below 350 db, AOU has decreased by 30 $\mu$mol kg$^{-1}$ in the AAIW ($27.1 < \gamma^a < 27.6$). This also corresponds to a decrease in TCO$_2$ (Figure 5.6).

Regarding the changes in CO$_{2}^{\text{bio}}$ (Figure 5.8b), the trend is similar to that in the AOU except for the Bay of Bengal where CO$_{2}^{\text{bio}}$ has mainly decreased. Because AOU has increased in the Bay of Bengal, the decrease in CO$_{2}^{\text{bio}}$ is due to a decrease in alkalinity (Figure 5.5) as described in Equation (4.7).
Figure 5.8 Changes between 2007 and 1995 in the measured AOU and in the biological CO$_2$ calculated using Equation (4.7) along the line I9N in the Indian Ocean. Values are given in $\mu$mol kg$^{-1}$ and the black contour overlay lines represent neutral density surfaces $\gamma^a$.

### 5.3.3 Anthropogenic CO$_2$

#### 5.3.3.1 Comparison between the 2004 and 2007 TrOCA methods

The anthropogenic CO$_2$ concentrations (Figure 5.9) were calculated using the I9N 2007 data from the Indian Ocean and the 2004 and 2007 TrOCA methods. Concentrations range from 5 to 70+ $\mu$mol kg$^{-1}$ depending on the TrOCA method used. Overall, the 2007 TrOCA method yields higher concentrations.
Figure 5.9 Anthropogenic CO$_2$ concentrations calculated using the 2004 (a) and 2007 (b) TrOCA methods for waters below the surface $\gamma^p = 24$ kg m$^{-3}$. The 2007 data for I9N were used for the calculation. Areas in white have values less than 5 $\mu$mol kg$^{-1}$. Black contours are for the neutral density surfaces, $\gamma^p$.

A comparison has been made between the two TrOCA methods for the Atlantic Ocean data along the line A16 (Chapter 4). The following compares the anthropogenic CO$_2$ calculated using the two TrOCA methods of 2004 and 2007, $C^{\text{TrOCA}}_{2004}$ and $C^{\text{TrOCA}}_{2007}$ respectively, for the I9N line (Figure 5.10). The difference in the methods is only
significant for more than two times the standard error of the difference. In this study the standard error of the difference is 7.2 \( \mu \text{mol kg}^{-1} \), estimated by quadratic error addition using the \( C_{\text{TrOCA}2004} \) and \( C_{\text{TrOCA}2007} \) errors. At the surface the TrOCA methods of 2004 and 2007 are not conservative and should not be applied (Touratier and Goyet, 2004a). A property is considered conservative in a mixture of water masses when its value remains on a straight mixing line. Any deviation from the conservative line indicates a local transformation (e.g. chemical or biological processes) or an interaction with the surrounding environment (e.g. atmosphere or sediments). From Figure 5.10, the average difference in the two TrOCA methods between 200 and 1000 db decreases from 35 \( \mu \text{mol kg}^{-1} \) to around 15 \( \mu \text{mol kg}^{-1} \). This means that the \( C_{\text{TrOCA}2007} \) gives higher values than \( C_{\text{TrOCA}2004} \). Note that the results obtained for the Indian Ocean are similar to those in the Atlantic Ocean. The exception is that significant differences were observed extending to 3000 db in the Atlantic Ocean, this is expected since the whole water column was ventilated in the past few decades in the Atlantic. The calculated \( C_{\text{TrOCA}2004} \) values of this study are in good agreement with those of Goyet et al. (1999), Sabine et al. (1999), Coatanoan et al. (2001) and Hall et al. (2004). However, these values were proven to be overestimated in relatively young waters and underestimated in older waters (Hall et al., 2004; Matsumoto and Gruber, 2005). Figure 5.11 shows that the difference between \( C_{\text{TrOCA}2007} \) and \( C_{\text{TrOCA}2004} \) is significant in the AAIW and in the ICW. Therefore, because \( C_{\text{TrOCA}2004} \) concentrations are biased in relatively young or ventilated waters, the bias in \( C_{\text{TrOCA}2007} \) would be greater. Below 1000 db and in the ITF, there is a non-significant
average difference of 5 $\mu$mol kg$^{-1}$, even though waters with very low or zero CFC concentration still contain a significant amount of anthropogenic CO$_2$ (Körtzinger et al., 1999; Wallace, 2001; Matsumoto and Gruber, 2005; Tanhua et al., 2006). This implies that choosing the oldest water masses to determine TrOCA$_{2007}$ (section 4.2.4) appears to be unnecessary.
Figure 5.10 Difference in anthropogenic CO$_2$ concentrations, in µmol kg$^{-1}$, calculated as $C_{2007}^{\text{TrOCA}}$ minus $C_{2004}^{\text{TrOCA}}$. CO$_2$ differences are considered significant if greater than 15 µmol kg$^{-1}$. Data collected during the 2007 I9N cruise were used for the computation of anthropogenic CO$_2$. 
Figure 5.11 Section of the difference in \( \mu \text{mol kg}^{-1} \) between the anthropogenic CO\(_2\) concentrations calculated as \( C_{\text{TrOCA}2004} \) minus \( C_{\text{TrOCA}2007} \). CO\(_2\) differences are considered significant if greater than 15 \( \mu \text{mol kg}^{-1} \). Data used are those from the I9N 2007 transect. Black contours are the neutral density surfaces, \( \gamma^p \).

