Ocean Acidification

Present Conditions and Future Changes in a High-CO₂ World


**ABSTRACT**

The uptake of anthropogenic CO$_2$ by the global ocean induces fundamental changes in seawater chemistry that could have dramatic impacts on biological ecosystems in the upper ocean. Estimates based on the Intergovernmental Panel on Climate Change (IPCC) business-as-usual emission scenarios suggest that atmospheric CO$_2$ levels could approach 800 ppm near the end of the century. Corresponding biogeochemical models for the ocean indicate that surface water pH will drop from a pre-industrial value of about 8.2 to about 7.8 in the IPCC A2 scenario by the end of this century, increasing the ocean’s acidity by about 150% relative to the beginning of the industrial era. In contemporary ocean water, elevated CO$_2$ will also cause substantial reductions in surface water carbonate ion concentrations, in terms of either absolute changes or fractional changes relative to pre-industrial levels. For most open-ocean surface waters, aragonite undersaturation occurs when carbonate ion concentrations drop below approximately 66 µmol kg$^{-1}$. The model projections indicate that aragonite undersaturation will start to occur by about 2020 in the Arctic Ocean and 2050 in the Southern Ocean. By 2050, all of the Arctic will be undersaturated with respect to aragonite, and by 2095, all of the Southern Ocean and parts of the North Pacific will be undersaturated. For calcite, undersaturation occurs when carbonate ion concentration drops below 42 µmol kg$^{-1}$. By 2095, most of the Arctic and some parts of the Bering and Chukchi seas will be undersaturated with respect to calcite. However, in most of the other ocean basins, the surface waters will still be saturated with respect to calcite, but at a level greatly reduced from the present.

**INTRODUCTION**

Since the beginning of the industrial revolution in the mid-eighteenth century, the release of carbon dioxide (CO$_2$) from humankind’s combined industrial and agricultural activities has resulted in an increase in atmospheric CO$_2$ concentrations from approximately 280 to 387 parts per million (ppm), with as much as 50% of the increase occurring in the last three decades. Earth’s atmospheric concentration of CO$_2$ is now higher than it has been for more than 800,000 years (Lüthi et al., 2008), and it is expected to continue to rise at an accelerating rate, leading to significant temperature increases in the atmosphere and the surface ocean in the coming decades. Over the industrial era, the ocean has absorbed about one-quarter of anthropogenic carbon emissions (Sabine and Feely, 2007; Canadell et al., 2007). This absorption has benefited mankind by significantly curtailing the growth of CO$_2$ levels in the atmosphere, thereby reducing the global warming realized to date.

However, when the anthropogenic CO$_2$ is absorbed by seawater, chemical reactions occur that reduce seawater pH, carbonate ion (CO$_3^{2-}$) concentration, and saturation states of the biologically important CaCO$_3$ minerals calcite (Ω$_{calc}$) and aragonite (Ω$_{ar}$) in a process commonly referred to as “ocean acidification” (Broecker and Clarke, 2001; Caldeira and Wickett, 2003, 2005; Orr et al., 2005; Doney et al., 2009; Figure 1). The pH of ocean surface waters has already decreased by about 0.1 since the industrial era began (Caldeira and Wickett, 2003, 2005; Orr et al., 2005), with a decrease of ~ 0.0018 yr$^{-1}$ observed over the last quarter century at several open-ocean time-series sites (Bates, 2007; Bates and Peters, 2007; Santana-Casiano et al., 2007; Dore et al., 2009). By the middle of this century, atmospheric CO$_2$ levels could reach more than 500 ppm, and exceed 800 ppm by the end of the century (Friedlingstein et al., 2006). These CO$_2$ levels would result in an additional decrease in surface water pH of 0.3 units from current conditions, 0.4 from pre-industrial, by 2100, which represents an increase in the ocean’s hydrogen ion (H$^+$) concentration by 2.5 times relative to the beginning of the industrial era. Results from large-scale ocean CO$_2$ surveys and time-series studies over the past two decades show that ocean acidification is a predictable consequence of rising atmospheric CO$_2$ (Feely et al., 2004; Bates and Peters, 2007; Santana-Casiano et al., 2007; Dore et al., 2009; Takahashi et al., 2009) that is independent of the uncertainties and outcomes of climate change.

