Decadal changes in the aragonite and calcite saturation state of the Pacific Ocean

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[1] Based on measurements from the WOCE/JGOFS global CO_2 survey, the CLIVAR/CO_2 Repeat Hydrography Program and the Canadian Line P survey, we have observed an average decrease of 0.34% yr^{-1} in the saturation state of surface seawater in the Pacific Ocean with respect to aragonite and calcite. The upward migrations of the aragonite and calcite saturation horizons, averaging about 1 to 2 m yr^{-1}, are the direct result of the uptake of anthropogenic CO_2 by the oceans and regional changes in circulation and biogeochemical processes. The shoaling of the saturation horizon is regionally variable, with more rapid shoaling in the South Pacific where there is a larger uptake of anthropogenic CO_2. In some locations, particularly in the North Pacific Subtropical Gyre and in the California Current, the decadal changes in circulation can be the dominant factor in controlling the migration of the saturation horizon. If CO_2 emissions continue as projected over the rest of this century, the resulting changes in the marine carbonate system would mean that many coral reef systems in the Pacific would no longer be able to sustain a sufficiently high rate of calcification to maintain the viability of these ecosystems as a whole, and these changes perhaps could seriously impact the thousands of marine species that depend on them for survival.

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1. Introduction

[2] Carbon dioxide is one of the most important of the "green-house" gases in the atmosphere, contributing to the heat balance of the earth as well as affecting the calcium carbonate ($CaCO_3$) equilibrium in the oceans. As a result of the industrial and agricultural activities of humans since the beginning of the industrial era, atmospheric CO_2 concentrations have increased about 40% [*Prentice et al.*, 2001; *Royal Society*, 2005; *Solomon et al.*, 2007; *Sabine and Feely*, 2007]. Atmospheric CO_2 concentrations are now higher than has been experienced for at least the last 800,000 years [*Keeling and Whorf*, 2004; *Lüthi et al.*, 2008]. The global oceans are the largest natural long-term reservoir for the excess CO_2, currently absorbing 26% of the combined carbon released from deforestation and fossil fuel combustion up to the present and could absorb as much as 90% of the excess CO_2 over the next several millennia [*Archer et al.*, 1998; *Canadell et al.*, 2007; *Le Quéré et al.*, 2009; *Sabine et al.*, 2011]. Seawater chemistry is now changing in response to continually rising atmospheric CO_2 levels. For example, the mean surface ocean pH has decreased by about 0.1 units since the beginning of the industrial revolution [*Caldeira and Wickett*, 2003, 2005; *Feely et al.*, 2004, 2009a; *Orr et al.*, 2005]. If current carbon dioxide emission trends continue this process, commonly known as "ocean acidification," will occur at rates and extents that have not been observed for tens of millions of years [*Feely et al.*, 2004, 2009a; *Kump et al.*, 2009]. A doubling of atmospheric carbon dioxide concentration from pre-industrial levels, which could occur in as little as 50 years, is predicted to correspond with an average sea surface pH decrease of about 0.25 [*Caldeira and Wickett*, 2005].

[3] A growing number of research studies have demonstrated that under increasing ocean acidification conditions

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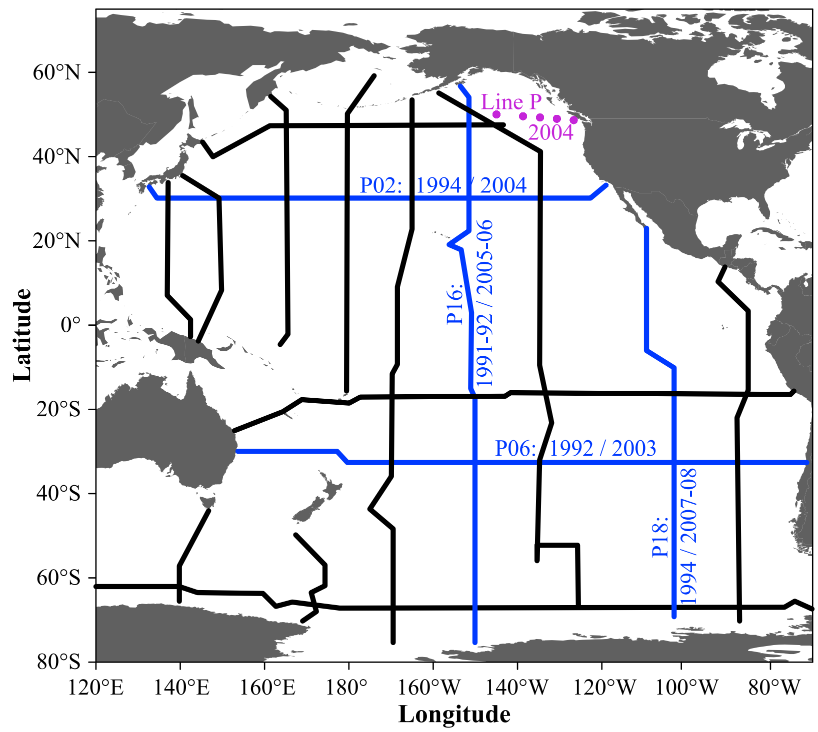

Figure 1. Map of the cruise sections used in this study from the international WOCE/JGOFS/OACES Global CO_2 Survey, the CLIVAR/CO_2 Repeat Hydrography survey lines and the Line P stations in the Pacific Ocean.

many marine $CaCO_3$-secreting species will soon be suffering adverse impacts. For example, the rate at which reef-building corals make their skeletons has been shown to decrease under increasing ocean acidification [*Gattuso et al.*, 1998; *Marubini and Atkinson*, 1999; *Marubini and Thake*, 1999; *Ohde and Van Woesik*, 1999; *Langdon et al.*, 2000, 2003; *Leclercq et al.*, 2000, 2002; *Marubini et al.*, 2003; *Guinotte et al.*, 2003; *Ohde and Hossain*, 2004; *Langdon and Atkinson*, 2005; *Silverman et al.*, 2007, 2009; *Anthony et al.*, 2008]. These reduced growth rates could make many reef ecosystems unsuitable for calcification by the end of this century. Similar decreases in the calcification rates of planktonic coccolithophores and foraminifera have been observed when the organisms were subjected to CO_2-enriched waters [*Spero et al.*, 1997; *Riebesell et al.*, 2000; *Zondervan et al.*, 2001, 2002; *Sciandra et al.*, 2003; *Seibel and Fabry*, 2003; *Riebesell*, 2004; *Delille et al.*, 2005; *Engel et al.*, 2005; *Fabry et al.*, 2008; *Guinotte and Fabry*, 2008; *Doney et al.*, 2009; *Riebesell and Tortell*, 2011]. Most of these studies have demonstrated a close positive correlation between the rate of marine calcification and the aragonite/calcite saturation state of seawater. Saturation state with respect to aragonite and calcite carbonate minerals is calculated as the product of the concentrations of Ca^{2+} and CO_3^{2-} divided by the apparent (i.e., relevant to seawater conditions) stoichiometric solubility product:

$$\Omega\text{arag} = \left[Ca^{+2}\right]\left[CO_3^{-2}\right]/\text{Ksp*arag} \tag{1}$$

$$\Omega\text{cal} = \left[Ca^{+2}\right]\left[CO_3^{-2}\right]/\text{Ksp*cal} \tag{2}$$

where Ωarag and Ωcal are calculated using the CO2SYS program developed by *Lewis and Wallace* [1998]. As atmospheric pCO_2 increases and equilibrates with seawater, carbonate ion is consumed via a series of reactions:

$$CO_{2(aq)} + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \tag{3}$$

$$\text{and } H^+ + CO_3^{-2} \rightleftarrows HCO_3^- \tag{4}$$

where the reaction of $CO_{2(aq)}$ with H_2O (3) leads to an initial increase in dissolved H_2CO_3 from the gas exchange process. These reactions are reversible and the thermodynamics of these reactions in seawater are well established [*Millero et al.*, 2002, and references therein]. It is these reactions in combination with the slow circulation and primary production throughout the global oceans that control pH over timescales of hundreds to thousands of years. By the end of this century, ocean acidification could decrease surface ocean pH by as much as 0.4 pH units relative to pre-industrial values [*Orr et al.*, 2005; *Meehl et al.*, 2007; *Joos et al.*, 2011]. The corresponding carbonate ion decrease in the surface waters would be approximately 50% [*Kleypas et al.*, 2006; *Feely et al.*, 2009b]. Thus, an increase in pCO_2 and a corresponding reduction in CO_3^{2-} concentration will result in a reduction of saturation state with respect to $CaCO_3$ phases. In this paper, we document the decreases in the aragonite and calcite saturation state of the Pacific Ocean between the time of the WOCE/JGOFS Global CO_2 Survey and CLIVAR/CO_2 Repeat Hydrography Program. We will show how the changes in saturation state are affected by both the influx of anthropogenic CO_2 as well as

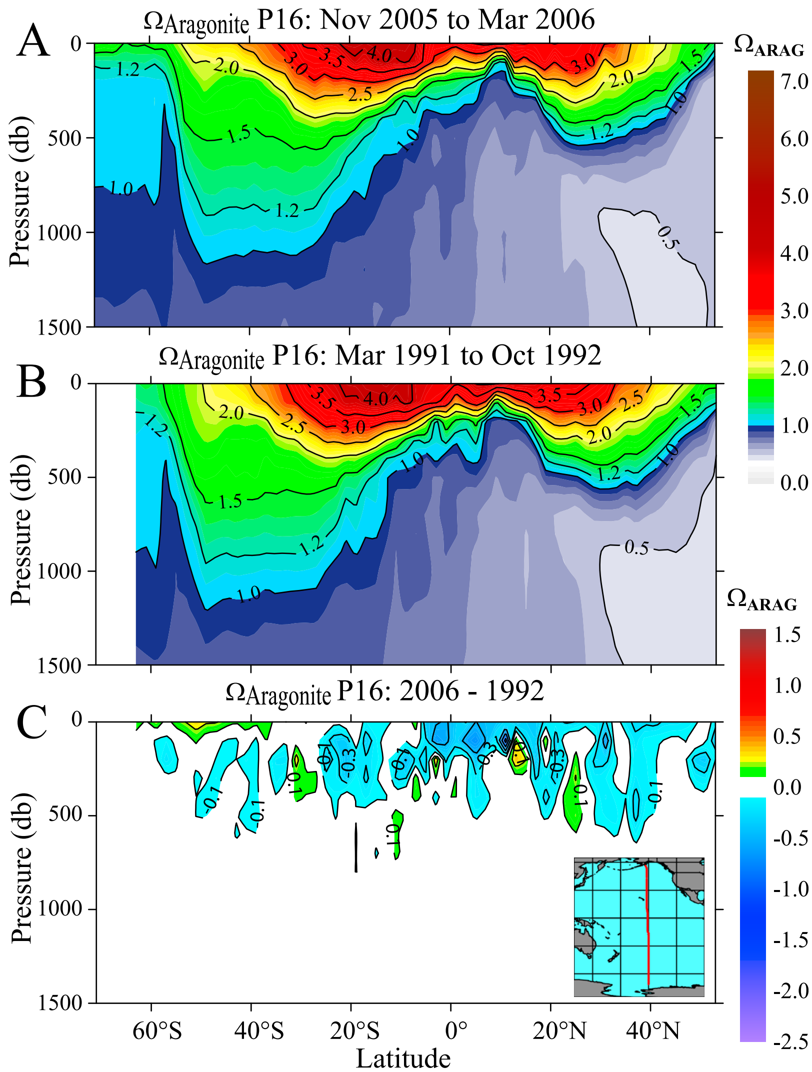

Figure 2. Aragonite saturation state for (a) (Ωarag) for 2005/06, (b) 1991/02, and (c) Ωarag difference (2005/06–1991/02) along the P16 section from Antarctica to Alaska.

changes in overturning circulation over the time interval between the observations.