5.3.3.2 The column inventory of the change in anthropogenic CO\(_2\)

In this section \( \Delta C_{\text{TrOCA}2004} \) is defined as the changes in anthropogenic CO\(_2\) calculated using the 2004 TrOCA method at time 1 (2007) minus that at time 0 (1995). Similarly, \( \Delta C_{\text{TrOCA}2007} \) is defined as the anthropogenic CO\(_2\) calculated using the 2007 TrOCA method.
at time 1 – time 0. The changes in anthropogenic CO₂ are shown for one of the methods, \( \Delta C_{\text{TrOCA}}^{2004} \). Figure 5.12 shows an increase of about 5 to 10 \( \mu \text{mol kg}^{-1} \) in the Bay of Bengal, more than 10 \( \mu \text{mol kg}^{-1} \) in the AAIW and ICW, and no change in the ITF.

Figure 5.12 Change in anthropogenic CO₂ concentration calculated using the 2004 TrOCA method over the period 1995-2007 in the Indian Ocean. Values are given in \( \mu \text{mol kg}^{-1} \) and black contours are neutral density surfaces, \( \gamma^n \).

Estimates of the annual changes of the column inventories in all the forms of CO₂ (total, anthropogenic, biological and mixing) are shown in Figure 5.13. Mixing CO₂ was
calculated from a conservation of mass technique (4.2.5). Depth integration of the CO$_2$ forms was performed from 200 db to the bottom. There are no data between the equator and 10$^\circ$N since both 1995 and 2007 I9N stations did not overlap. Overall, total CO$_2$ and anthropogenic CO$_2$ have a positive inventory. Anthropogenic CO$_2$ is higher in the tropical South Indian Ocean than towards the equator. This is similar to the general trends observed in the Atlantic (previous chapter) and Pacific oceans (Sabine et al., 2008). At around 30 $^\circ$S, the South Indian Ocean inventory is higher ($\sim$ 0.2 mol m$^{-2}$ yr$^{-1}$) than that in the South Atlantic Ocean ($\sim$ 0.17 mol m$^{-2}$ yr$^{-1}$), but lower than that of the South Pacific Ocean ($\sim$ 0.55 mol m$^{-2}$ yr$^{-1}$ in Sabine et al. (2008)). Increased ventilation in the South Indian Ocean subtropical gyre in the period before the 2007 cruise caused anthropogenic CO$_2$ to increase in the ICW. This is consistent with atmospheric forcing and other Southern Hemisphere observations. The 1995 cruise was after a period of relatively low SAM, while the 2007 cruise followed a period of high SAM (Lenton and Matear, 2007; Roemmich et al., 2007). This means that in both cases, the SAMs were in a positive mode but with a different index number. During a positive SAM, the subpolar westerly winds increase while the tropical westerly winds decrease. As a result of these two features, wind stress in mid-latitude ocean gyres (e.g. ICW) increase (Roemmich et al., 2007), increasing ventilation, hence, increasing CO$_2^{\text{anth}}$ uptake. The study of Lenton and Matear (2007) shows the impact of the SAM in the Southern Ocean on the CO$_2$ uptake and its interannual variability in the three ocean sectors (Indian, Atlantic and Pacific). Their results show that CO$_2$ uptake by the oceans will decrease as the SAM is increasing. The total interannual variability variance of the air-sea CO$_2$ flux is explained
by 22%, 21% and 0% by the SAM in the Indian, Pacific and Atlantic oceans, respectively (Lenton and Matear, 2007).