Seawater carbonate chemistry is governed by a series of abiotic chemical reactions (CO$_2$ dissolution, acid/base chemistry) and biologically mediated reactions (photosynthesis, respiration, and CaCO$_3$ precipitation and dissolution). The first key reaction occurs when CO$_2$ gas from the atmosphere dissolves into seawater:

$$\text{CO}_2^{(\text{atm})} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3^{(\text{aq})}. \quad (1)$$

This exchange is relatively rapid, with atmosphere-ocean equilibration on a time scale of several months, so that surface waters in most ocean regions increase in CO$_2$ concentration from year to year in proportion to the increased
CO₂ concentration in the atmosphere. The second set of reactions involves the hydration of water to form H₂CO₃, which dissociates in subsequent acid-base reactions:

\[
\text{CO}_2(aq) + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- + 2H^+ + CO_3^{2-}. \tag{2}
\]

These reactions are very rapid, on time scales of tens of seconds for CO₂ hydration and microseconds for subsequent acid-base reactions (Zeebe and Wolf-Gladrow, 2001; Dickson et al., 2007). In most applications, the partitioning of inorganic carbonate species can be assumed to be in equilibrium. For typical surface ocean conditions, about 90% of the total dissolved inorganic carbon (DIC) occurs as bicarbonate ions (HCO₃⁻) and ~9% as carbonate ions (CO₃²⁻), with only ~1% remaining as dissolved CO₂(aq) and H₂CO₃. The third key reaction involves the formation and dissolution of solid calcium carbonate minerals (CaCO₃(s)):

\[
Ca^{2+} + CO_3^{2-} \rightarrow \text{CaCO}_3(s). \tag{3}
\]

At equilibrium, the calcium concentration times the carbonate concentration is equal to a constant called the apparent solubility product.

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(\([\text{Ca}^{2+} \times \text{CO}_3^{2-}] = K_{\text{sp}}\)). The saturation state of calcium carbonate mineral phases is defined by
\[\Omega = \frac{[\text{Ca}^{2+}] [\text{CO}_3^{2-}]}{K_{\text{sp}}}\] The apparent solubility product varies with temperature, salinity, and pressure, and differs among calcium carbonate minerals (e.g., calcite, aragonite, and high-Mg calcite; Mucci, 1983). The final important reaction is photosynthesis and respiration/decomposition:
\[\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{O}_2. \quad (4)\]
As CO₂ concentrations increase in seawater, the CO₂ gas reacts with water to form H₂CO₃. Most of the H₂CO₃ dissociates to form a H⁺ and a HCO₃⁻, and most of the resulting H⁺ reacts with CO₃²⁻ to produce additional HCO₃⁻ ions. As a result, CO₂ dissolution in the ocean increases H⁺ (and thus decreases pH) and decreases CO₃²⁻ concentrations.

The decrease in CO₃²⁻ reduces the saturation state of CaCO₃, which directly affects the ability of some CaCO₃-secreting organisms, such as planktonic coccolithophores and pteropods, and invertebrates such as mollusks and corals, to produce their shells or skeletons (Equation 3, and Doney et al., 2009). This is true even though most surface waters in the global ocean are currently supersaturated with respect to CaCO₃ (e.g., oceanic Ω values of 2–4 for aragonite and 4–6 for calcite, where Ω = 1 expresses saturation), because of the exceedingly slow abiotic precipitation rates for CaCO₃ minerals (Table 1). When seawater is supersaturated with respect to aragonite and calcite (saturation levels > 1), calcification is favored more than dissolution. Many organisms have optimal calcium carbonate precipitation rates at the supersaturated states for these minerals that are characteristic of the pre-industrial ocean, and therefore decreasing CO₃²⁻ concentrations could decrease calcification rates for a number of these species.

Over longer time scales, the ocean's capacity for absorbing more CO₂ from the atmosphere also depends on the extent of marine carbonate interactions with CO₂ via the dissolution reaction:
\[\text{CO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{HCO}_3^- + \text{Ca}^{2+}. \quad (5)\]
The increase in total alkalinity (TA) from this reaction enhances the ocean's capacity to absorb more CO₂ from the atmosphere (Zeebe and Wolf-Gladrow, 2001). TA is a measure of the excess cations (such as Ca²⁺ and Mg²⁺) that are balanced by the anions formed by dissociations of carbonic, boric, and other weak acids in seawater. The primary contributors to the dissolution reaction in Equation 5 are the carbonate shells that are produced in the euphotic zone. Upon a calcifying organism’s death, its carbonate shell falls through the water column and is either deposited in sediments or dissolved.

