

## Effect of CO<sub>2</sub> on Ocean pH

Carbon dioxide (CO<sub>2</sub>) is a gas that occurs naturally in the atmosphere, but because of its solubility in water, there is an even greater mass dissolved in the oceans. The amount in the atmosphere has been increasing fairly steadily from the mid 1800s, and increasingly so since 1950 - probably due to Mankind burning coal and oil for energy production, and is now greater than it has been in the past hundreds of thousand years (Chapter 1, figure 1).

There's been concern – hysteria even – that this increase in oceans' CO<sub>2</sub> will create acidity to endanger life in the oceans. The topic has even been given the name “**Ocean Acidification**” or **OA**. This Chapter will discuss this AGW proposition.

### A Bit of Chemistry

Seawater is a slightly alkaline solution about 3.5% w/w (aka Salinity, S= 35, ie parts per thousand) of many soluble substances (typical concentrations shown in Table 1). Its density varies between about 1020 to 1029 kg/m<sup>3</sup>. These dissolved substances are mostly ionic, ie they break apart, “dissociate”, into their constituent components – ions - on being dissolved in water. Carbon dioxide produces a weakly acid solution when it dissolves in water, and reduces the alkalinity of seawater.

<u>Ion</u>	<u>Concentration (mol/kg)</u>
Cl <sup>-</sup>	0.546
Na <sup>+</sup>	0.469
Mg <sup>2+</sup>	0.0528
SO <sub>4</sub> <sup>2-</sup>	0.0282
Ca <sup>2+</sup>	0.0103
K <sup>+</sup>	0.0102
Ionic carbon, C <sub>T</sub>	0.00206
Br <sup>-</sup>	0.000844
Total Borates	0.000416
Sr <sup>2+</sup>	0.000091

Table 1: Major ions of Seawater (Salinity = 35)

Acidity of aqueous solutions arises from hydrated hydrogen ions released by dissociation of the solvent, water. The concentration (in molarity, moles/**litre**) is represented as [H<sup>+</sup>]. (Table 1 units need to be divided by density.) Molarity is the number of formula weights per litre of solution. For example, 0.1 molarity sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>, solution contains 0.1 x (2 x 23 + 12 + 3 x 16) = 10.6 g/l.

The acidity of aqueous solutions encountered can vary over a huge range, and so to keep things meaningful, S.P.L. Sorensen introduced the pH scale (1909).

**Definition:**  $\text{pH} = -\log_{10}[\text{H}^+]$

A *neutral* aqueous solution, for example a solution of NaCl, has equal concentrations of [H<sup>+</sup>] & [OH<sup>-</sup>], ie 10<sup>-7</sup> each and pH of 7. A 0.1M solution of a *strong acid*, for example HCl or HNO<sub>3</sub>, has pH = 1. The scale also works for alkalinity (or basicity), so that a 0.1M solution of a *strong alkali*, for example KOH, has a pH = 14 (or pOH = 1). The equivalence between pH scale and [H<sup>+</sup>] is shown in the table.

pH	[H <sup>+</sup> ]
0	1
1	1 x 10 <sup>-1</sup>
6	1 x 10 <sup>-6</sup>
7	1 x 10 <sup>-7</sup>
8	1 x 10 <sup>-8</sup>
14	1 x 10 <sup>-14</sup>

The worldwide ocean average is generally reckoned to be between 8.1 and 8.2, and so is slightly alkaline. The oceans' pH varies with locality from 8.2 to 7.90 (Figure 1), and these pH differences have been taken as evidence of OA, ie due to Mankind's contribution to increasing CO<sub>2</sub>. A pH range of 0.3 is equivalent to the [H<sup>+</sup>] range of 6.3 x 10<sup>-9</sup> to 12.6 x 10<sup>-9</sup>, about a 100% range.