The annual CO\textsubscript{2} inventory between the equator and 10°S is also positive and higher in the Indian Ocean (~ 0.15 mol m\textsuperscript{-2} yr\textsuperscript{-1}) than in the Atlantic (~ -0.25 mol m\textsuperscript{-2} yr\textsuperscript{-1}) but lower than that in the Pacific (~0.25 mol m\textsuperscript{-2} yr\textsuperscript{-1}) oceans. Overall, the annual anthropogenic inventories are higher than the mixing CO\textsubscript{2} annual changes, except in the Bay of Bengal. The column inventory of the change in CO\textsubscript{2}\textsuperscript{mix} in this water (BB) shows that CO\textsubscript{2}\textsuperscript{mix} caused pH to decrease. In the south Indian Ocean convergence zone or in the ICW, ventilation has a larger role in increasing anthropogenic CO\textsubscript{2}. Around the equator, conditions (e.g. upwelling, equatorial current, warmer temperatures etc.) are more favorable for respiration and oxidation of organic matter.
Figure 5.13 Column inventory of the change in mol C m$^{-2}$ yr$^{-1}$ of TCO$_2$ (black), CO$_2^{\text{anth}}$ (red), CO$_2^{\text{bio}}$ (green) and CO$_2^{\text{mix}}$ (blue) over the period 1995-2007, below 200 db and in the Indian Ocean. There are no data between the equator and 10 °N since the transects I9N 1995 and I9N 2007 did not overlap there.
5.4 Chapter summary

In summary, this chapter focuses on the changes in the CO$_2$ system in the Indian Ocean thermocline and intermediate waters along the 95 °E meridian. The 2007 I9N cruise was a repeat hydrographic section of the 1995 WOCE program. The 2007 cruise occurred in the inter-monsoon period just before the beginning of the summer monsoon, while the 1995 cruise occurred during the winter monsoon. Stations overlapped in the south but not between the Equator and 10°N. During the cruises, four water masses were surveyed: AAIW, ICW, ITF and BB.

The measured TA and TCO$_2$ were used to calculate pCO$_2$ and pH using the CO2SYS program and the in situ conditions of the hydrographic parameters. The same hydrographic parameters were used as dependent variables to determine TA and TCO$_2$ in water within the neutral density surface ranges 24 to 27 kg m$^{-3}$, and $> 27$ kg m$^{-3}$. The RSME of the TA and TCO$_2$ fits ranged from 2.7 to 4.0 µmol kg$^{-1}$ and 3.5 to 5.8 µmol kg$^{-1}$ respectively. The extended MLR (eMLR) calculation of Friis et al. (2005) was used to estimate the difference in MLR TA and MLR TCO$_2$ over the period 1995-2007 in the Indian Ocean. The error of the eMLR was calculated using the general propagation error formula for a linear equation, which resulted in high values for eMLR TCO$_2$ at the surface of the Indian Ocean. Therefore, the MLR TCO$_2$ at the surface was not analyzed.

The increase in CO$_2^{bio}$ contributed to most of the changes in TCO$_2$ observed at the surface of the ICW and ITF (top 350 db). On the contrary, CO$_2^{bio}$ decreased in the bottom waters of the Bay of Bengal by about 20 to 40 µmol kg$^{-1}$. Along the density surface of
this water mass, there was a decreasing gradient of the changes in CO$_2^{\text{bio}}$ from the north
(60+ $\mu$mol kg$^{-1}$) to the south (20 $\mu$mol kg$^{-1}$). This suggests that the bottom water of BB
has become less productive or more rapidly flushed in 2007 compared to 1995.

Furthermore, CO$_2^{\text{anth}}$ (anthropogenic CO$_2$) has increased by 5 $\mu$mol kg$^{-1}$ in the Bay
of Bengal. Thus, this region has become more acidic, and this is supported by the fact
that the estimated pH has decreased by 0.05 to 0.1 units. CO$_2^{\text{anth}}$ has also increased by 5
to 10 $\mu$mol kg$^{-1}$ in the ICW and AAIW but no change was observed in the ITF. Increased
ventilation in the South Indian Ocean subtropical gyre in the period before the 2007
cruise caused anthropogenic CO$_2$ to increase in the ICW. This is consistent with
atmospheric forcing and other Southern Hemisphere observations. The 1995 cruise was
after a period of relatively low Southern Annular Mode (SAM), while the 2007 cruise
followed a period of high SAM (Roemmich et al., 2007). In general, in the India Ocean,
changes in CO$_2^{\text{bio}}$ are larger than CO$_2^{\text{anth}}$. 