2. The Data Sets

2.1. WOCE/JGOFS Global CO_2 Survey

[4] Carbon system measurements were made on 26 WOCE/JGOFS Global CO_2 Survey cruises between 1991 and 1996 in the Pacific Ocean [*Feely et al.*, 2004; *Sabine et al.*, 2004]. Dissolved inorganic carbon (DIC) was analyzed on all cruises using a coulometric titration [*U.S. Department of Energy (DOE)*, 1994; *Johnson and Wallace*, 1992; *Johnson et al.*, 1985, 1987; *Ono et al.*, 1998]. Total alkalinity [*DOE*, 1994; *Millero et al.*, 1993; *Ono et al.*, 1998] was the most common second carbon parameter on the cruises. However, on the P16N cruise, pH was measured as the second parameter [*Feely et al.*, 2009c; *Byrne et al.*, 2010]. Total alkalinity (TA) was calculated for these cruises using the *Mehrbach et al.* [1973] carbonate constants as refit by *Dickson and Millero* [1987]. The overall accuracy of the DIC data was ~3 μmol kg^{-1} and ~5 μmol kg^{-1} for the TA data [*Lamb et al.*, 2002]. The final Pacific data set, containing about 35,000 sample locations with DIC and TA values, has been described in detail [*Key et al.*, 2004; *Sabine et al.*, 2005]. Both the WOCE/JGOFS Global CO_2 data set and the CLIVAR/CO_2 Repeat Hydrography data set are available from the CLIVAR and Carbon Hydrographic Data Office (http://whpo.ucsd.edu/) and the Carbon Dioxide Information Analysis Center (http://cdiac.ornl.gov/oceans/home.html).

2.2. CLIVAR/CO_2 Repeat Hydrography Data

[5] For the CLIVAR/CO_2 Repeat Hydrography cruises, samples were collected and analyzed for DIC, TA, oxygen, nutrient, tracer, and hydrographic data at repeat sections along the P02 (from Japan to the United States along 30°N; 2004), P16S (152°W from Tahiti to 71°S; 2005), P16N (along 152°W from Tahiti to Alaska; 2006), P6 (along 30°S from Australia to Chile; 2003), and P18 (along 110°W; 2007–2008 and 1994) transects (Figure 1). As a minimum, DIC and TA were measured on all the cruises. The CLIVAR/CO_2 data quality was confirmed by daily analyses of Certified Reference Materials [*Dickson*, 2001; *Dickson et al.*,

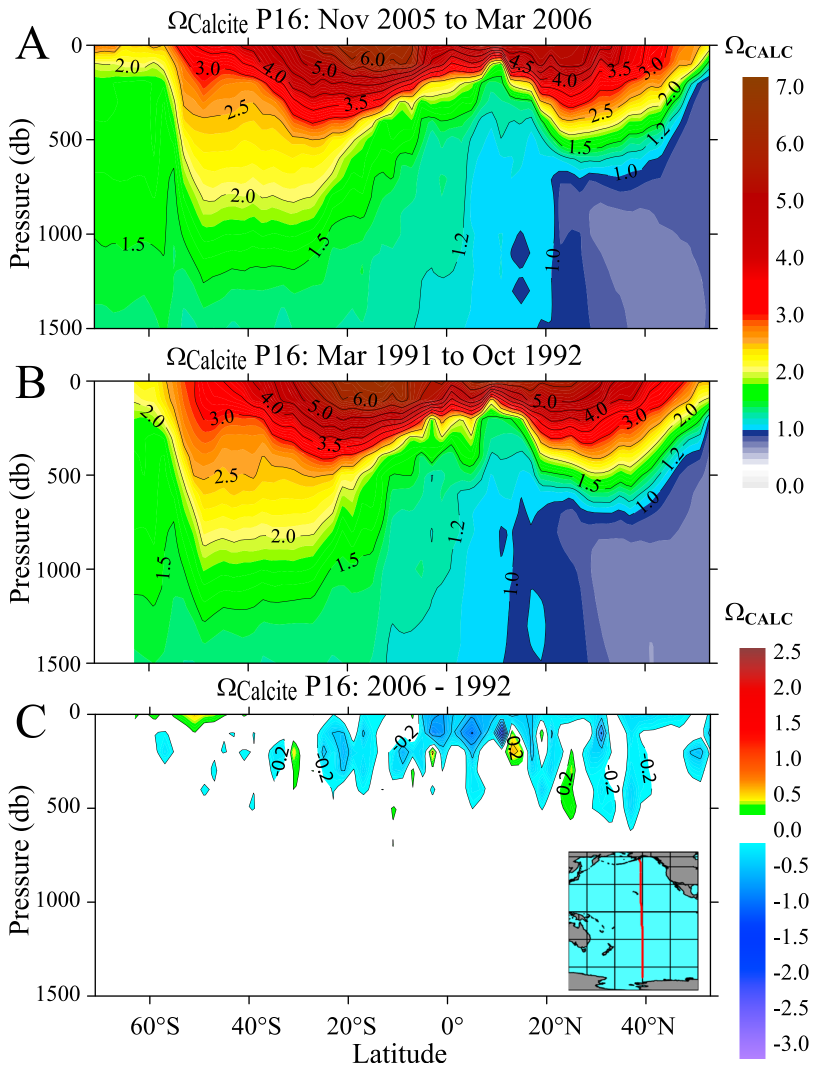

Figure 3. Calcite saturation state (Ωcal) for (a) 2005/06, (b) 1991/02, and (c) Ωcal difference (2005/06 – 1991/02) along the P16 section from Antarctica to Alaska.

2007]. The consistency of the individual cruises was checked by comparing deepwater (>2000 m) values at stations that overlapped on P16S and P16N, and at the intersection of P16N and P02 [*Sabine et al.*, 2008]. These quality checks suggest that the DIC data are accurate within ~1 μmol kg^{-1} and the TA data are accurate within ~3 μmol kg^{-1}. The P16 pH measurements were made spectrophotometrically with an overall precision of ±0.0015 [*Byrne et al.*, 2010]. The CLIVAR/CO_2 Repeat Hydrography physical and chemical data were compared to the 1990s WOCE/JGOFS data along the two P16N and P02 sections by examining values on isopycnal surfaces in deep water. The only observed offsets were found in the 1994 P02 TA data that required an adjustment of +10 μmol kg^{-1}.

2.3. Line P

[6] For the 2004 February Line P data [*Miller et al.*, 2009], samples were collected and analyzed for DIC, TA, oxygen, nutrient, and hydrographic data along Line P (Figure 1). DIC and TA were measured employing the CLIVAR/CO_2 methodology (Section 2.1 above), and were confirmed by daily analyses of Certified Reference Materials and secondary standards directly calibrated against the certified materials [*Dickson*, 2001; *Dickson et al.*, 2007]. The consistency of the data were checked by comparing deepwater (>2000 m) values at stations that were close to the P16N section. These quality checks suggest that the DIC data are accurate within ~2 μmol kg^{-1} and the TA data are accurate within ~3 μmol kg^{-1}.

3. Data Analysis

3.1. Total Change in Aragonite/Calcite Saturation State Between Cruises

[7] Total changes in aragonite and calcite saturation levels were calculated using the CO2SYS program developed by *Lewis and Wallace* [1998]. The in situ degree of seawater saturation with respect to aragonite and calcite calculated from equations (1) and (2), where the Ca^{+2} concentrations are estimated from salinity and carbonate ion concentrations, are calculated from the dissolved inorganic carbon (DIC) and total alkalinity (TA) data. The pressure effect on the

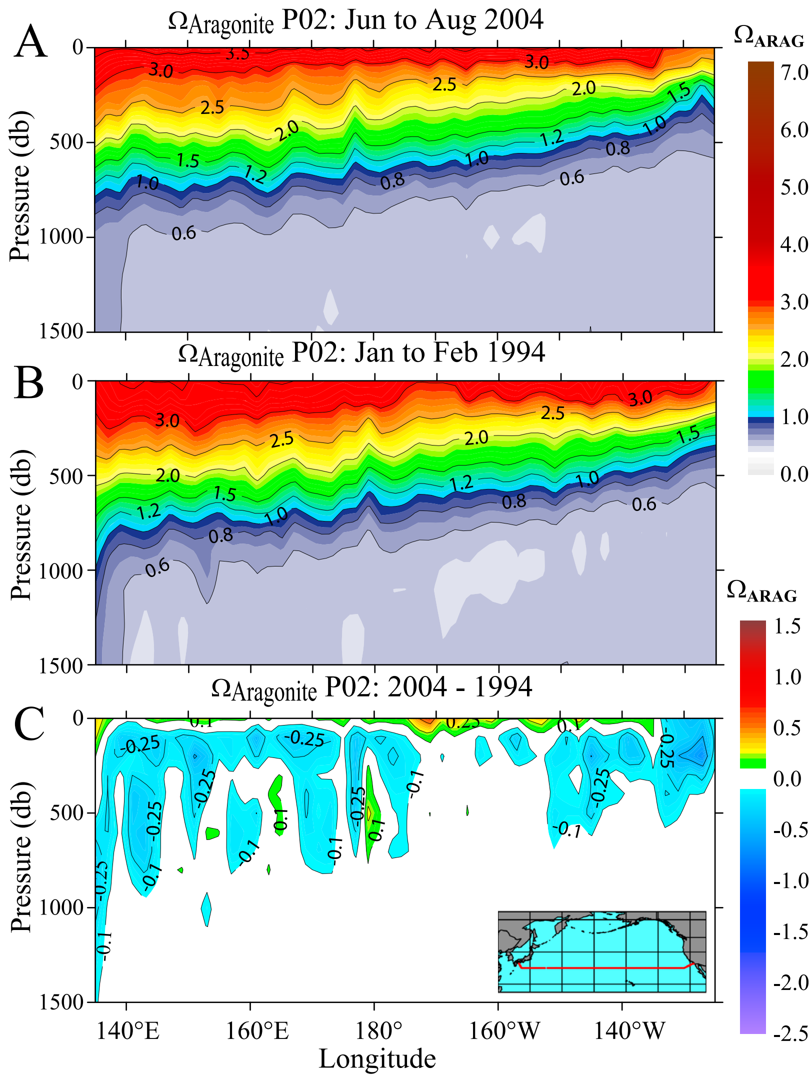

Figure 4. Aragonite saturation state for (a) (Ωarag) for 2004, (b) 1994, and (c) Ωarag difference (2004–1994) along the P02 section from Japan to Mexico.

solubility is estimated from the equation of *Mucci* [1983] that includes the adjustments to the constants recommended by *Millero* [1995]. The overall uncertainties of aragonite and calcite saturation state are on the order of ± 0.03 and ± 0.05, respectively. The aragonite solubility calculations are in agreement with field experiments of the first instance of aragonite dissolution based on freshly collected pteropod shells placed into a spectrophotometer under conditions of ambient temperature and pressure [*Feely et al.*, 1988]. The total changes in aragonite or calcite saturation state were calculated as the gridded and interpolated differences between saturation values estimated for each pair of repeat cruises.