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DATA SETS AND MODELING APPROACH

From 1990 through 1998, carbon system measurements were made on 99 WOCE/JGOFS (World Ocean Circulation Experiment/Joint Global Ocean Flux Study) CO₂ survey cruises in the global ocean (Key et al., 2004; Sabine et al., 2005). These cruises were conducted as a collaborative effort among 15 laboratories from eight countries. At least two carbon parameters were measured on all the cruises, but the carbon system pairs that were measured varied between cruises. The overall accuracy of the DIC data was ±3 µmol kg⁻¹, and for TA, the second most common carbon parameter analyzed, the overall accuracy was ±5 µmol kg⁻¹.

The data were corrected for systematic biases between cruises and maintained as a unique corrected data set (hereafter called GLODAP), which consists of about 72,000 sample locations where DIC and TA were collected. The data are available from the Carbon Dioxide Information Analysis Center (http://cdiac.esd.ornl.gov/oceans/).

The National Center for Atmospheric Research (NCAR) Community Climate System Model 3.1 (CCSM3) was used to estimate the long-term changes in the saturation state of seawater with

<table>
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<th>Ocean</th>
<th>¹Salinity</th>
<th>¹Temperature (°C)</th>
<th>²Dissolved Inorganic Carbon (µmol kg⁻¹)</th>
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<th>³pH (Seawater Scale)</th>
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<td>± 48</td>
<td>8.108 ± 0.05</td>
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Note: the ± values in the table give the standard deviations about the regional means.

⁴ Arctic Ocean data (N=70) from GLODAP version 1.1 bottle data, http://cdiac.ornl.gov/oceans/glomap/data_files.htm
respect to aragonite and calcite (Doney et al., 2006; Steinacher et al., 2009). The modeled decadal mean values were calculated using modeled monthly dissolved inorganic carbon, alkalinity, temperature, and salinity output from CCSM3, which uses full carbon cycle–climate radiative feedbacks and assumes historical fossil fuel emissions and the IPCC Special Report on Emissions Scenarios (SRES) nonintervention future A2 scenario (Thornton et al., 2009). The model’s variable grid (0.9–3.6° latitude x 3.6° longitude) was interpolated to a 2° x 2° regular grid for analysis. GLODAP 1° x 1° gridded surface dissolved inorganic carbon and total alkalinity (http://cdiac.ornl.gov/oceans/glodap/Glodap_home.htm) and World Ocean Atlas 2005 (http://www.nodc.noaa.gov/OC5/WOA05/pr_woa05.html) 1° x 1° gridded temperature and salinity data were used to calculate GLODAP-based carbonate system parameters. For both CCSM3 and GLODAP-based data sets, carbonate system parameters were calculated using a standard polynomial solver by Richard Zeebe (University of Hawaii) for Matlab (http://www.soest.hawaii.edu/oceanography/faculty/zebe_files/CO2_System_in_Seawater/csyls.html) and the thermodynamic carbonate dissociation constants from Mehrbach et al. (1973) (refit by Lueker et al., 2000), total pH scale, and other dissociation constants reviewed in Zeebe and Wolf-Gladrow (2001). Before calculating the difference between GLODAP and CCSM-based carbonate system parameters, GLODAP data were interpolated to the same 2° x 2° regular grid as CCSM3 data.

RESULTS AND DISCUSSION

Calcification or dissolution of both planktonic and benthic calcifying organisms commonly depends on the carbonate ion concentration, often expressed by the degree of saturation of the biominerals aragonite and calcite (see Feely et al., 2004, and references therein). Consequently, spatial and temporal changes in saturation state with respect to these mineral phases are important for understanding how ocean acidification might impact future ecosystems. Figures 2 and 3 show mean ocean surface pH and CO$_3^{2−}$ concentrations for the Pacific, Atlantic, and