Chapter 6: Summary and conclusions

Since the industrial revolution, CO₂ has increased in the atmosphere and about 40% of the increase has been taken up by the ocean. Once in the ocean, CO₂ is quickly transformed into carbonic acid, which reacts with bicarbonate and carbonate ions, releasing hydrogen ions and lowering the pH of the seawater. The carbonate and bicarbonate ion proportions consequently change. An artifact of increasing CO₂ in the ocean is ocean acidification; it changes the calcium carbonate saturation state, which in turn alters the calcification rate of shelled organisms.

The purpose of this dissertation is to estimate the changes in the carbonate system in the oceans, and whether these changes are due to natural (biological activity, chemical transformation or mixing of water masses) or anthropogenic (human activities) perturbations. Firstly, the solubility of boric acid in electrolyte solutions at 25 °C was derived. Subsequent to this, the effect of filtration on total alkalinity measurement in the open ocean was explored. Finally, a synthesis and analysis of the carbonate parameters in the Atlantic and Indian oceans were undertaken. For this task, an analysis of the change of the carbonate parameters due to changes of the biology and the distribution of water masses in the thermocline and intermediate waters was examined.

In order to estimate the changes in the carbonate system in the oceans it is first important to understand the chemistry of CO₂ in the oceans. For example, in Chapter 2 a formulated hypothesis was that the important thermodynamic constants of CO₂, pK*₁ and
pK*₂ change when boric acid is present in solution. To attempt to solve this problem, the solubility of boric acid in seawater or artificial seawater should be determined. A first step here is to determine the solubility of boric acid in the major sea salts solutions. However, in Chapter 2, due to experimental limitations, only LiCl, NaCl, KCl, RbCl and CsCl were used as the sea salt solutions. Results showed that the solubility of boric acid in LiCl, NaCl, and KCl solutions is not a strong function of temperature. Furthermore, the results can only be applied over a limited temperature range (5 to 35°C). Boric acid is soluble in the order SO₄ > NO₃ and F > Cl > Br > I in common cation solutions. In common anion salt solutions, the order is Cs > Rb > K > Na > Li > H and Ba > Sr > Ca > Mg. The results can be used to estimate the boric acid activity coefficients γₐ and solubility [B] in natural mixed electrolyte solutions using the more general Pitzer equation (2.27).

This approach resulted in a partial determination of the solubility of boric acid in seawater. To complete the analysis, it is recommended that this study be repeated under different temperature conditions, and in other salts solutions so that the derived coefficients could be used for in situ natural water environments. For example, the other salts solutions would be the major sea salts (Na₂SO₄, MgCl₂ and MgSO₄) and then the minor sea salts (Na₂CO₃ and NaHCO₃). The titration of boric acid in MgCl₂ solutions, with sodium or potassium hydroxide for example, would cause the solution to precipitate and fail the experiments. Other methods should be investigated in order to solve the solubility of boric acid in seawater. Once complete, one can then determine the changes
in pK*₁ and pK*₂ due to the interaction of B(OH)₄ and CO₃²⁻ and BOH₃ and HCO₃⁻, respectively.