3.2. Changes in Aragonite/Calcite Saturation State Due to Changes in Anthropogenic CO_2 and Changes in Circulation and Mixing Processes

[8] The extended multiple linear regression (e-MLR) approach developed by *Friis et al.* [2005] was used for this analysis. In this procedure, the observed DIC and TA data are fitted as a function of physical (e.g., temperature, salinity) and chemical (e.g., phosphate, nitrate, silicate) parameters. Multiple linear regression fits are determined for each cruise using the same set of independent physical and chemical parameters [*Sabine et al.*, 2008]. The coefficients of these two fits are then subtracted, such that the resulting equation directly determines the net DIC and TA change between the two cruises. Using this method, much of the random variability in the independent parameter measurements is minimized for both cruises, and the propagation of errors that results from a particular independent parameter's inability to describe completely the dependent parameter are partially canceled out when the coefficients are subtracted [*Friis et al.*, 2005; *Sabine et al.*, 2008; *Wanninkhof et al.*, 2010; *Goodkin et al.*, 2011]. The determination of which parameters are selected for use is based on the statistical fits of the field data. Almost all studies to date have used salinity (S) and potential temperature (θ) to characterize the conservative characteristics. For our study, all repeat cruises were fit as a function of: S, θ, potential density, phosphate (P) and silicate (Si). Oxygen, or apparent oxygen utilization (AOU), was specifically not used for the fit in anticipation of

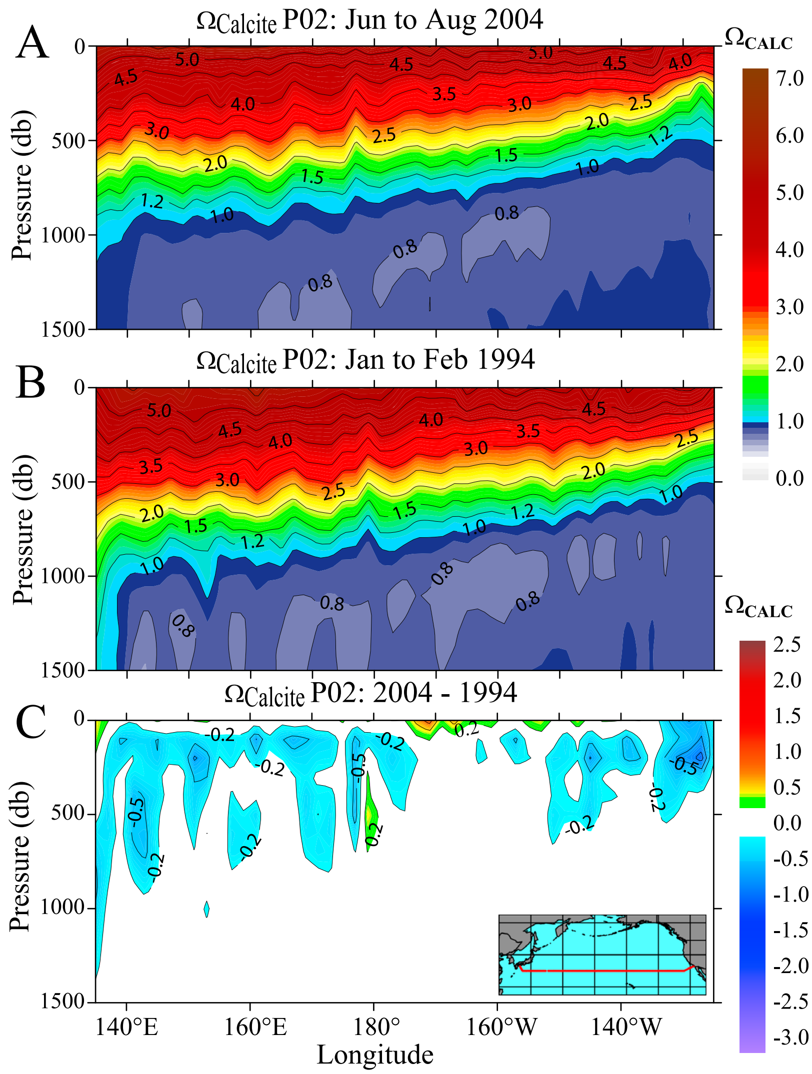

Figure 5. Calcite saturation state for (a) (Ωcal) for 2004, (b) 1994, and (c) Ωcal difference (2004–1994) along the P02 from Japan to Mexico.

using AOU to characterize the difference in the circulation changes as described below. The P16 and P02 lines were subdivided into three segments and fit with three independent e-MLR functions [*Sabine et al.*, 2008]. The divisions were chosen by first fitting all of the data along a section with a single function and plotting the residuals as a function of latitude (P16 and P18) or longitude (P02). The residuals resulted in a pattern, which indicated that the tropical Pacific (15°S–15°N) had a different pattern of residuals, and that of P02 should be divided at 145°E and 140°W. To estimate the circulation effects, AOU was fit using the same e-MLR approach that was applied to the carbon data. The coefficients and standard errors for the AOU fits are given by *Sabine et al.* [2008], employing a carbon to oxygen stoichiometric ratio of 117/170 [*Anderson and Sarmiento*, 1994]. *Sabine et al.* [2008] determined that approximately 80% of the DIC change in the North Pacific over the last decade is the result of circulation/ventilation changes and that circulation effects resulted in almost no change in the South Pacific [*Sabine et al.*, 2008, Figure 2]. The central core of the maximum AOU change appears to be associated with the 26.6 potential density surface in the subtropical North Pacific, consistent with previous studies [*Emerson et al.*, 2001; *Ono et al.*, 2001; *Deutsch et al.*, 2006]. The change in aragonite/calcite saturation state that is due to the uptake of anthropogenic CO_2 is then determined by subtracting this circulation and/or ventilation change in DIC from the total change in DIC and getting the anthropogenic CO_2 change by difference. These new values are then used to estimate the change in saturation state that is due to the anthropogenic component. The technique is based on the assumption of constancy of the processes controlling the coefficients in the e-MLR equations. Significant changes in elemental ratios over time could lead to an underestimation of anthropogenic CO_2 contribution [*Wanninkhof et al.*, 2010].

4. Results

4.1. The P16 South-North Transects (2005–06 Versus 1991)

[9] There is significant shoaling of the aragonite and calcite saturation horizons from south to north in the Pacific

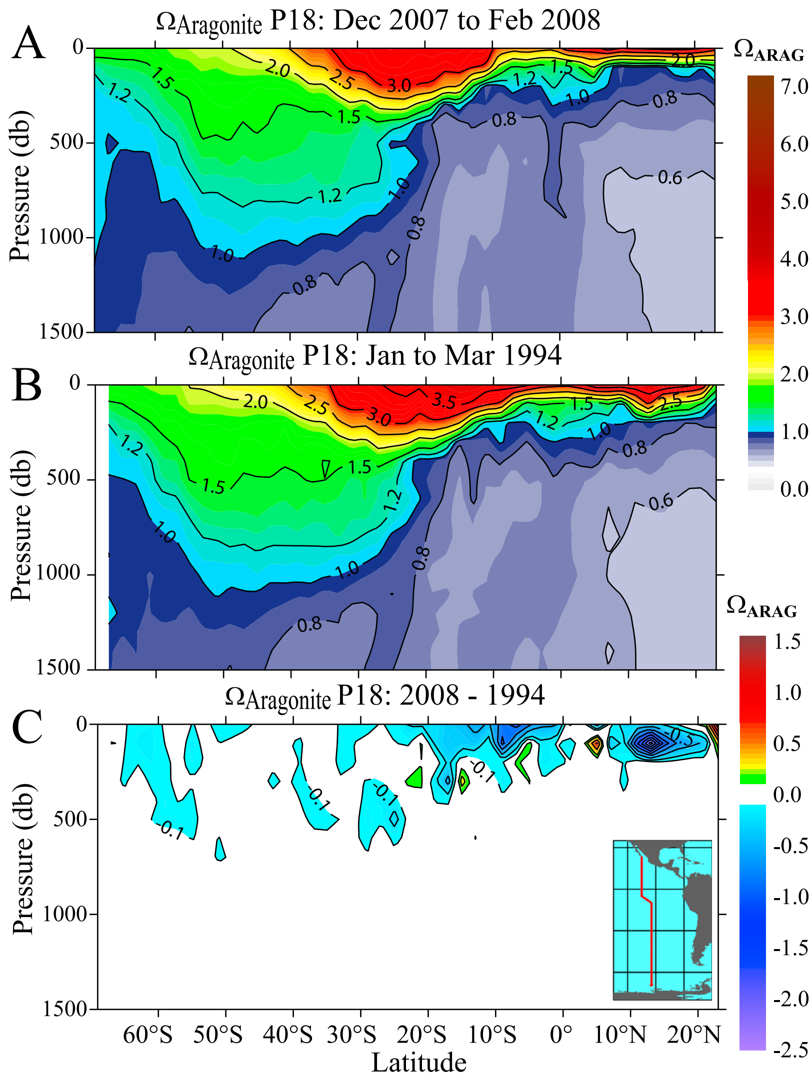

Figure 6. Aragonite saturation state for (a) (Ωarag) for 2008, (b) 1994, and (c) Ωarag difference (2008–1994) along the P18 section from Antarctica to Mexico.

because of the higher DIC concentrations relative to TA at shallower depths in the northern hemisphere that result from enhanced upwelling at the equator, at 10°N, and north of about 40°N in the subarctic North Pacific (Figures 2 and 3, respectively). The 2005–06 CLIVAR/CO_2 Repeat Hydrography cruise data show a general upward migration of the aragonite saturation horizon of about 1–2 m yr^{-1} along the entire cruise track and an average decrease in the overall aragonite saturation state of about 4.5% in near-surface waters over the 14-year interval between the two cruises. Most of the change in the aragonite saturation state, ranging from +0.3 to −0.5, occurred in the upper 600 m of the water column (Figure 2). The positive changes in saturation state are observed near frontal zones associated with the North Equatorial Current at about 12–14°N where mesoscale changes in salinity and temperature predominate [*Fine et al.*, 2001]. The calcite saturation horizon (Ωcal = 1.0) rose from depths greater than 2800 m in the South Pacific and shoaled to depths less than 200 m between 40°N and 50°N (Figure 3). On average, the calcite saturation horizon in the Pacific shoaled about 1 m yr^{-1} from 1991 to 2006.