Figure 2. (Top and middle rows) National Center for Atmospheric Research Community Climate System Model 3.1 (CCSM3)-modeled decadal mean pH at the sea surface centered around the years 1875, 1995, 2050, and 2095. (Bottom left) Global Ocean Data Analysis Project (GLODAP)-based pH at the sea surface, nominally for 1995. (Bottom right) The difference between the GLODAP-based and CCSM-based 1995 fields. Note the different range of the difference plot. Deep coral reefs are indicated by darker gray dots; shallow-water coral reefs are indicated with lighter gray dots. White areas indicate regions with no data.
Indian oceans from the CCSM3 model projections for the decades centered on 1875, 1995, 2050, and 2095, as well as the difference between the GLODAP gridded data and the 1995 model results, respectively. Based on the GLODAP data set, open-ocean surface water pH ranges from about 7.95–8.35 (mean = 8.11); CO$_3^{2-}$ concentrations range from about 80–300 µmol kg$^{-1}$ (mean = 191 µmol kg$^{-1}$); aragonite saturation values range from approximately 2.4–3.9; and calcite saturation from approximately 3.8–5.9 (Table 1). GLODAP pH and carbonate ion values are higher in highly productive regions of the western North and South Atlantic, western North and South Pacific, South Indian Ocean, Bering Sea, and most of the Southern Ocean (Figures 2 and 3). These regions have a large uptake of CO$_2$ (high pH, high CO$_3^{2-}$) during the spring–summer months when productivity is strongest and when most of the surveys occurred. Because the modeled results for 1995 are decadal averages, it is not too surprising that the largest data-model differences occur in these highly productive subpolar regions.

Model projections indicate that surface ocean pH will drop from a pre-industrial average of about 8.2 to a mean of about 7.8 in the IPCC A2 scenario by the end of this century. For CO$_3^{2-}$, the highest concentrations are in the tropical and subtropical regions, particularly on the western side of each basin where the waters are warmer and saltier. For most open-ocean surface waters, aragonite undersaturation occurs when CO$_3^{2-}$ concentrations drop below approximately 66 µmol kg$^{-1}$. Model projections suggest that this will start to occur at about 2020 in the Arctic Ocean (Steinacher et al., 2009) and 2050 in the Southern Ocean south of 65°S (Orr et al., 2005) in the A2 business-as-usual scenario. By 2050, all of the Arctic will be undersaturated with respect to aragonite (Figure 4), and by 2095, all of the Southern Ocean south of 60°S and parts of the North Pacific will be undersaturated. In the Arctic Ocean, the rapid decrease in saturation state occurs, in part, as a direct result of the decrease in TA in surface waters due to the increase in freshwater inflow from low-alkalinity river water and from ice melt (Orr et al., 2005). For calcite, undersaturation occurs when CO$_3^{2-}$ drops below 42 µmol kg$^{-1}$ (Figure 5). By 2095, most of the Arctic and some parts of the Bering and Chukchi seas will be undersaturated.
Figure 4. (Top and middle rows) CCSM3-modeled decadal mean $\Omega_\text{ar}$ at the sea surface, centered around the years 1875, 1995, 2050, and 2095. (Bottom left) GLDAP-based $\Omega_\text{ar}$ at the sea surface, nominally for 1995. (Bottom right) The difference between the GLDAP-based and CCSM-based 1995 fields. Note the different range of the difference plot. Deep coral reefs are indicated by darker gray dots; shallow-water coral reefs are indicated with lighter gray dots. White areas indicate regions with no data.

Figure 5. (Top and middle rows) CCSM3-modeled decadal mean $\Omega_\text{ca}$ at the sea surface centered around the years 1875, 1995, 2050, and 2095. (Bottom left) GLDAP-based $\Omega_\text{ca}$ at the sea surface, nominally for 1995. (Bottom right) The difference between the GLDAP-based and CCSM-based 1995 fields. Note the different range of the difference plot. Deep coral reefs are indicated by darker gray dots; shallow-water coral reefs are indicated with lighter gray dots. White areas indicate regions with no data.
with respect to calcite. However, in most of the other ocean basins the surface waters will still be oversaturated with respect to calcite, but at a level greatly reduced from the present.