The second focus in this study was to assess the quality of the parameter sampling and measurements, i.e., quality assessment and control (Chapter 3). Uncertainties in TCO₂ and TA measurements were ~ 15 µmol kg⁻¹ in the 1980s, but improved to 2 and 4 µmol kg⁻¹ respectively in the 1990s and to 1.5 µmol kg⁻¹ in the 2000s. A study in Young-II Bay, Korea, showed that phytoplankton and bacterial cells affect the measured alkalinity of unfiltered seawater (Kim et al., 2006). This same study also suggests that alkalinity measurements made at sea should be made on filtered seawater, questioning the validity of the earlier measurements. Following their recommendation, this dissertation tested the hypothesis that filtering seawater sampled in the open ocean is necessary for the determination of TA. Total alkalinity of filtered and unfiltered samples was measured during the P16N 2006 cruise in the Pacific Ocean and the I9N 2007 cruise in the Indian Ocean (Chapter 3). Although filtering coastal water samples may be important to remove the contributions of phytoplankton and bacteria on the measured TA, it is not the case for open ocean samples. The results showed that the at-sea measured TA of filtered and unfiltered samples were not statistically different. Measurement of 180 samples of surface, oxygen minimum, and deep waters in the Pacific and Indian oceans for unfiltered and filtered agreed to ± 2 µmol kg⁻¹. The measurements showed that it is not necessary to filter seawater samples when measuring total alkalinity in the open ocean. And more importantly, that the unfiltered measurements made on seawater over the last 20 years are not affected when samples are not filtered.
In Chapters 4 and 5, an estimate was made of the changes in the carbonate system in the Atlantic and Indian oceans, and whether these changes were due to natural or anthropogenic perturbations. With the high quality CO$_2$ measurements derived earlier, changes over a decade in the carbonate parameters were examined for the eastern Atlantic Ocean along the transect A16 (Chapter 4), and for the eastern Indian Ocean along the transect I9N (Chapter 5). The data were collected during the WOCE/JGOFS (1990s) and CLIVAR (2000s) programs. All of the CO$_2$ measurements made on these cruises were examined for internal consistencies. Parameters pCO$_2$ and pH were not measured on some of the earlier cruises. In this instance they were calculated using the CO2SYS program with inputs of TA, TCO$_2$ and the in situ hydrographic conditions.

Parameters TA and TCO$_2$ for both oceans were fitted to multi linear regressions (MLR) using hydrographic parameters. In the Atlantic Ocean, these MLR were performed from south to north, in both the 0-200 db pressure range and below 200 db. In the Indian Ocean, these MLR were performed in both the 24-27 kg m$^{-3}$ neutral density range and below 27 kg m$^{-3}$. The results obtained for the MLR yielded better RMSE in the Indian Ocean than in the Atlantic Ocean. In the Indian Ocean, RSME of the TA and TCO$_2$ fits ranged from 2.7 to 4.0 $\mu$mol kg$^{-1}$ and 3.5 to 5.8 $\mu$mol kg$^{-1}$, respectively. In contrast, the RSME of the Atlantic Ocean TA and TCO$_2$ fits range from 5.8 to 6.9 $\mu$mol kg$^{-1}$ and 5.4 to 9.6 $\mu$mol kg$^{-1}$, respectively. The extended MLR (eMLR) method of Friis et al. (2005) was used to estimate the difference in MLR TA and MLR TCO$_2$ over the period 1989-2005 in the Atlantic Ocean and 1995-2007 in the Indian Ocean. The error of the eMLR was calculated using the general propagation error formula for a linear
equation, which resulted in high values for eMLR TCO$_2$ at the surface of the Indian Ocean. The dependent variable phosphate was not available for the Atlantic Ocean data. It appears that phosphate is an important variable in the MLR TCO$_2$, as it has the highest correlation coefficient with TCO$_2$ in the Indian Ocean. To summarize, on one hand, the error (deviations) of MLR TCO$_2$ fits are higher in the Atlantic Ocean than in the Indian Ocean surface waters, i.e., the fits in the Atlantic Ocean are worse. On the other hand, the error of eMLR TCO$_2$, which gives an indication of the accuracy of the difference in the MLR TCO$_2$ across different years, is lower in the Atlantic Ocean than in the Indian Ocean surface waters. To avoid applying an accurate result to a poor fit (in the Atlantic Ocean), the eMLR TCO$_2$ at the surface of both oceans were not analyzed. It is recommended that the relationships between TCO$_2$ and other hydrographic parameters at the surface be further investigated. These relationships may not be linear at the surface. In this case another method should be used. For example, Neural Network statistical analyses (NN) are powerful for estimating parameters when there are non-linear relationships. NN have been used to determine surface pCO$_2$ in the Atlantic Ocean with inputs of remotely sensed sea surface temperature, chlorophyll and mixed layer depth (Friedrich and Oschlies, 2009). Surface TCO$_2$ can then be derived from this estimated pCO$_2$ and TA estimated from eMLR or other global relationships (Lee et al., 2006).

The TA and TCO$_2$ data collected during the WOCE and CLIVAR programs in the Atlantic and Indian oceans were also used to calculate the biological and anthropogenic forms of CO$_2$, and the aragonite and calcite degree of saturation with respect to seawater. The back calculation method of Chen and Millero (1979) was used to determine the
biological CO₂, while the TrOCA methods (Touratier and Goyet, 2004b; Touratier et al., 2007) were used to calculate the anthropogenic CO₂. The mixing form of CO₂ (e.g. upwelling, ventilation, water mass property change etc.) was derived using a conservation of mass approach.