4.2. The P02 West-East Sections (2004 Versus 1994) in the North Pacific

[10] The west-to-east shoaling of the aragonite and calcite saturation horizons (Figures 4 and 5) is consistent with the shoaling of the TA concentrations shown in *Feely et al.* [2002]. This shoaling is the result of the deep ventilation in the western Pacific and anticyclonic circulation in the North Pacific. The 2004 P02 aragonite saturation horizon (Ωarag = 1.0) shoaled from depths of about 750 m near 140°E to 150 m near 122°W. From there, it deepened slightly to about 300 m near the North American coast. The data indicate a distinct upward migration of the saturation horizon along portions of the section. In particular, for the California Current region between 135°W and 120°W, the saturation horizon in the eastern subtropical Pacific west of the continental shelf has risen more than 100 m since the previous WOCE cruise in 1994. Most of the changes of the saturation state (ranging from +0.5 to −0.5 for aragonite and +0.8 to −0.8 for calcite) occurred in the upper 800 m of the water column, deepening toward the west (Figures 4 and 5). The

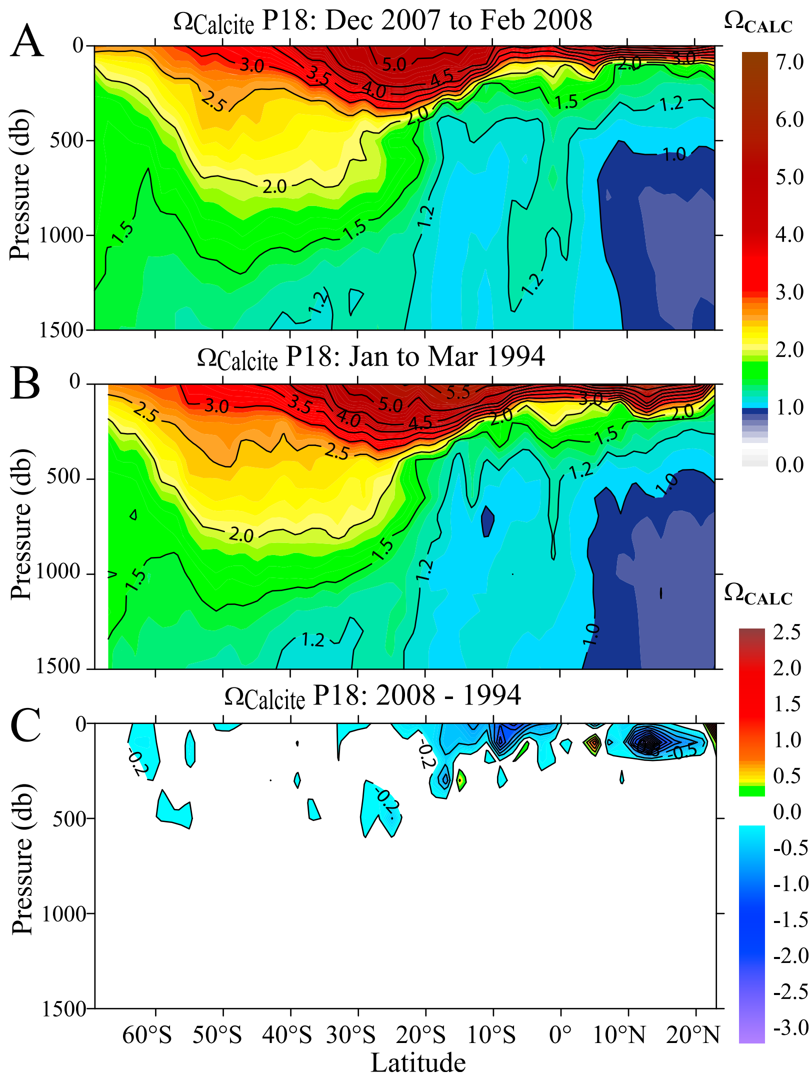

Figure 7. Calcite saturation state for (a) (Ωcal) for 2008, (b) 1994, and (c) Ωcal difference (2008–1994) along the P18 section from Antarctica to Mexico.

decreases in saturation state occurred between 100 and 600 m and are located in regions where changes in ventilation and uptake of anthropogenic CO_2 have major negative impacts on saturation state.

4.3. P18 South-North Transects Along 110°W (2007–2008 Versus 1994)

[11] The P18 sections show similar shoaling of the aragonite and calcite saturation horizons from south to north compared with the P16 sections (Figures 6 and 7). The 2007–2008 aragonite saturation depth shoaled from about 1000 m near 40°S to <250 m near 10°S, deepened to ~300 m at the equator, and shoaled to ~150 m near 10°N. The general pattern of aragonite and calcite saturation along the 2007–2008 P18 transect is generally consistent with previous results for 1994 along the same section (Figure 6). The 2007–2008 P18 cruise data show a general upward migration of the aragonite saturation horizon of about 1–2 m yr^{-1} along the cruise track and an average decrease in the overall aragonite saturation state of ~4.5% in near-surface waters over the 14-year period between the two cruises. Most of the change in the aragonite saturation state, ranging from +0.2 to −0.8, occurred in the upper 500 m of the water column (Figure 6). The calcite saturation horizon rose from depths greater than 2800 m in the South Pacific and shoaled to about 550 m near 10°N in the North Pacific (Figure 7).

4.4. The P06 West-East Section (2003) in the South Pacific

[12] The distributions of temperature, salinity, DIC, and aragonite saturation for the P06 west-east 2003 section in the South Pacific are plotted in Figure 8. Since insufficient alkalinity data were collected for the previous WOCE section, it is not possible to make aragonite saturation state comparisons with the earlier data. Nevertheless, this is the first complete east-west aragonite saturation section for the South Pacific. As with the North Pacific, the aragonite saturation horizon shoals from west to east in the South Pacific, starting from depths around 1200 m near 160°W to 800 m near 80°W in the deeper waters. In the eastern South Pacific, there is a large mass of eastward increasing high-DIC, high-salinity, undersaturated water ranging in depths

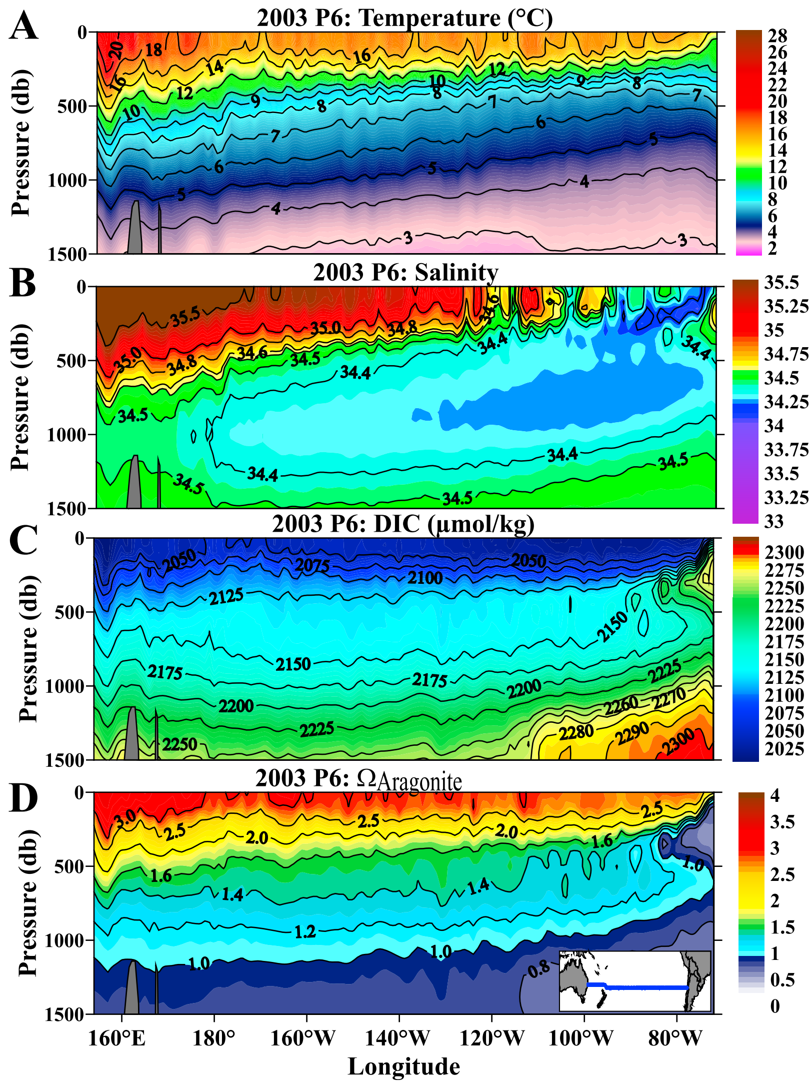

Figure 8. West-east distribution of (a) temperature, (b) salinity, (c) DIC, and (d) Ωarag along the P06 Repeat Hydrography section in the South Pacific. The data were collected during the Japanese Repeat Hydrography Section in 2003.

from about 100 to 600 m near the coast of South America. This extremely shallow undersaturated water is probably the result of the uptake of anthropogenic CO_2 combined with high amounts of remineralized organic matter along the South American coast, leading to an unusual, heretofore unrecognized, ocean acidification site close to the coast. This site is similar to what has been observed off the west coast of Africa in the South Atlantic [*Chung et al.*, 2003; *Feely et al.*, 2004] and off the west coast of North America [*Feely et al.*, 2008]. In those cases, the oxidation of organic matter augmented by the uptake of anthropogenic CO_2 accounted for the observed local reduction in the aragonite saturation state.

4.5. Line P

[13] The Line P aragonite and calcite saturation sections for February 2004 are shown in Figures 9a and 9b. At that time the aragonite saturation horizon (Ωarag = 1.0) was shallowest (∼160 m) at the westernmost Station "P" From there, it deepened slightly to about 190 m near the North American coast off Vancouver Island. The calcite saturation data also suggested a distinct shoaling of the Ωcal = 1 horizon to a depth of about 200 m near station "P" and a gradual deepening of the saturation horizon toward the east. This is consistent with the predominance of downwelling of water properties and carbon system parameters along the coast during the winter months [*Ianson and Allen*, 2002; *Ianson et al.*, 2009]. The shallow depths of the aragonite and calcite saturation horizons occur in regions where uptake of anthropogenic CO_2 produces a significant shoaling effect on saturation state (see Section 5 below).

