

## OCB-OA: The chemistry of ocean acidification

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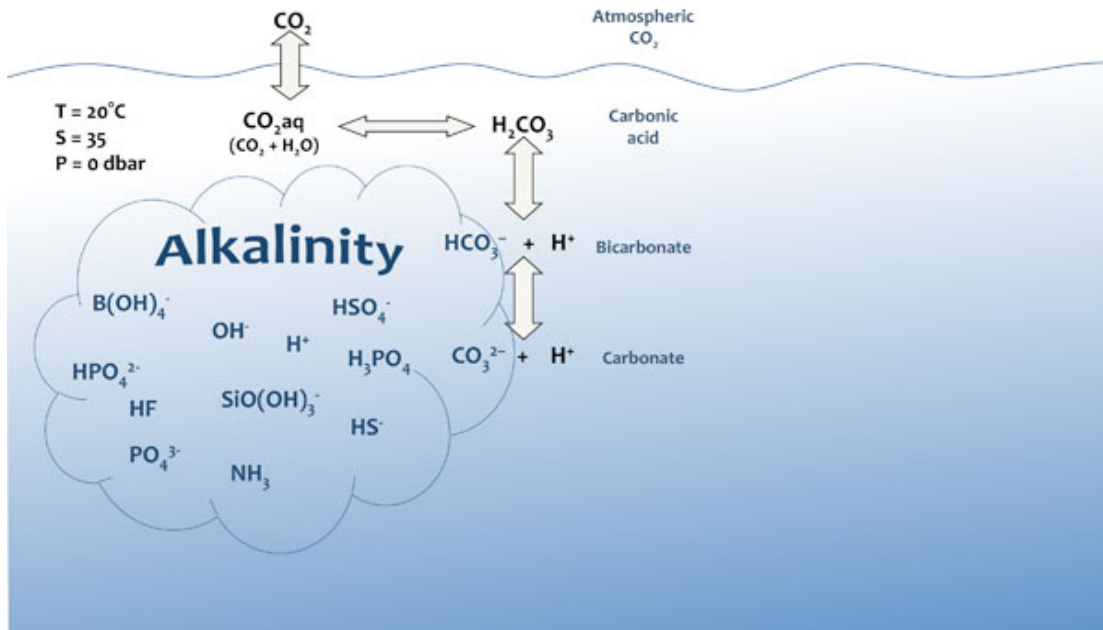
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**Table: Concentrations of carbonate system species in seawater**

	Preindustrial atmospheric CO <sub>2</sub>	2x Preindustrial CO <sub>2</sub>
Atmospheric CO <sub>2</sub> (μatm)	280 μatm	560 μatm
Carbonic acid H <sub>2</sub> CO <sub>3</sub> (μmol/kg seawater)	9	18
Bicarbonate HCO <sub>3</sub> <sup>-</sup> (μmol/kg seawater)	1757	1975
Carbonate CO <sub>3</sub> <sup>2-</sup> (μmol/kg seawater)	239	151
Total carbon species TCO <sub>2</sub> (μmol/kg seawater)	2005	2144
Total alkalinity TA (μmol/kg seawater)	2345	2345
pH	8.18	7.93
?-aragonite	3.72	2.35

These values were calculated using the “Mehrbach refit” carbonate system constants (Dickson and Millero, 1987, Deep-Sea Research), KSO<sub>4</sub> dissociation constant from Dickson (1990, Journal of Chemical Thermodynamics), and the total pH scale.—J. Kleypas, A. Dickson, D. McCorkle

Figure 3: Carbonate chemistry and seawater alkalinity. Schematic of the carbonate system species in seawater and some of the equilibrium reactions that occur among them. Seawater total alkalinity (TA) is commonly defined as “the excess base” in seawater, or the sum of excess proton acceptors, and its component ions are illustrated in light blue. Seawater TA slows down, or buffers, changes in ocean pH because it includes so many different acid-base pairs. TA stays constant even when CO<sub>2</sub> is added to seawater because the charge balance of the solution stays the same, meaning that the number of positive ions generated equals the number of negative ions generated by these reactions.



### How much has CO<sub>2</sub> already decreased pH and how much change is expected?

*Basic:* Surface ocean pH has fallen by about 0.11 pH unit since the Industrial Revolution. Computer models forecast a drop of 0.3-0.4 pH units more by the end of the century if we continue to burn fossil fuels as we are today.

*Intermediate:* Scientists estimate that surface ocean pH has fallen by about 0.11 pH units from preindustrial times to today. Because pH is a measure of hydrogen ion concentration and the pH scale is logarithmic — for a decrease of 1 pH unit, the hydrogen ion concentration increases by a factor of 10 — a 0.11-unit pH decrease is equivalent to about a 29% increase in the ocean hydrogen ion concentration. If we continue on the expected trajectory for fossil-fuel use and rising atmospheric CO<sub>2</sub>, pH is likely to drop by 0.3-0.4 units by the end of the 21st century and increase ocean hydrogen ion concentration (or acidity) by 100-150% above what it was in preindustrial times. — S. Doney

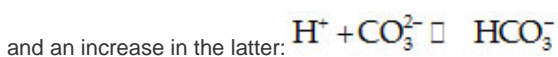
### How does ocean acidification decrease the amount of carbonate ions in seawater?