The changes in TCO₂ revealed that an increase in biological activity was of the main contributor to the changes in TCO₂ observed in the thermocline of the Atlantic Ocean equatorial waters, the ICW and ITF. On the contrary, CO₂\textsuperscript{bio} has decreased in the Bay of Bengal and in the south and north Atlantic subtropical gyres. In the South Atlantic subtropical gyre (42°S – 5°S), CO₂\textsuperscript{bio} decreased by 0 to 40 µmol kg\textsuperscript{-1}. Because the A16S 1991 cruise occurred in boreal summer and the A16S 2005 cruise occurred in boreal winter, this sampling difference could be due to seasonal changes in CO₂\textsuperscript{bio}.

Furthermore, anthropogenic CO₂ has increased in the ICW. This may have been caused by increased ventilation in the South Indian Ocean subtropical gyre (Roemmich et al., 2007). In addition, anthropogenic CO₂ increased by 5 µmol kg\textsuperscript{-1} in the Bay of Bengal, and caused a decrease in pH by 0.05 to 0.1 units. CO₂\textsuperscript{anth} also increased between 5 to 10 µmol kg\textsuperscript{-1} in the ICW, LSW and AAIW of both the Atlantic and Indian oceans. A negative change in CO₂\textsuperscript{anth} in the Atlantic Ocean around the equator could be attributed to an increase of anthropogenic-free upwelling waters during the period 1989-2005. This implies that the observed changes in CO₂ in this region should be dominated by the CO₂\textsuperscript{mix} contribution.
The changes in the different forms of CO$_2$ have caused a change in pH in both oceans. For example, the increase in CO$_2^{\text{mix}}$ was mainly responsible for the decrease in pH in the Bay of Bengal. As another example, the decrease in CO$_2^{\text{bio}}$ due to the change in seasons decreased pH by about 0.15 units in the thermocline of the Atlantic Ocean, south of the Equator i.e it acidified the ocean. In comparison, anthropogenic CO$_2$ has decreased pH by 0.1 units since the industrial era (Haugan and Drange, 1996). The acidification of the deep waters caused the shoaling of the aragonite 100% saturation horizon of ~200 db in the North Atlantic and ~50 db in the South Atlantic. The upward migration of the aragonite 100% saturation depth was caused mainly by the oxidation of organic matter and mixing as opposed to anthropogenic CO$_2$. This study also showed that there was no significant change in the calcite 100% saturation depth.

In the process of calculating the anthropogenic CO$_2$, a difference in the distribution and column inventory was found while using the TrOCA approaches of 2004 (Touratier and Goyet, 2004b) and 2007 (Touratier et al., 2007). Overall, the revisited version of 2007 yielded ~20 μmol kg$^{-1}$ more anthropogenic CO$_2$ at 200 db than the 2004 method. The anthropogenic CO$_2$ calculated with the 2004 TrOCA version agreed with other studies (Chen and Millero, 1979; Gruber 1998; Lee et al., 2003). The difference in the two methods was significant above 3000 db in the Atlantic Ocean but only above 1000 db in the Indian Ocean. Below these pressures in their respective oceans, water with very low or zero CFC signal still contains a significant amount of anthropogenic CO$_2$ (Körtzinger et al., 1999; Wallace, 2001; Matsumoto and Gruber, 2005; Tanhua et al., 2006) but the difference between the 2004 and 2007 TrOCA methods are statistically
insignificant. The significant differences in are located in the LSW, in the south and north subtropical gyres of the Atlantic Ocean, above 1200 db, and in the AAIW and ICW of the Indian Ocean. The TrOCA method is supposed to be valid for determining anthropogenic CO$_2$ in intermediate, deep and bottom waters. However, the anthropogenic CO$_2$ values of Gruber et al. (1998), Lee et al. (2003) and Touratier and Goyet (2004b) were shown to be overestimated in relatively young waters and underestimated in older waters (Hall et al., 2004; Matsumoto and Gruber, 2005) from using alternate methods. Therefore, since C$_{\text{TrOCA}}^{\text{2004}}$ values are positively biased in young or recently ventilated waters, the values of C$_{\text{TrOCA}}^{\text{2007}}$ would be even more overestimated because the difference between C$_{\text{TrOCA}}^{\text{2007}}$ and C$_{\text{TrOCA}}^{\text{2004}}$ are positive in these waters. In summary, the results of this dissertation showed that the TrOCA 2004 and TrOCA 2007 methods do not work in intermediate waters, such as the AAIW in the Indian Ocean and the LSW in the Atlantic Ocean. Indeed, an optimal multi-parameter analysis using time series in the LSW showed that the water mass properties have changed and fluctuated over time (Leffanue and Tomczak, 2004; Henry-Edwards and Tomczak, 2006). Because LSW is not at steady state, most of the models that estimate anthropogenic CO$_2$, including the TrOCA and MLR methods, should not be used. Models that estimate the anthropogenic CO$_2$ must be investigated further.