5. Discussion

5.1. Estimates of the Relative Role of Anthropogenic CO_2 and Circulation Changes on the Vertical Migration of the Aragonite/Calcite Saturation Horizons

[14] The repeat sections allow us to determine the changes in saturation state and upward migration of the saturation horizons over the time intervals of the cruises. These changes can be caused by: 1) uptake of anthropogenic CO_2;

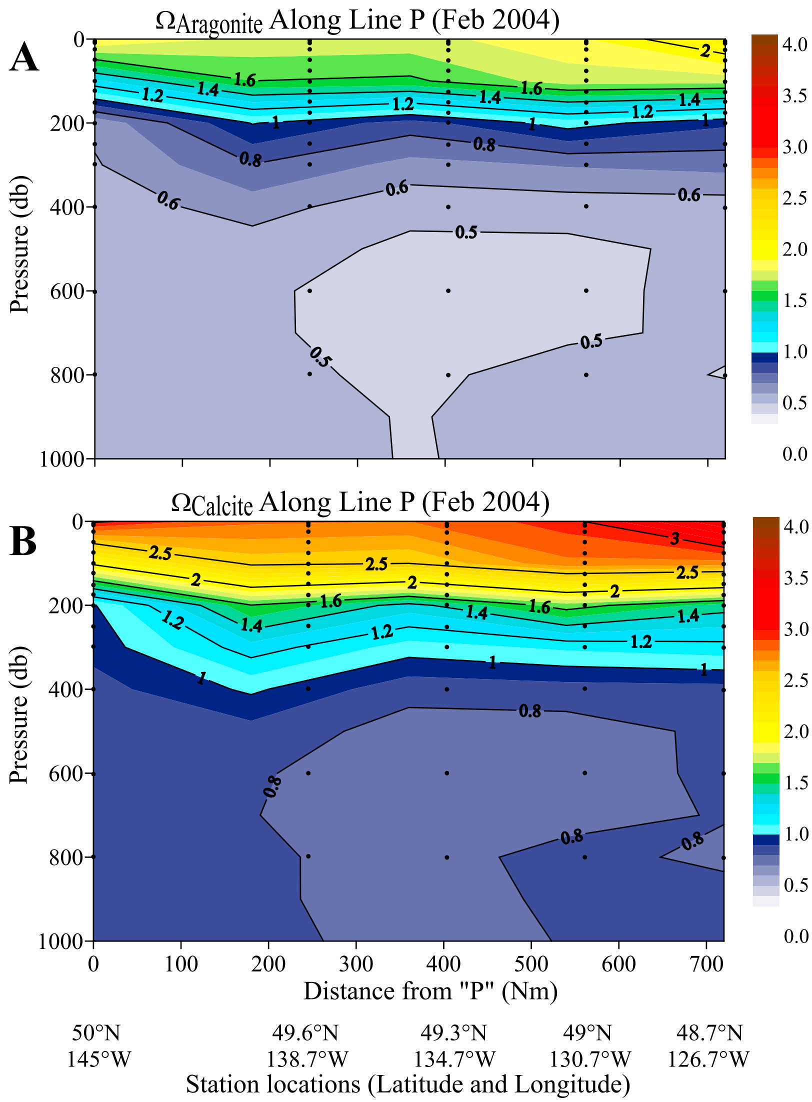

Figure 9. Line P sections of (a) aragonite saturation and (b) calcite saturation from Vancouver Island to Ocean Station "Papa" for February 2004.

2) changes in circulation and/or ventilation; and 3) changes in biogeochemical processes. The calculated change in aragonite saturation state between the decadal cruises for each of the transects, which is based on the increase in anthropogenic CO_2 as calculated by *Sabine et al.* [2008], is shown in Figure 10. The decrease of the saturation state is regionally variable, with much deeper changes in the South Pacific and western North Pacific than the eastern North Pacific. This is largely due to the fact that the South Pacific and western North Pacific take up more anthropogenic CO_2 than the eastern North Pacific [*Sabine et al.*, 2004, 2008]. The situation in the North Pacific is complicated by the fact that in the subpolar North Pacific most of the DIC increase was caused by a decrease in the overturning circulation due to reduced winds since the 1970s, causing an increase in apparent oxygen utilization (AOU) rather than uptake of anthropogenic CO_2 [*McPhaden and Zhang*, 2002; *Deutsch et al.*, 2006; *Mecking et al.*, 2008; *Sabine et al.*, 2008; *Sabine and Tanhua*, 2010].

[15] The average shoaling rate of the Ωarag = 1.0 horizon and the average change in saturation state in the upper 100 m due to uptake of anthropogenic CO_2 are given in Table 1. The results indicate an upward migration of the aragonite saturation horizon on the order of 1–2 m yr^{-1}, with higher shoaling rates in the South Pacific than in the North Pacific because of the higher anthropogenic CO_2 uptake in the South Pacific. These rates are roughly consistent with the model estimates for the Pacific Ocean given in *Orr et al.* [2005] for an IPCC IS92a "business as usual" scenario.

[16] The far eastern Pacific data indicate an average upward migration of the aragonite saturation horizon of more than 5 m yr^{-1} in the California Current (Figure 4). This large and unexpected change is primarily due to a significant change in the circulation and water mass properties of the California Current since 1998. A careful analysis of the CalCOFI data [*Di Lorenzo et al.*, 2005] noted large-scale cooling and freshening of the water from 50 to 200 m within the California Current. The authors interpreted these observations

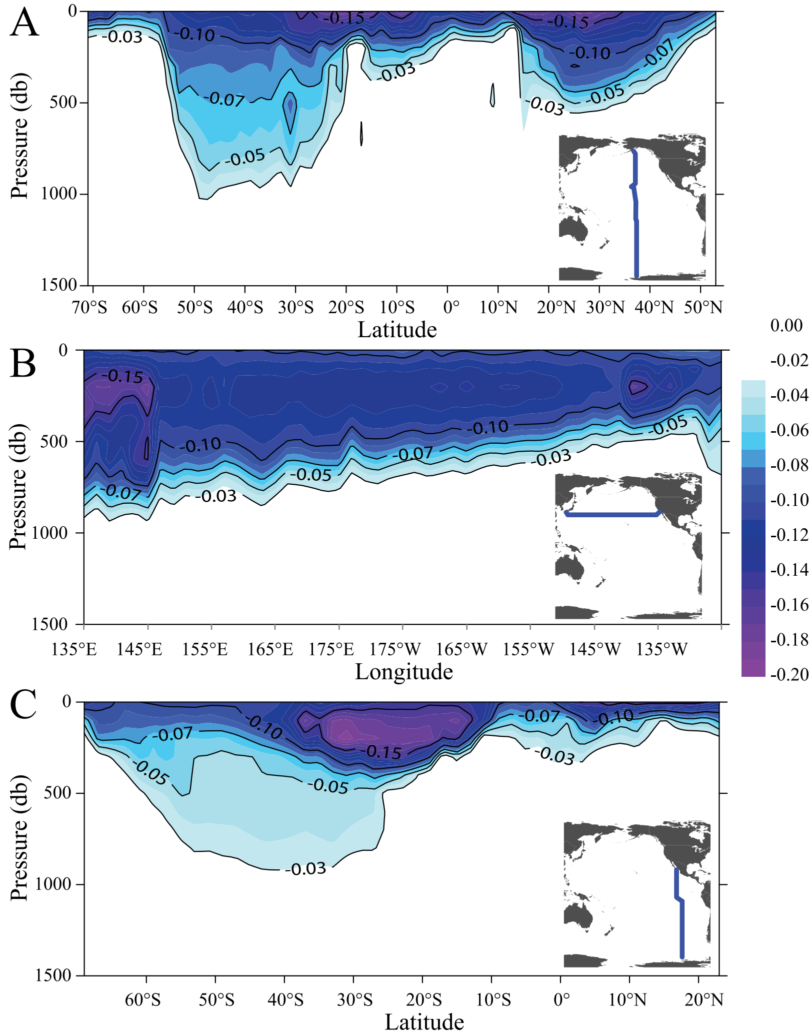

Figure 10. Change in aragonite saturation state (Ωarag) along the (a) P16, (b) PO2, and (c) P18 sections based on the anthropogenic CO_2 differences from *Sabine et al.* [2008].

as indicating an enhancement of the southward advection of cool, lower-salinity subarctic water coming from the subarctic North Pacific. This interpretation is consistent with our observations of increased amounts of cool, CO_2-rich water at the same depths in the 2004 data set compared with the 1994 data. Physical and chemical changes of the water mass properties in the California Current were apparently the major factors controlling the upward migration of the aragonite saturation horizon and probably played a significant role in controlling the seasonal upwelling of corrosive "ocean-acidified" water onto the continental shelf [*Feely et al.*, 2008]. These results suggest that large-scale changes in circulation can be as important as, or in some cases, more important than, the direct effects of anthropogenic CO_2 uptake in affecting the location of corrosive water in some parts of the eastern Pacific. More detailed information on the temporal variability of the physical and chemical properties of the California Current is required before we can accurately predict how these long-term changes will affect our coastal ecosystems. In particular, recent modeling of primary production and nitrate transport processes in the California Current ecosystem suggests that increased nitrate supply and upwelling of lower pH source waters resulting from increased stratification of the North Pacific will cause an enhanced intensification of the acidification in this region over the next century [*Rykaczewski and Dunne*, 2010].

5.2. Potential Impacts of the Changes in Aragonite and Calcite Saturation State in the Pacific Ocean

[17] To date, there has been an overall decrease of about 16% in the aragonite saturation state of North and South Pacific surface and intermediate waters since the beginning

Table 1. Average Shoaling of the Aragonite Saturation Horizon (Ωarag = 1.0) and Decrease in the Aragonite Saturation State in the Upper 100 m in the South and North Pacific Due to the Uptake of Anthropogenic CO_2

Region	P16 (m yr^{-1})	P18 (m yr^{-1})	P16 Ωarag Decrease (% yr^{-1})	P18 Ωarag Decrease (% yr^{-1})
South Pacific	2.01 ± 0.80	1.81 ± 0.85	0.34 ± 0.05	0.35 ± 0.05
North Pacific	0.81 ± 0.71[a]	1.14 ± 0.55	0.34 ± 0.07[a]	0.33 ± 0.01

[a]Includes PO2 value at the crossover point.