*Basic:* Ocean acidification decreases carbonate ion levels because some of the additional hydrogen ions combine with carbonate ions (CO<sub>3</sub><sup>2-</sup>) to form bicarbonate (HCO<sub>3</sub><sup>-</sup>).

*Intermediate:* When CO<sub>2</sub> dissolves in seawater it combines with water to form hydrogen (H<sup>+</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>) ions:



Some of the hydrogen ions combine with carbonate (CO<sub>3</sub><sup>2-</sup>) ions to form additional bicarbonate ions resulting in a decrease in the former



Thus, the net effect when is added to seawater is for the concentrations of H<sup>+</sup>, CO<sub>2</sub>, and HCO<sub>3</sub><sup>-</sup> to increase, and the concentration of CO<sub>3</sub><sup>2-</sup> to decrease. —A. Dickson

*Advanced:* The essence of *anthropogenic ocean acidification* is that there is an increase in the concentration of the unionized species, CO<sub>2</sub> in seawater as a result of the growth in the atmospheric concentration of carbon dioxide, and its subsequent dissolution into seawater.

Seawater itself contains a variety of acid-base species (including those of the carbon dioxide system) that can be assumed to be at chemical equilibrium, because of the rapid kinetics of coupled aqueous acid-base reactions (see Dickson *et al.*, 2007). The position of chemical equilibrium, that is the detailed chemical composition of the solution at equilibrium, is governed by a number of parameters, comprising a set of appropriate equilibrium constants (for seawater these are usually considered to be functions of salinity, temperature, and pressure) for a set of stoichiometrically independent reactions, and the initial concentrations of the various components that make up the system. (The number of such components, *k*, depends on the number of species considered, *q*, and the number of stoichiometrically

independent equilibria,  $n$ , i.e.  $k = q - n$ .)

The response of such an equilibrium state to a particular perturbation is not inherently obvious. Although Le Chatelier's Principle can be applied to the response of each one of a series of coupled reactions individually, the net effect of the coupling can be harder to interpret. Here therefore we seek to show that, in natural seawater, the sensitivity parameter

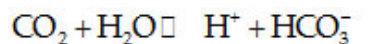
$$\left( \frac{\partial[\text{CO}_3^{2-}]}{\partial[\text{CO}_2]} \right) < 0$$

brackets refer to the concentrations of the enclosed species.

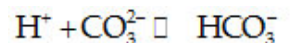
This could be done rigorously using the approach of sensitivity analysis (Fishtik *et al.*, 1994; 1995). It is probably simpler to calculate this sensitivity parameter numerically using a computer program such as CO2CALC (Robbins *et al.*, 2010). In either case it will be necessary to state just what acid-base systems are being considered and to assign appropriate equilibrium constants (typically for the acid-dissociation reactions) and initial concentrations for the various *components*. For a normal seawater composition (see below), this sensitivity parameter will indeed be negative, i.e. "ocean acidification decreases the amount of carbonate ions in seawater".

The reason for this depends essentially on the initial composition of the seawater before it is perturbed. In the surface waters of the North Atlantic, for example, the concentration of total dissolved inorganic carbon (the sum of the concentrations of the three coexisting species: bicarbonate ion, carbonate ion, and unionized dissolved carbon dioxide) is only about  $2 \times 10^{-3} \text{ mol kg}^{-1}$ . About 90% of this is present as bicarbonate ion, the proportion of carbonate ion is about a factor of 10 less ( $\sim 2 \times 10^{-4} \text{ mol kg}^{-1}$ ), and that of unionized carbon dioxide yet another factor of 10 less ( $\sim 2 \times 10^{-5} \text{ mol kg}^{-1}$ ). As a result of the equilibria between these various species (and others such as the boric acid and water systems), seawater is weakly buffered with respect to changes in hydrogen ion which is itself present at much lower concentrations:  $\sim 10^{-8} \text{ mol kg}^{-1}$ .

If one adds some  $\text{CO}_2$  to seawater, it reacts with the water in accordance with the acid-dissociation equilibrium:

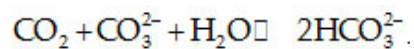


If one looks at this equation, and at the initial concentrations noted in the paragraph above, one can see that if the forward reaction occurs even to a relatively small degree (as Le Chatelier's principle would imply) there will be a much larger proportional change in the concentration of  $\text{H}^+$  than there is in that of  $\text{HCO}_3^-$ . In seawater, a coupled independent reaction largely uses up this "excess"  $\text{H}^+$ :



The net effect when  $\text{CO}_2$  is added to seawater, is thus for the concentrations of  $\text{H}^+$ ,  $\text{HCO}_3^-$ , and  $\text{H}_2\text{O}$  to increase, and the concentration of  $\text{CO}_3^{2-}$  to decrease.