The tracers used in models are not conservative at the surface or biased in young or recently ventilated waters. The CO$_2$ parameters and hydrographic data vary seasonally at the surface because of the physical and biological effects. Biological processes do not affect tracers such as CFCs, still their decreasing atmospheric source has complicated the
calculation of water ages and anthropogenic CO$_2$. Another tracer, SF$_6$, has been increasing in the atmosphere for the last 30 years and may be used as a proxy for anthropogenic CO$_2$ (Tanhua, 2008) in recently ventilated waters but not in waters older than 30 years. Oceanic SF$_6$ measurements are becoming more available and should be used as another standard parameter when measuring during the carbon.

To conclude, changes in the carbonate system due to natural and anthropogenic perturbations were revealed. Only the changes in pK$^*$$_1$ and pK$^*$$_2$ due to presence of boric acid in solution were not conclusively evaluated. Because boric acid is a major ion in seawater, its solubility should be analyzed in the major and minor sea salts solutions across wider temperature and ionic strength ranges. To do so, other methods than the one described in Chapter 2 should be investigated in order to solve the problem. The filtration study described in Chapter 3 shows that filtering open ocean water samples did not have any significant effect on the TA measurements. This supports the validity and quality of the TA measured in the last 20 years. In Chapters 4 and 5, predicting TA using the hydrographic properties in a multi linear regression scheme has proven to be successful. On the other hand, this was not the case for TCO$_2$ at the surface of the ocean. Other methods should be investigated. An example is the use neural networks, which can be successful for solving complex non-linear relationships. Finally, the changes in CO$_2$ due to natural and anthropogenic perturbations were successfully identified in the Atlantic and Indian oceans. Overall, the increase in biological activity increased the acidity of the ocean at the surface and the increase in anthropogenic CO$_2$ signal increased the acidity of the ocean in deep waters. The acidification of the ocean has caused the
aragonite saturation horizon to shoal. Because the methods used to calculate $\text{CO}_2^{\text{anth}}$ are invalid at the surface, changes in surface anthropogenic CO$_2$ and its effect on the carbonate system were not identified. This study also showed that these same methods, TrOCA 2004 and 2007, are invalid in intermediate and recently ventilated water masses. The Transit Time Distribution (TTD) method (Waugh et al., 2004; Waugh et al., 2006) that calculates $\text{CO}_2^{\text{anth}}$ at the surface is also biased. This method assumes that the disequilibrium of carbon between the atmosphere and the surface ocean did not change during the last few hundred years. This assumption is a source of error for the estimation of $\text{CO}_2^{\text{anth}}$ (Alvarez et al., 2009). Therefore, it is essential to develop a method that can accurately measure or estimate the anthropogenic CO$_2$ at the surface and in relatively young and ventilated waters.
References


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Touratier, F., Azouzi, L., Goyet, C. 2007. CFC-11, $\delta^{14}$C and $^3$H tracers as a means to assess anthropogenic CO$_2$ concentrations in the ocean. Tellus B 59(2), 318-325.


Appendix 1: pH measurement and accuracy

During the CLIVAR A16N 2003, A16S 2005 and I9N 2005 cruises, pH was measured using an m-cresol purple indicator with an absorbance at 578 nm and 434 nm ratio of 1.625. This method, described in SOP 6b (Dickson et al., 2007), yields a pH value on the total scale, pH_t. The latter was then converted to pH_{sws}, which is the pH on the seawater scale. On the total scale, the concentration of hydrogen ion considered, H^+, is equal to the concentration of free H^+ ions plus those associated with sulfate (SO_4^{2-}). The seawater scale considers the interaction of H^+ with both sulfate (SO_4^{2-}) and fluoride (F^-) ions. To convert pH from the total to seawater scale, the following relationship is used