of the industrial revolution, and a decrease of about 0.34% yr^{-1} over the last two decades (Table 1) [*Feely et al.*, 2004, 2009b; *Caldeira and Wickett*, 2005; *Orr et al.*, 2005; *Kleypas et al.*, 2006]. These rates of decrease are in excellent agreement with those reported by *Ishii et al.* [2011] for the near-surface waters off Japan in the western Pacific. If continued or enhanced over the coming decades, changes in saturation state like this can cause significant changes in overall calcification rates for many species of open-ocean and coastal marine calcifiers including corals, foraminifera, coccolithophores, pteropods, and oyster larvae [*Spero et al.*, 1997; *Bijma et al.*, 1999, 2002; *Kleypas et al.*, 1999a, 1999b; *Marubini and Atkinson*, 1999; *Langdon et al.*, 2000, 2003; *Riebesell et al.*, 2000; *Marubini et al.*, 2001; *Zondervan et al.*, 2001, 2002; *Guinotte et al.*, 2003, 2006; *Reynaud et al.*, 2003; *Sciandra et al.*, 2003; *Seibel and Fabry*, 2003; *Green et al.*, 2004; *Marshall and Clode*, 2004; *Riebesell*, 2004; *Delille et al.*, 2005; *Engel et al.*, 2005; *Langdon and Atkinson*, 2005; *Kleypas et al.*, 2006; *Hoegh-Guldberg et al.*, 2007; *Guinotte and Fabry*, 2008; *De'ath et al.*, 2009; *Hoegh-Guldberg and Bruno*, 2010; *Lischka et al.*, 2011; *Barton et al.*, 2012]. If CO_2 emissions continue as projected over the rest of this century, based on the Intergovernmental Panel on Climate Change (IPCC) IS92a CO_2 emission scenario ($\sim$800 μatm CO_2 in the year 2100), recent models predict that by the end of this century the surface water DIC could probably increase by more than 12%, and the carbonate ion concentration would decrease by almost 50% [*Orr et al.*, 2005; *Kleypas et al.*, 2006; *McNeil and Matear*, 2006, 2008; *Feely et al.*, 2009b; *Joos et al.*, 2011]. This extent of change in the carbonate species concentrations would cause aragonite undersaturation in all of the Southern Ocean (south of 50°S) sector of the South Pacific and portions of the subarctic North Pacific throughout the entire water column [*Caldeira and Wickett*, 2005; *Orr et al.*, 2005; *Cao and Caldeira*, 2008; *McNeil and Matear*, 2008; *Steinacher et al.*, 2009; *Joos et al.*, 2011]. Throughout the rest of the Pacific, the surface waters would be supersaturated with respect to aragonite and calcite, but the overall saturation state would decrease by as much as 30–40% depending on location [*Cao and Caldeira*, 2008; *Steinacher et al.*, 2009; *Feely et al.*, 2009a; *Joos et al.*, 2011]. These changes would likely be sufficient to cause major changes in calcification rates [*Kleypas et al.*, 1999b; *Hoegh-Guldberg et al.*, 2007; *Hoegh-Guldberg and Bruno*, 2010]. For example, the model output of *Caldeira and Wickett* [2005] predicts a 34% drop in aragonite saturation for a tripling of the pre-industrial CO_2 levels by the end of this century. Such a drop in aragonite saturation would cause many coral reef ecosystems to fall well below their normal environmental limit (aragonite saturation $<\sim$3.2) for reef calcification under natural conditions [*Kleypas et al.*, 1999b; *Silverman et al.*, 2009]. For many reefs in the Pacific, changes like these would make calcification unsustainable for corals, possibly compromising the viability of these ecosystems [*Fabricius et al.*, 2011]. Similar decreases in calcification rates would be expected for mussels, clams, and oysters in coastal regions affected by ocean acidification [*Green et al.*, 2004; *Gazeau et al.*, 2007; *Talmage and Gobler*, 2009; *Barton et al.*, 2012]. Other research indicates that many species of shellfish are highly sensitive to higher-than-normal CO_2 levels, and that high rates of mortality appear to be directly correlated with the higher CO_2 levels [*Kurihara and Shirayama*, 2004; *Fabry et al.*, 2008; *Guinotte and Fabry*, 2008; *Kurihara*, 2008; *Kroeker et al.*, 2010]. However, it should be noted that aragonite and calcite saturation conditions in coastal waters are more difficult to predict over the long-term because of higher degree of complexity of the physical and biogeochemical processes that cause enhanced localized spatial and temporal variability [*Bates et al.*, 2010; *Andersson et al.*, 2005, 2006; *Feely et al.*, 2008; *Shamberger et al.*, 2011]. Nevertheless, it seems certain that as the levels of dissolved CO_2 in seawater rise, the skeletal growth rates of many calcium-secreting species will be reduced in many oceanic regions as a result of the effects of ocean acidification. Thus, if we continue to rapidly increase the CO_2 levels in the oceans, there will very likely be direct and profound impacts on marine ecosystems.

6. Conclusions

[18] Over the past 250 years, since the beginning of the industrial revolution, there has been about a 16% decrease in aragonite and calcite saturation state in the Pacific Ocean. From repeat oceanographic surveys, we have observed an average 0.34% yr^{-1} decrease in the saturation state of surface seawater with respect to aragonite and calcite over a 14-year period. This has caused an upward migration of the aragonite and calcite saturation horizons toward the ocean surface on the order of 1–2 m yr^{-1}. These changes are the result of the uptake of anthropogenic CO_2 by the oceans, as well as other smaller scale regional changes in circulation over decadal time scales. If CO_2 emissions continue as projected out to the end this century, the resulting changes in the marine carbonate system would mean that many coral reef systems in the Pacific would probably no longer be able to maintain the necessary rate of calcification required to sustain their vitality.

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References

Anderson, L. A., and J. L. Sarmiento (1994), Redfield ratios of remineralization determined by nutrient data analysis, *Global Biogeochem. Cycles*, *8*, 65–80, doi:10.1029/93GB03318.

Andersson, A. J., F. T. Mackenzie, and A. Lerman (2005), Coastal ocean and carbonate ecosystems in the high CO_2 world of the Anthropocene, *Am. J. Sci.*, *305*, 875–918, doi:10.2475/ajs.305.9.875.

Andersson, A. J., F. T. Mackenzie, and A. Lerman (2006), Coastal ocean CO_2-carbonic acid-carbonate sediment system of the Anthropocene, *Global Biogeochem. Cycles*, *20*, GB1S92, doi:10.1029/2005GB002506.

Anthony, K. R. N., D. I. Kline, G. Diaz-Pulido, S. Dove, and O. Hoegh-Guldberg (2008), Ocean acidification causes bleaching and productivity loss in coral reef builders, *Proc. Natl. Acad. Sci. U. S. A.*, *105*(45), 17,442–17,446, doi:10.1073/pnas.0804478105.

Archer, D., H. Kheshgi, and E. Maier-Reimer (1998), Dynamics of fossil fuel CO_2 neutralization by marine $CaCO_3$, *Global Biogeochem. Cycles*, *12*, 259–276, doi:10.1029/98GB00744.

Barton, A., B. Hales, G. G. Waldbusser, C. Langdon, and R. A. Feely (2012), The Pacific oyster, Crassostrea gigas, shows negative correlation to naturally elevated carbon dioxide levels: Implications for near-term ocean acidification effects, *Limnol. Oceanogr.*, *57*(3), 698–710, doi:10.4319/lo.2012.57.3.0698.

Bates, N. R., A. Amat, and A. J. Andersson (2010), Feedbacks and responses of coral calcification on the Bermuda reef system to seasonal changes in biological processes and ocean acidification, *Biogeosciences*, *7*(8), 2509–2530, doi:10.5194/bg-7-2509-2010.

Bijma, J., H. J. Spero, and D. W. Lea (1999), Reassessing foraminiferal stable isotope geochemistry: Impact of the oceanic carbonate systems (experimental results), in *Use of Proxies in Paleoceanography: Examples From the South Atlantic*, edited by G. Fisher and G. Wefer, pp. 489–512, Springer, New York, doi:10.1007/978-3-642-58646-0_20.

Bijma, J., B. Hönisch, and R. E. Zeebe (2002), Impact of the ocean carbonate chemistry on living foraminiferal shell weight: Comment on "Carbonate ion concentration in glacial-age deepwaters of the Caribbean Sea" by W. S. Broecker and E. Clark, *Geochem. Geophys. Geosyst.*, *3*(11), 1064, doi:10.1029/2002GC000388.

Byrne, R. H., S. Mecking, R. A. Feely, and X. Liu (2010), Direct observations of basin-wide acidification of the North Pacific Ocean, *Geophys. Res. Lett.*, *37*, L02601, doi:10.1029/2009GL040999.

Caldeira, K., and M. E. Wickett (2003), Anthropogenic carbon and ocean pH, *Nature*, *425*, 365, doi:10.1038/425365a.

Caldeira, K., and M. E. Wickett (2005), Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean, *J. Geophys. Res.*, *110*, C09S04, doi:10.1029/2004JC002671.

Canadell, J. G., C. Le Quéré, M. R. Raupach, C. B. Field, E. T. Buitenhuis, P. Ciais, T. J. Conway, N. P. Gillett, R. A. Houghton, and G. Marland (2007), Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity, and efficiency of natural sinks, *Proc. Natl. Acad. Sci. U. S. A.*, *104*, 18,866–18,870, doi:10.1073/pnas.0702737104.

Cao, L., and K. Caldeira (2008), Atmospheric CO_2 stabilization and ocean acidification, *Geophys. Res. Lett.*, *35*, L19609, doi:10.1029/2008GL035072.

Chung, S.-N., K. Lee, R. A. Feely, C. L. Sabine, F. J. Millero, R. Wanninkhof, J. L. Bullister, R. M. Key, and T.-H. Peng (2003), Calcium carbonate budget in the Atlantic Ocean based on water column inorganic carbon chemistry, *Global Biogeochem. Cycles*, *17*(4), 1093, doi:10.1029/2002GB002001.

De'ath, G., J. M. Lough, and K. E. Fabricius (2009), Declining coral calcification on the Great Barrier Reef, *Science*, *323*, 116–119, doi:10.1126/science.1165283.

Delille, B., et al. (2005), Response of primary production and calcification to changes of $p$$CO_2$ during experimental blooms of the coccolithophorid *Emiliania huxleyi*, *Global Biogeochem. Cycles*, *19*, GB2023, doi:10.1029/2004GB002318.

Deutsch, C., S. Emerson, and L. Thompson (2006), Physical-biological interactions in North Pacific oxygen variability, *J. Geophys. Res.*, *111*, C09S90, doi:10.1029/2005JC003179.

Dickson, A. G. (2001), Reference materials for oceanic CO_2 measurements, *Oceanography*, *14*(4), 21–22.

Dickson, A. G., and F. J. Millero (1987), A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, *Deep Sea Res., Part A*, *34*(10), 1733–1743, doi:10.1016/0198-0149(87)90021-5.

Dickson, A. G., C. L. Sabine, and J. R. Christian (Eds.) (2007), *Guide to Best Practices for Ocean CO_2 Measurements*, *PICES Spec. Publ.*, vol. 3, 191 pp., N. Pac. Mar. Sci. Organ., Sidney, B. C., Canada.

Di Lorenzo, E., A. J. Miller, N. Schneider, and J. C. McWilliam (2005), The warming of the California Current system dynamics and ecosystem implications, *J. Phys. Oceanogr.*, *35*, 336–362, doi:10.1175/JPO-2690.1.

Doney, S. C., V. J. Fabry, R. A. Feely, and J. A. Kleypas (2009), Ocean acidification: The other CO_2 problem, *Annu. Rev. Mar. Sci.*, *1*, 169–192, doi:10.1146/annurev.marine.010908.163834.

Emerson, S., S. Mecking, and J. Abell (2001), The biological pump in the subtropical North Pacific Ocean: Nutrient sources, Redfield ratios, and recent changes, *Global Biogeochem. Cycles*, *15*(3), 535–554, doi:10.1029/2000GB001320.

Engel, A., et al. (2005), Testing the direct effect of CO_2 concentration on a bloom of the coccolithophorid Emiliania huxleyi in mesocosm experiments, *Limnol. Oceanogr.*, *50*, 493–507, doi:10.4319/lo.2005.50.2.0493.

Fabricius, K. A., et al. (2011), Losers and winners in coral reefs acclimatized to elevated carbon dioxide concentrations, *Nat. Clim. Change*, *1*(3), 165, doi:10.1038/nclimate1122.

Fabry, V. J., B. A. Seibel, R. A. Feely, and J. C. Orr (2008), Impacts of ocean acidification on marine fauna and ecosystem processes, *ICES J. Mar. Sci.*, *65*(3), 414–432, doi:10.1093/icesjms/fsn048.

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

Feely, R. A., et al. (2002), In situ calcium carbonate dissolution in the Pacific Ocean, *Global Biogeochem. Cycles*, *16*(4), 1144, doi:10.1029/2002GB001866.

Feely, R. A., C. L. Sabine, K. Lee, W. Berelson, J. Kleypas, V. J. Fabry, and F. J. Millero (2004), Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans, *Science*, *305*, 362–366, doi:10.1126/science.1097329.

Feely, R. A., C. L. Sabine, J. M. Hernandez-Ayon, D. Ianson, and B. Hales (2008), Evidence for upwelling of corrosive "acidified" water onto the Continental Shelf, *Science*, *320*(5882), 1490–1492, doi:10.1126/science.1155676.