In Figure 6, average basin-wide saturation state profiles for aragonite (solid line) and calcite (dashed line) are plotted along with depth profiles of pH and $\text{CO}_3^{2-}$ concentrations for each of the basins (Figure 6). The depth profiles show that both pH and $\text{CO}_3^{2-}$ decrease rapidly in subsurface waters because of the release of $\text{CO}_2$, primarily from circulation and respiration processes within the subsurface water masses. Portions of the eastern subtropical Atlantic become undersaturated with respect to aragonite between 400 and 1000 m, and all of the Atlantic becomes undersaturated with respect to calcite below a depth of approximately 3000–3500 m (Chung et al., 2004; Feely et al., 2004). In the Indian and Pacific oceans, undersaturation of aragonite begins at much shallower depths where the $\text{CO}_3^{2-}$ drops below a value of about 66 $\mu$mol kg$^{-1}$ (depth range of 100–1200 m, depending on location) because the waters are much older and have acquired more $\text{CO}_2$ from the cumulative effects of respiration while they travel along the transport pathway of the deeper water masses. The calcite saturation depths in the Indian and Pacific are generally about 50–200 m deeper than the aragonite saturation depth. The addition of anthropogenic $\text{CO}_2$ over the past 250 years has caused the aragonite saturation horizons to shoal toward the surface in all ocean basins by varying amounts, ranging from about 50–200 m, depending on location (Feely et al., 2004; Orr et al., 2005).

Because aragonite and calcite saturation values are highest in warm tropical and subtropical oceans, these regions might also experience the largest absolute changes in saturation state by the end of the century. Figure 7 and Table 2 show the projected absolute and relative changes, or fractional changes, of aragonite state from 1865 to 2095. The largest projected decreases in aragonite saturation between 1865 and 2095 are observed in warm tropical and subtropical waters (Figure 7, top). For example,

![Figure 6. Distribution of: (A) pH and (B) $\text{CO}_3^{2-}$ concentration in the Pacific, Atlantic, and Indian oceans. The data are from the World Ocean Circulation Experiment/Joint Global Ocean Flux Study/Ocean Atmosphere Carbon Exchange Study global $\text{CO}_2$ survey data (Sabine et al., 2005). The lines show the average aragonite (solid line) and calcite (dashed line) saturation $\text{CO}_3^{2-}$ concentration for each of these basins. The color coding shows the latitude bands for the data sets (after Feely et al., 2009).](image-url)
in the tropical and subtropical Atlantic, the average decrease in aragonite saturation state between the present-day levels and a 3XCO₂-world (~ 840 µatm) is -0.81, whereas in the high-latitude North Atlantic, it is only -0.39 (Table 2). The temperate latitude differences are generally somewhere in the middle between these two extremes. In the tropics and subtropics, many species of tropical corals are extremely sensitive to any decreases in saturation state (Langdon, 2002). In these same locations, natural variability in the ocean carbonate system is much smaller than forecasted anthropogenically driven changes (Cooley et al., 2009), implying that future low-latitude conditions could stress tropical species by significantly altering the conditions to which they have adapted.

On the other hand, the relative changes in CO₃²⁻ concentrations and aragonite and calcite saturation states are highest in the high latitudes. There, the large changes in carbonate chemistry relative to historical conditions, which are captured in both the large percent changes in modeled carbonate system parameters and the saturation state changes from supersaturation (Ω > 1) to undersaturation (Ω < 1), might have large impacts on high-latitude calcifying planktonic and benthic organisms such as pteropods, mussels, and oysters (Fabry et al., 2008; Doney et al., 2009). Whether absolute or relative changes in CO₃²⁻ concentrations and/or aragonite and calcite saturation state play a controlling role in overall ecosystem changes has yet to be determined. Nevertheless, the striking decreases in aragonite and calcite saturation state projected by the end of this century over the entire ocean clearly indicate that there is a reasonable cause for concern.

CONCLUSIONS
The oceanic uptake of anthropogenic CO₂ from the atmosphere is decreasing the pH and lowering the CO₃²⁻ concentration and CaCO₃ saturation states of aragonite and calcite in the upper ocean. Ocean acidification is expected to result in a pH decrease of ~ 0.3–0.4 units relative to pre-industrial values by the end of this century. Based on the best available information and model projections, it appears that as levels of dissolved CO₂ in seawater rise, the skeletal growth rates of calcium-secreting organisms will be...
reduced due to the effects of decreased ocean CO$_3^{2–}$ concentrations. If anthropogenic CO$_2$ emissions are not dramatically reduced in the coming decades, there is the potential for direct and profound impacts on our living marine ecosystems.

ACKNOWLEDGEMENTS

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