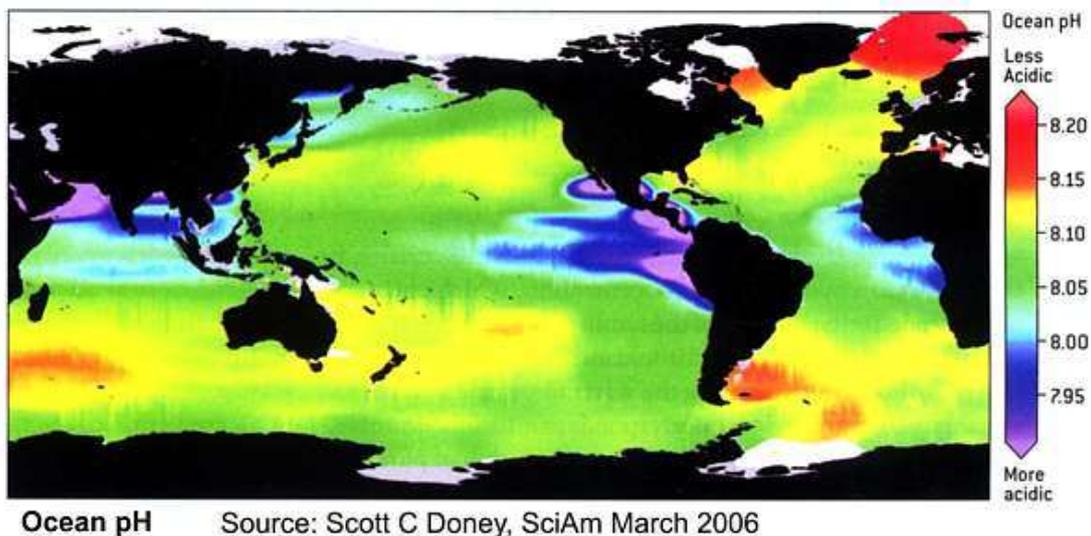


Figure 1: Variation of pH with locality in oceans (for nominal year 1994).

Such a range in most physical quantities would represent a tremendous change in properties but such an acidity range in the oceans for example, is not usually noticeable and one could certainly not feel any difference. Therefore, as opposed to the doomsayers, ie AGW followers, one should be concerned with the (realistic) pH scale rather than the amplifying [H<sup>+</sup>] when one is discussing ocean alkalinity changes.

### Quantitative change of pH with atmospheric CO<sub>2</sub>.

Carbon dioxide produces a slightly acidic solution in pure water and this is due to the weak acid, carbonic acid, H<sub>2</sub>CO<sub>3</sub>, produced. However, only a small proportion – a couple of molecules in a thousand - of the total dissolved CO<sub>2</sub> becomes H<sub>2</sub>CO<sub>3</sub>.

The hydration equilibrium:



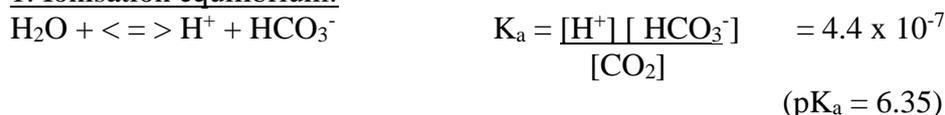
The total of [CO<sub>2</sub> + H<sub>2</sub>CO<sub>3</sub>] in solution is also represented as H<sub>2</sub>CO<sub>3</sub>\* or [CO<sub>2</sub>]<sub>aq</sub>.

Cr is the total dissolved inorganic carbon, aka CO<sub>2</sub>/H<sub>2</sub>O or Dissolved Inorganic Carbon (DIC). It is comprised of three interacting species, **CO<sub>2</sub>**, **carbonate CO<sub>3</sub><sup>2-</sup>**, and **bicarbonate HCO<sub>3</sub><sup>-</sup>**. Equilibria are established between these 3 chemical species plus H<sup>+</sup>, and each has an equilibrium constant, K.

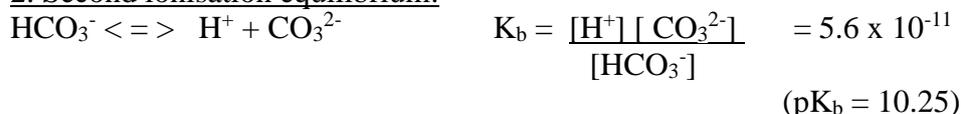
(These “constants” vary with temperature, and slightly with pressure and the total concentration of other non-reacting ions. This last variable is known as ionic strength; in seawater, it is usually known as salinity, S.)

The following two equations can be found in undergraduate textbooks, and as they have experimental data, the values can vary a little. The familiar values are as quoted by J.N. Butler<sup>i</sup> for *pure water* (extrapolated to zero ionic strength) at 25°C.

1. Ionisation equilibrium:



2. Second ionisation equilibrium:



Typical values for **seawater** at 25°C, Salinity = 35 and atmospheric pressure are K<sub>a</sub> = 1.380E-06, and K<sub>b</sub> = 1.122E-09, used in the following calculations. (From Lower<sup>ii</sup>).