Feely, R. A., S. C. Doney, and S. R. Cooley (2009a), Ocean acidification: Present conditions and future changes in a high-CO_2 world, *Oceanography*, *22*(4), 36–47, doi:10.5670/oceanog.2009.95.

Feely, R. A., J. Orr, V. J. Fabry, J. A. Kleypas, C. L. Sabine, and C. Langdon (2009b), Present and future changes in seawater chemistry due to ocean acidification, in *Carbon Sequestration and Its Role in the Global Carbon Cycle*, *Geophys. Monogr. Ser.*, vol. 183, edited by B. J. McPherson and E. T. Sundquist, pp. 175–188, AGU, Washington, D. C., doi:10.1029/2005GM000337.

Feely, R. A., et al. (2009c), Carbon dioxide, hydrographic, and chemical data obtained during the R/Vs *Roger Revelle* and *Thomas Thompson* repeat hydrography cruises in the Pacific Ocean: CLIVAR CO_2 sections P16S_2005(6 January–19 February, 2005) and P16N_2006(13 February–30 March, 2006), edited by A. Kozyr, *Rep. ORNL/CDIAC-155*, 56 pp., Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., U.S. Dep. of Energy, Oak Ridge, Tenn.

Fine, R. A., K. A. Maillet, K. F. Sullivan, and D. Willey (2001), Circulation and ventilation flux of the Pacific Ocean, *J. Geophys. Res.*, *106*(C10), 22,159–22,178, doi:10.1029/1999JC000184.

Friis, K., A. Körtzinger, J. Pätsch, and D. W. R. Wallace (2005), On the temporal increase of anthropogenic CO_2 in the subpolar North Atlantic, *Deep Sea Res., Part I*, *52*, 681–698, doi:10.1016/j.dsr.2004.11.017.

Gattuso, J.-P., M. Frankignoulle, I. Bourge, S. Romaine, and R. W. Buddemeier (1998), Effect of calcium carbonate saturation of seawater on coral calcification, *Global Planet. Change*, *18*, 37–46, doi:10.1016/S0921-8181(98)00035-6.

Gazeau, F., C. Quibler, J. M. Jansen, J.-P. Gattuso, J. J. Middelburg, and C. H. R. Heip (2007), Impact of elevated CO_2 on shellfish calcification, *Geophys. Res. Lett.*, *34*, L07603, doi:10.1029/2006GL028554.

Goodkin, N. F., N. M. Levine, S. C. Doney, and R. Wanninkhof (2011), Impacts of temporal CO_2 and climate trends on the detection of anthropogenic CO_2 accumulation, *Global Biogeochem. Cycles*, *25*, GB3023, doi:10.1029/2010GB004009.

Green, M. A., M. E. Jones, C. L. Boudreau, R. L. Moore, and B. A. Westman (2004), Dissolution mortality of juvenile bivalves in coastal marine deposits, *Limnol. Oceanogr.*, *49*(3), 727–734, doi:10.4319/lo.2004.49.3.0727.

Guinotte, J. M., and V. J. Fabry (2008), Ocean acidification and its potential effects on marine ecosystems, *Ann. N. Y. Acad. Sci.*, *1134*, 320–342, doi:10.1196/annals.1439.013.

Guinotte, J. M., R. W. Buddemeier, and J. A. Kleypas (2003), Future coral reef habitat marginality: Temporal and spatial effects of climate change in the Pacific basin, *Coral Reefs*, *22*, 551–558, doi:10.1007/s00338-003-0331-4.

Guinotte, J. M., J. Orr, S. Cairns, A. Freiwald, L. Morgan, and R. George (2006), Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals?, *Front. Ecol. Environ*, *4*(3), 141–146, doi:10.1890/1540-9295(2006)004[0141:WHCISC]2.0.CO;2.

Hoegh-Guldberg, O., and J. F. Bruno (2010), The impact of climate change on the world's marine ecosystems, *Science*, *328*(5985), 1523–1528, doi:10.1126/science.1189930.

Hoegh-Guldberg, O., et al. (2007), Coral reefs under rapid climate change and ocean acidification, *Science*, *318*(5857), 1737–1742, doi:10.1126/science.1152509.

Ianson, D., and S. E. Allen (2002), A two-dimensional nitrogen and carbon flux model in a coastal upwelling region, *Global Biogeochem. Cycles*, *16*(1), 1011, doi:10.1029/2001GB001451.

Ianson, D., R. A. Feely, C. L. Sabine, and L. W. Juranek (2009), Features of coastal upwelling that determine net air-sea CO_2 flux, *J. Oceanogr.*, *65*(5), 677–687, doi:10.1007/s10872-009-0059-z.

Ishii, M., N. Kosugi, D. Sasano, S. Saito, T. Midorikawa, and H. Y. Inoue (2011), Ocean acidification off the south coast of Japan: A result from time series observations of CO_2 parameters from 1994 to 2008, *J. Geophys. Res.*, *116*, C06022, doi:10.1029/2010JC006831.

Johnson, K. M., and D. W. R. Wallace (1992), The single operator multiparameter metabolic analyzer for total carbon dioxide with coulometric detection, *Res. Summ., 19*, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., Oak Ridge, Tenn., doi:10.2172/10194787.

Johnson, K. M., A. E. King, and J. M. Sieburth (1985), Coulometric TCO_2 analyses for marine studies; an introduction, *Mar. Chem.*, *16*(1), 61–82, doi:10.1016/0304-4203(85)90028-3.

Johnson, K. M., P. J. B. Williams, L. Brändström, and J. M. Sieburth (1987), Coulometric total carbon dioxide analysis for marine studies:

Automation and calibration, *Mar. Chem.*, *21*(2), 117–133, doi:10.1016/0304-4203(87)90033-8.

Joos, F., T. L. Frölicher, M. Steinacher, and G.-K. Plattner (2011), Impact of climate change mitigation on ocean acidification projections, in *Ocean Acidification*, edited by J.-P. Gattuso and L. Hannson, pp. 272–290, Oxford Univ. Press, New York.

Keeling, C. D., and T. P. Whorf (2004), Atmospheric CO_2 records from sites at the SIO air sampling network, in *Trends Online: A Compendium of Data on Global Change*, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., U.S. Dep. of Energy, Oak Ridge, Tenn., doi:10.3334/CDIAC/atg.012.

Key, R. M., A. Kozyr, C. L. Sabine, K. Lee, R. Wanninkhof, J. L. Bullister, R. A. Feely, F. J. Millero, C. Mordy, and T.-H. Peng (2004), A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), *Global Biogeochem. Cycles*, *18*, GB4031, doi:10.1029/2004GB002247.

Kleypas, J. A., R. W. Buddemeier, D. Archer, J.-P. Gattuso, C. Langdon, and B. N. Opdyke (1999a), Geochemical consequences of increased atmospheric carbon dioxide on coral reefs, *Science*, *284*, 118–120, doi:10.1126/science.284.5411.118.

Kleypas, J. A., J. W. McManus, and L. A. B. Meñez (1999b), Environmental limits to coral reef development: Where do we draw the line?, *Am. Zool.*, *39*, 146–159.

Kleypas, J. A., R. A. Feely, V. J. Fabry, C. Langdon, C. L. Sabine, and L. L. Robbins (2006), Impacts of ocean acidification on coral reefs and other marine calcifiers: A guide to future research, report, 88 pp., Natl. Sci. Found., Arlington, Va.

Kroeker, K. J., R. L. Kordas, R. N. Crim, and G. G. Singh (2010), Meta-analysis reveals negative yet variable effects of ocean acidification on marine organisms, *Ecol. Lett.*, *13*(11), 1419–1434, doi:10.1111/j.1461-0248.2010.01518.x.

Kump, L. R., T. J. Bralower, and A. Ridgewell (2009), Ocean acidification in deep time, *Oceanography*, *22*(4), 94–107, doi:10.5670/oceanog.2009.100.

Kurihara, H. (2008), Effects of CO_2-driven ocean acidification on the early developmental stages of invertebrates, *Mar. Ecol. Prog. Ser.*, *373*, 275–284, doi:10.3354/meps07802.

Kurihara, H., and Y. Shirayama (2004), Effects of increased atmospheric CO_2 on sea urchin early development, *Mar. Ecol. Prog. Ser.*, *274*, 161–169, doi:10.3354/meps274161.

Lamb, M. F., et al. (2002), Consistency and synthesis of Pacific Ocean CO_2 survey data, *Deep Sea Res., Part II*, *49*(1–3), 21–58, doi:10.1016/S0967-0645(01)00093-5.

Langdon, C., and M. J. Atkinson (2005), Effect of elevated pCO_2 on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment, *J. Geophys. Res.*, *110*, C09S07, doi:10.1029/2004JC002576.

Langdon, C., T. Takahashi, C. Sweeney, D. Chipman, J. Goddard, F. Marubini, H. Aceves, H. Barnett, and M. J. Atkinson (2000), Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef, *Global Biogeochem. Cycles*, *14*, 639–654, doi:10.1029/1999GB001195.

Langdon, C., W. S. Broecker, D. E. Hammond, E. Glenn, K. Fitzsimmons, S. G. Nelson, T.-H. Peng, I. Hadjas, and G. Bonani (2003), Effect of elevated CO_2 on the community metabolism of an experimental coral reef, *Global Biogeochem. Cycles*, *17*(1), 1011, doi:10.1029/2002GB001941.

Leclercq, N., J.-P. Gattuso, and J. Jaubert (2000), CO_2 partial pressure controls the calcification rate of a coral community, *Global Change Biol.*, *6*, 329–334, doi:10.1046/j.1365-2486.2000.00315.x.

Leclercq, N., J.-P. Gattuso, and J. Jaubert (2002), Primary production, respiration, and calcification of a coral reef mesocosm under increased CO_2 partial pressure, *Limnol. Oceanogr.*, *47*(2), 558–564, doi:10.4319/lo.2002.47.2.0558.

Le Quéré, C., et al. (2009), Trends in the sources and sinks of carbon dioxide, *Nat. Geosci.*, *2*(12), 831–836, doi:10.1038/ngeo689.

Lewis, E., and D. W. R. Wallace (1998), Program developed for CO_2 system calculations, *Rep. 105*, 33 pp., Oak Ridge Natl. Lab., Oak Ridge, Tenn. [Available at http://cdiac.esd.ornl.gov/oceans/co2rprt.html]

Lischka, S., J. Büdenbender, T. Boxhammer, and U. Riebesell (2011), Impact of ocean acidification and elevated temperatures on early juveniles of the polar shelled pteropod *Limacina helicina*: Mortality, shell degradation, and shell growth, *Biogeosciences*, *8*, 919–932, doi:10.5194/bg-8-919-2011.

Lüthi, D., et al. (2008), High-resolution carbon dioxide concentration record 650,000–800,000 years before present, *Nature*, *453*, 379–382, doi:10.1038/nature06949.

Marshall, A. T., and P. Clode (2004), Calcification rate and the effect of temperature in a zooxanthellate and an azooxanthellate scleractinian reef coral, *Coral Reefs*, *23*, 218–224, doi:10.1007/s00338-004-0369-y.

Marubini, F., and M. Atkinson (1999), Effects of lowered pH and elevated nitrate on coral calcification, *Mar. Ecol. Prog. Ser.*, *188*, 117–121, doi:10.3354/meps188117.