\[
\text{pH}_{\text{sws}} = \text{pH}_t + \log(1+ \frac{[\text{SO}_4^{2-}]}{K_{\text{HSO}_4}}) - \log(1+ \frac{[\text{SO}_4^{2-}]}{K_{\text{HSO}_4}} + \frac{[\text{F}^-]}{K_{\text{HF}}})
\]

with the concentration of sulfate and fluoride ions estimated from salinity S, the dissociation constants of HSO_4, K_{\text{HSO}_4} (Dickson, 1990a) and the dissociation constants of HF, K_{HF} (Dickson and Riley, 1979). Measurements made on duplicate samples and TRIS buffers prepared as per the recipe of Millero (1986a), provided validation of the precision (± 0.003) and accuracy (± 0.008) of the pH measurements. The reproducibility of the pH systems was monitored throughout the cruises by making measurements on CRM, Tris
buffers and duplicates on the same sample. The results are given in Table A1.1. The reproducibility of pH measurements made on CRM, Tris buffer and on duplicates were quite good. The measurements made on the manual system were slightly better than the automatic system. Occasionally, samples drawn from the syringe on the automatic system entrained an air bubble because the valve was improperly opened, tubing was pinched, or the syringe plunger was dry and became stuck in the barrel. Sporadically, the software would lose communication with the microprocessor-controlled syringe pumps and stop the analysis. This problem was resolved by following the steps outlined in the software to reestablish communication. During the I9N 2007 cruise, the ambient temperature of the hydrolab reached 30°C and stayed like this for almost three weeks. This high temperature caused the valves to malfunction and draw samples from the wrong syringe. The Automated analyzer was shut down after station 123 and replaced by the manual one. The spectroscopic values of pH were compared to those measured by the titration systems. The mean values are reasonable (0.003), but the scatter is quite large (± 0.012) due to problems with the electrode discussed in Chapter 3.

Table A1.1 Accuracy and precision of pH measurements using CRM and Tris buffer.

<table>
<thead>
<tr>
<th></th>
<th>CRM</th>
<th>Tris</th>
<th>Duplicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automated system</td>
<td>8.081 ± 0.006</td>
<td>0.001 ± 0.005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n = 41</td>
<td>n = 19</td>
<td></td>
</tr>
<tr>
<td>Manual system</td>
<td>7.869 ± 0.005</td>
<td>8.084 ± 0.007</td>
<td>0.000 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>n = 77</td>
<td>n = 36</td>
<td>n = 183</td>
</tr>
</tbody>
</table>
Appendix 2: Neutral density surfaces $\gamma^n$

A neutral surface is the surface where a fluid parcel advects adiabatically and isentropically without doing any work against gravity (McDougall, 1987). The neutral density $\gamma^n$ is defined as the continuous analogue version of the discrete potential density, $\sigma$. This means that instead of analyzing data in several potential density ranges, at different pressure references (e.g. $\sigma_0$, $\sigma_3$, $\sigma_4$… with 0 db, 3000 db and 4000 db as pressure reference), interpreting any property or result along one neutral density surface $\gamma^p$ would become more appropriate. The property $\gamma^p$ is a function of hydrographic (salinity, temperature, and pressure) and geographic data (latitude and longitude). It therefore accounts for the compressibility nature of seawater and is easier to use than the potential density at different levels in the ocean (e.g. 1000 db or 4000 db). At 2000 db for instance, the pressure difference between $\gamma^p$ and $\sigma_0$ could be 200 db because of the nonlinear nature of the equation of state (You, 1998a). Jackett and McDougall (1997) used the Levitus climatology data sets to derive the world’s oceans $\gamma^n$. Chapters 4 and 5 use the hydrographic parameters of the A16 and I9N cruises, respectively to derive $\gamma^n$. For quick comparison purposes, the potential densities of the Atlantic and Indian oceans in the literature can be converted to neutral densities using the linear relationship given in Figure A2.1 and Figure A2.2, respectively. The potential densities $\sigma_0$, $\sigma_1$, $\sigma_3$ and $\sigma_4$ are those calculated at the pressure reference 0, 1000, 3000 and 4000 db, respectively.
Figure A2.1 Relationship between potential density ($\sigma_0$, $\sigma_1$, $\sigma_3$, and $\sigma_4$) and neutral surface density $\gamma^n$ based on the 2003-2005 A16 cruises.
Figure A2.2 Relationship between potential density ($\sigma_0$, $\sigma_1$, $\sigma_3$, and $\sigma_4$) and neutral surface density $\gamma^n$ based on the 2007 I9N cruise.