Two more independent equations are required to link the four species.

3. Mass balance on C<sub>T</sub> (Total carbon) → C<sub>s</sub>:

$$C_T = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3^*]$$

and is determined from chemical analyses. A useful approximation is to include borates here, effectively as an additional ca 20% to C<sub>T</sub>, (as they would do anyway in some titrations). This reduces a difficult higher order polynomial down to a quadratic (see below), plus prevents a pH error of up to 0.1. Other minor interacting species, eg phosphates and silicates, are insignificant. As pH is the primary interest, the newly defined C<sub>s</sub> will replace C<sub>T</sub> with little error.

$$C_s = 0.0020 \text{ (from carbon)} + 0.0004 \text{ (from borates)} = 0.0024 \text{ M}$$

4. Henry's Law relates the concentration of CO<sub>2</sub> in air to that of water in equilibrium with it. At 25°C and up to 5 atm pressure, the solubility follows Henry's Law,

$$[\text{CO}_2]_{\text{aq}} = K_H \cdot P_{\text{CO}_2}$$

where K<sub>H</sub> = 0.034 and P<sub>CO<sub>2</sub></sub> is the partial pressure (ie fraction) of CO<sub>2</sub> in air, currently about 0.0004 and rising.

There are thus 4 independent equations connecting 4 unknown concentrations, ie [H<sup>+</sup>], [CO<sub>2</sub>]<sub>aq</sub>, [HCO<sub>3</sub><sup>-</sup>] and [CO<sub>3</sub><sup>2-</sup>]. These give the quadratic in [H<sup>+</sup>] readily solved in a spreadsheet,

$$[\text{H}^+]^2 \cdot A - [\text{H}^+] \cdot K_a - K_a \cdot K_b = 0 \quad \text{where } A = \frac{C_s}{[\text{H}_2\text{CO}_3^*]} - 1$$

then substituting that value gives the remaining 3 concentrations.

## Results and Discussion

	%CO <sub>2</sub>	CO <sub>2(aq)</sub>	Cs	H+	pH	[HCO <sub>3</sub> <sup>-</sup> ]	[CO <sub>3</sub> <sup>2-</sup> ]	[Ca <sup>2+</sup> ]
Vostok low	0.018	5.184E-06	0.002405	3.850E-09	8.41	1.858E-03	5.415E-04	8.86E-04
pre-industrial	0.028	8.064E-06	0.002408	5.572E-09	8.25	1.998E-03	4.023E-04	1.19E-03
50s	0.035	1.008E-05	0.00241	6.760E-09	8.17	2.058E-03	3.416E-04	1.40E-03
Now	0.04	1.152E-05	0.002412	7.604E-09	8.12	2.091E-03	3.086E-04	1.56E-03
Double Mankind	0.052	1.498E-05	0.002415	9.618E-09	8.02	2.149E-03	2.507E-04	1.91E-03
Double	0.08	2.304E-05	0.002423	1.429E-08	7.84	2.225E-03	1.747E-04	2.75E-03
Breath	5.0	1.440E-03	0.00384	8.294E-07	6.08	2.397E-03	3.243E-06	1.48E-01
100% CO <sub>2</sub>	100	2.880E-02	0.0312	1.657E-05	4.78	2.40E-03	1.63E-07	2.95E+00

**Table 2: Variation of Seawater pH with Atmospheric [CO<sub>2</sub>]**  
(carbonate and bicarbonate include ca 20% borates)

Table examples:

1. "Vostok min" levels of CO<sub>2</sub> (0.018%) in Vostok ice-cores (Fig 1, Chapter 1).
2. "Pre-industrial" are the maximum levels of CO<sub>2</sub> (0.028%) from Vostok. It was about this level in mid-1800s but rising ever since.
3. "Now". The *additional* contribution of Man is (0.04 – 0.028 = 0.012)%.
4. "Double Mankind" is Now plus another Mankind's current contribution (0.04 + 0.012 => 0.052%), resulting in a pH drop of only **0.102**.
5. "Double Total" is double current *total* CO<sub>2</sub>, an overstatement of the case, but is still a drop of only **0.279 - less than the pH spread worldwide**.
6. "Breath" is for interest. However, I've seen a prominent researcher on (eg David Attenborough) TV presentations by blowing – supposedly as a representative source of CO<sub>2</sub> - into seawater to illustrate "Ocean Acidification"! Clearly this is a vast exaggeration, as at this 5% level we'd all be asphyxiated; it's exhaled breath after all. As a further exaggeration, human breath can be contaminated – deliberately or otherwise - by very acid (HCl) stomach vapours.