Marubini, F., and B. Thake (1999), Bicarbonate addition promotes coral growth, *Limnol. Oceanogr.*, *44*(3), 716–720, doi:10.4319/lo.1999.44.3.0716.

Marubini, F., H. Barnett, C. Langdon, and M. J. Atkinson (2001), Dependence of calcification on light and carbonate ion concentration for the hermatypic coral Porites compressa, *Mar. Ecol. Prog. Ser.*, *220*, 153–162, doi:10.3354/meps220153.

Marubini, F., C. Ferrier-Pages, and J.-P. Cuif (2003), Suppression of skeletal growth in scleractinian corals by decreasing ambient carbonate-ion concentration: A cross-family comparison, *Proc. R. Soc. London, Ser. B*, *270*(1511), 179–184, doi:10.1098/rspb.2002.2212.

McNeil, B. I., and R. J. Matear (2006), Projected climate change impact on oceanic acidification, *Carbon Balance Manage.*, *1*, paper 2, doi:10.1186/1750-0680-1-2.

McNeil, B. I., and R. J. Matear (2008), Southern Ocean acidification: A tipping point at 450-ppm atmospheric CO_2, *Proc. Natl. Acad. Sci. U. S. A.*, *105*(48), 18,860–18,864, doi:10.1073/pnas.0806318105.

McPhaden, M. J., and D. Zhang (2002), Slowdown of the meridional overturning circulation in the upper Pacific Ocean, *Nature*, *415*, 603–608, doi:10.1038/415603a.

Mecking, S., C. Langdon, R. A. Feely, C. L. Sabine, C. A. Deutsch, and D.-H. Min (2008), Climate variability in the North Pacific thermocline diagnosed from oxygen measurements: An update based on the U.S. CLIVAR/CO_2 repeat hydrography cruises, *Global Biogeochem. Cycles*, *22*, GB3015, doi:10.1029/2007GB003101.

Meehl, G. A., et al. (2007), Global climate projections, in *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by S. Solomon et al., pp. 747–845, Cambridge Univ. Press, Cambridge, U. K.

Mehrbach, C., C. H. Culberson, J. E. Hawley, and R. M. Pytkowicz (1973), Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol. Oceanogr.*, *18*, 897–907, doi:10.4319/lo.1973.18.6.0897.

Miller, L. A., M. Davelaar, and J. Linguanti (2009), Line P inorganic carbon data set, cruise 2004–05, February 2004, Inst. of Ocean Sci., Fish. and Oceans Can., Sidney, B. C., Canada.

Millero, F. J. (1995), Thermodynamics of the carbon dioxide system in the oceans, *Geochim. Cosmochim. Acta*, *59*(4), 661–677, doi:10.1016/0016-7037(94)00354-O.

Millero, F. J., J.-Z. Zhang, K. Lee, and D. M. Campbell (1993), Titration alkalinity of seawater, *Mar. Chem.*, *44*(2–4), 153–165, doi:10.1016/0304-4203(93)90200-8.

Millero, F. J., D. Pierrot, K. Lee, R. Wanninkhof, R. A. Feely, C. L. Sabine, R. M. Key, and T. Takahashi (2002), Dissociation constants for carbonic acid determined from field measurements, *Deep Sea Res., Part I*, *49*(10), 1705–1723, doi:10.1016/S0967-0637(02)00093-6.

Mucci, A. (1983), The solubility of calcite and aragonite in seawater at various salinities, temperatures and one atmosphere total pressure, *Am. J. Sci.*, *283*, 780–799, doi:10.2475/ajs.283.7.780.

Ohde, S., and M. M. M. Hossain (2004), Effect of $CaCO_3$ (aragonite) saturation state of seawater on calcification of Porites coral, *Geochem. J.*, *38*(6), 613–621, doi:10.2343/geochemj.38.613.

Ohde, S., and R. Van Woesik (1999), Carbon dioxide flux and metabolic processes of a coral reef, Okinawa, *Bull. Mar. Sci.*, *65*(2), 559–576.

Ono, T., S. Watanabe, K. Okuda, and M. Fukasawa (1998), Distribution of total carbonate and related properties in the North Pacific along 30°N, *J. Geophys. Res.*, *103*(C13), 30,873–30,883, doi:10.1029/1998JC900018.

Ono, T., T. Midorikawa, Y. W. Watanabe, K. Tadokoro, and T. Saino (2001), Temporal increases of phosphate and apparent oxygen utilization in the subsurface waters of western subarctic Pacific from 1968 to 1998, *Geophys. Res. Lett.*, *28*, 3285–3288, doi:10.1029/2001GL012948.

Orr, J. C., et al. (2005), Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms, *Nature*, *437*(7059), 681–686, doi:10.1038/nature04095.

Prentice, I. C., et al. (2001), The carbon cycle and atmospheric carbon dioxide, in *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J. T. Houghton et al., pp. 183–237, Cambridge Univ. Press, New York.

Reynaud, S., N. Leclercq, S. Romaine-Lioud, C. Ferrier-Pagès, J. Jaubert, and J.-P. Gattuso (2003), Interacting effects of CO_2 partial pressure and temperature on photosynthesis and calcification in a scleractinian coral, *Global Change Biol.*, *9*, 1660–1668, doi:10.1046/j.1365-2486.2003.00678.x.

Riebesell, U. (2004), Effects of CO_2 enrichment on marine phytoplankton, *J. Oceanogr.*, *60*, 719–729, doi:10.1007/s10872-004-5764-z.

Riebesell, U., and P. D. Tortell (2011), Effects of ocean acidification on pelagic organisms and ecosystems, in *Ocean Acidification*, edited by J.-P. Gattuso and L. Hansson, pp. 99–121, Oxford Univ. Press, Oxford, U. K.

Riebesell, U., I. Zondervan, B. Rost, P. D. Tortell, R. E. Zeebe, and F. M. M. Morel (2000), Reduced calcification of marine plankton in response to increased atmospheric CO_2, *Nature*, *407*, 364–367, doi:10.1038/35030078.

Royal Society (2005), Ocean acidification due to increasing atmospheric carbon dioxide, *Policy Doc., 12/05*, 223 pp., London.

Rykaczewski, R. R., and J. P. Dunne (2010), Enhanced nutrient supply to the California Current Ecosystem with global warming and increased stratification in an earth system model, *Geophys. Res. Lett.*, *37*, L21606, doi:10.1029/2010GL045019.

Sabine, C. L., and R. A. Feely (2007), The oceanic sink for carbon dioxide, in *Greenhouse Gas Sinks*, edited by D. Reay et al., pp. 31–49, CABI, Wallingford, U. K., doi:10.1079/9781845931896.0031.

Sabine, C. L., and T. Tanhua (2010), Estimation of anthropogenic CO_2 inventories in the ocean, *Annu. Rev. Mar. Sci.*, *2*, 175–198, doi:10.1146/annurev-marine-120308-080947.

Sabine, C. L., et al. (2004), The oceanic sink for anthropogenic CO_2, *Science*, *305*(5682), 367–371, doi:10.1126/science.1097403.

Sabine, C. L., R. M. Key, A. Kozyr, R. A. Feely, R. Wanninkhof, F. J. Millero, T.-H. Peng, J. L. Bullister, and K. Lee (2005), Global Ocean Data Analysis Project (GLODAP): Results and data, *Rep. ORNL/CDIAC-145*, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., U.S. Dep. of Energy, Oak Ridge, Tenn.

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

Sabine, C. L., R. A. Feely, R. Wanninkhof, T. Takahashi, S. Khatiwala, and G.-H. Park (2011), The global ocean carbon cycle, *Bull. Am. Meteorol. Soc.*, *92*(6), S100–S108, doi:10.1175/1520-0477-92.6.S1.

Sciandra, A., J. Harlay, D. Lefèvre, R. Lemée, P. Rimmelin, M. Denis, and J.-P. Gattuso (2003), Response of coccolithophorid Emiliania huxleyi to elevated partial pressure of CO_2 under nitrogen limitation, *Mar. Ecol. Prog. Ser.*, *261*, 111–122, doi:10.3354/meps261111.

Seibel, B. A., and V. J. Fabry (2003), Marine biotic response to elevated carbon dioxide, in *Climate Change and Biodiversity: Synergistic Impacts*, edited by L. Hannah and T. Lovejoy, *Adv. Appl. Biodivers. Sci.*, *4*, 59–67.

Shamberger, K. E. F., R. A. Feely, C. L. Sabine, M. J. Atkinson, E. H. DeCarlo, F. T. Mackenzie, P. S. Drupp, and D. A. Butterfield (2011), Calcification and organic production on a Hawaiian coral reef, *Mar. Chem.*, *127*(1–4), 64–75, doi:10.1016/j.marchem.2011.08.003.

Silverman, J., B. Lazar, and J. Erez (2007), Effect of aragonite saturation, temperature, and nutrients on the community calcification rate of a coral reef, *J. Geophys. Res.*, *112*, C05004, doi:10.1029/2006JC003770.

Silverman, J., B. Lazar, L. Cao, K. Caldeira, and J. Erez (2009), Coral reefs may start dissolving when atmospheric CO_2 doubles, *Geophys. Res. Lett.*, *36*, L05606, doi:10.1029/2008GL036282.

Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, and H. L. Miller (Eds.) (2007), *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge Univ. Press, Cambridge, U. K.

Spero, H. J., J. Bijma, D. W. Lea, and B. E. Bemis (1997), Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes, *Nature*, *390*, 497–500, doi:10.1038/37333.

Steinacher, M., F. Joos, T. L. Frölicher, G.-K. Plattner, and S. C. Doney (2009), Imminent ocean acidification in the Arctic projected with the NCAR global coupled carbon cycle-climate model, *Biogeosciences*, *6*, 515–533, doi:10.5194/bg-6-515-2009.

Talmage, S. C., and C. J. Gobler (2009), The effects of elevated carbon dioxide concentrations on the metamorphosis, size, and survival of larval hard clams (Mercenaria mercenaria), bay scallops (Argopecten irradians), and Eastern oysters (Crassostrea virginica), *Limnol. Oceanogr.*, *54*(6), 2072–2080, doi:10.4319/lo.2009.54.6.2072.

U.S. Department of Energy (1994), Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water, version 2, edited by A. G. Dickson and C. Goyet, *Rep. ORNL/CDIAC-74*, Carbon Dioxide Inf. and Anal. Cent., Oak Ridge Natl. Lab., Oak Ridge, Tenn.

Wanninkhof, R., S. C. Doney, J. L. Bullister, N. M. Levine, M. Warner, and N. Gruber (2010), Detecting anthropogenic CO_2 changes in the interior Atlantic Ocean between 1989 and 2005, *J. Geophys. Res.*, *115*, C11028, doi:10.1029/2010JC006251.

Zondervan, I., R. E. Zeebe, B. Rost, and U. Riebesell (2001), Decreasing marine biogenic calcification: A negative feedback on rising atmospheric pCO_2, *Global Biogeochem. Cycles*, *15*, 507–516, doi:10.1029/2000GB001321.

Zondervan, I., B. Rost, and U. Riebesell (2002), Effect of CO_2 concentration on the PIC/POC ratio in the coccolithophore Emiliania huxleyi grown under light-limiting conditions and different daylengths, *J. Exp. Mar. Biol. Ecol.*, *272*, 55–70, doi:10.1016/S0022-0981(02)00037-0.