Another way to think of this is to write an equilibrium reaction occurring between the various carbonate species:



where this reaction is the sum of the first two reactions. It is thus apparent from this reaction as written that increasing the amount of  $\text{CO}_2$  will result in a reaction that reduces the amount of  $\text{CO}_3^{2-}$  and increases the amount of  $\text{HCO}_3^-$ . Less apparent is that the hydrogen ion concentration will also increase (proportionally to the ratio between the concentrations of  $\text{HCO}_3^-$  and of  $\text{CO}_3^{2-}$ ). This increase in hydrogen ion concentration (a decrease in pH resulting from the addition of  $\text{CO}_2$ ) is the so-called *ocean acidification*. —A. Dickson

### Why doesn't ocean salt buffer away ocean acidification?

*Basic:* In the laboratory, when you mix a strong acid and base, salt and water form, and the fluids are neutralized. But ocean salt comes from rock weathering, which carries weak acid and base ions to the ocean. Over thousands of years these ions accumulate and make seawater "salty." Ocean acidification is happening over decades to centuries, which is too fast for rock weathering to overcome.

*Intermediate:* When acids and bases neutralize each other in a laboratory experiment, salt and water form. But in the ocean, the major ions that make seawater "salty" (like sodium, chloride, and magnesium) are derived from rock weathering, which provides a balanced amount of positive and negative ions to the seas over many millennia. Weak acids and bases, like bicarbonate or borate, control variations in ocean pH on shorter time scales of decades to centuries. Of these weak acids and bases, the dissolved inorganic carbon

species—carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3^-$ ), and carbonate ( $\text{CO}_3^{2-}$ )—have the largest impact on global ocean pH variations because their concentrations are changing quickly relative to other chemical species in the ocean. — C.L. Sabine

### Will melting ice caps dilute the acidity by adding freshwater to the ocean?

*Basic:* Fresh water from melting ice caps dilutes everything in the ocean somewhat. However, a layer of fresh water just released from melting would contain less  $\text{CO}_2$  than the atmosphere and the surrounding seawater. It would also have less alkalinity, or excess base, that helps guard against changes in pH. So the fresh water would take up atmospheric  $\text{CO}_2$  and contribute to more ocean acidification.

*Intermediate:* Fresh water from melting ice caps dilutes the concentrations of all the various components of the carbonate system in seawater (described above), as well as the total alkalinity and salinity (both of which affect pH). For example, a liter of “typical” Arctic seawater (temperature, 5°C; salinity, 35; total alkalinity, 2244 micromoles per kilogram of seawater) that is exposed to today’s atmospheric  $\text{CO}_2$  level of 390 ppm has a total carbon content of 2100 micromoles per kilogram of seawater and a pH of 8.04 (total scale, here and below). Adding a kilogram of freshwater to the kilogram of seawater would dilute the salinity, alkalinity, and carbon content to half of what they were, and the initial pH would increase to 8.21. However, this mixed seawater will now be out of equilibrium with the atmosphere, with a  $\text{pCO}_2$  of 151 ppm, while the  $\text{pCO}_2$  level of the overlying atmosphere is 390 ppm. Therefore, it will absorb  $\text{CO}_2$  until the seawater  $\text{pCO}_2$  also equals 390 ppm, at which point the pH will be 7.83.— R.A. Feely, J. Kleypas

### Will $\text{CO}_2$ outgas as the oceans warm and decrease ocean acidification?

*Basic:* Increasing temperature decreases  $\text{CO}_2$  solubility in the surface ocean and might slow  $\text{CO}_2$  uptake by the ocean slightly. But the excess  $\text{CO}_2$  will still be present in the atmosphere and continue to cause warming and acidification.

*Intermediate:* The  $\text{CO}_2$  content of the surface waters of the oceans responds to both changes in  $\text{CO}_2$  content of the atmosphere and changes in temperature. For example, if ocean temperatures were not changing, a doubling of preindustrial  $\text{CO}_2$  levels (from 280 to 560 ppm) would cause an increase in the total amount of dissolved inorganic carbon in the surface ocean from about 2002 to 2131 micromoles per kilogram of seawater (assuming salinity = 35, temperature = 15°C, and alkalinity = 2300 micromoles per kilogram of seawater). If ocean temperatures warmed by 2°C over that period, then less carbon would be taken up (the increase would be from 2002 to 2117 micromoles per kilogram of seawater). Thus, a 2°C increase in temperature results in about a 10% decrease in carbon uptake in surface waters. The expected warming of the oceans also may alter ocean circulation, further reducing their capacity to absorb  $\text{CO}_2$  from the atmosphere, but the excess  $\text{CO}_2$  will still remain in the atmosphere and drive further acidification (and atmospheric warming). For pH, the net effects of climate warming on atmospheric  $\text{CO}_2$ ,  $\text{CO}_2$  solubility, and chemical speciation approximately cancel out. — S. Doney, J. Kleypas

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