The table's calculated pH values are those that result immediately from direct exposure to atmospheric CO<sub>2</sub> of surface seawater – the upper 30m to 100m that are mixed by turbulence. They therefore represent the maximum effect of that initiating CO<sub>2</sub> concentration. Surface waters eventually recycle through the more alkaline depths - the ocean floor minerals are limestone, silicates and other basic minerals. In a slow but continuous process – maybe a thousand years for a complete circulation - the former surface waters will likely become more alkaline, opposing the overall effect of CO<sub>2</sub> shown in the Table. The ocean floor is a vast pH buffer.

Figure 1 shows that ocean pH varies from about 8.2 to 7.90, and is often cited to be examples of the perilous Ocean Acidification due to manmade CO<sub>2</sub>. However, this pH range is equivalent to a huge atmospheric CO<sub>2</sub> range of 0.032% to 0.0697%, whereas it is usually accepted that it is virtually homogeneous.

**It is beyond belief for this pH range to be due to CO<sub>2</sub>.**

Surprisingly perhaps, the lowest pH is in warm tropical waters where gases have lower solubility. The range is also unlikely due to pollution or runoff from rivers as, for example, (the biggest tongue, in blue) extends thousands of kilometres westwards

from equatorial Central and South America. This particular tongue is either over, or downstream, from the very seismically active areas of the Galapagos Ridge and the East Pacific Rise. Undersea volcanic activity at diverging tectonic plates releases hot magma, CO<sub>2</sub> and H<sub>2</sub>S (hydrogen sulphide). These are the areas responsible for El Nino and La Nina. Although H<sub>2</sub>S forms a neutral solution in water, its final oxidation product, H<sub>2</sub>SO<sub>4</sub>, is the strong sulphuric acid.

**This is the real cause of the so-called OA.**

Although the oceans will never become acid from CO<sub>2</sub>, an alternative concern<sup>iii, iv</sup> has been expressed that ocean problems do not so much arise from acidity as such, but from eg decreasing ocean carbonate (Table 2) and its effect on marine animals, eg oyster shells and coral, mostly calcium carbonate.

Calcium carbonate's solubility



is described by its solubility product, K<sub>sp</sub> (for a particular temperature and salinity) and defined by the simple equation

$$K_{\text{sp}} = [\text{Ca}^{2+}]_{\text{aq}} \times [\text{CO}_3^{2-}]_{\text{aq}}$$

[The solubility of an ionic substance is sqrt(K<sub>sp</sub>) for those conditions. K<sub>sp</sub> = 4.8 x 10<sup>-7</sup> for calcite (calcium carbonate's stable form to moderate depths) in seawater at 25°C. Aragonite, stable at higher pressure, is a little less soluble.]

Combining K<sub>sp</sub> with [CO<sub>3</sub><sup>2-</sup>]<sub>aq</sub> of equation 2 yields

$$[\text{Ca}^{2+}]_{\text{max}} = K_{\text{sp}} / K_{\text{b}} \times [\text{H}^+] / [\text{HCO}_3^-]$$

the level of [Ca<sup>2+</sup>]<sub>aq</sub> above which calcium carbonate no longer dissolves for the given bicarbonate level. Comparing the Ca<sup>2+</sup> levels (table 2) shows the much higher – 10x - typical ocean value of 0.01 (Table 1), it can be seen that the oceans are already greatly over-saturated with [Ca<sup>2+</sup>]<sub>aq</sub>. Therefore, shells, corals, etc will not corrode with any feasible pH drop or atmospheric CO<sub>2</sub> level, so that falling carbonate levels have **zero effect**.

[The very toxic hydrogen sulphide from undersea volcanic activity, rather than global warming or OA, is a likely source of the extensive fish kills in the El Nino areas and “pollution” problems at Australia's Great Barrier Reef and at the oyster industry at north-west USA's coastal areas.

**The discussion of this will be in the chapter on El Nino and another on the cause of climate changes.]**

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<sup>i</sup> Butler, James N: “Ionic Equilibrium” Addison –Wesley, 1964. A Classic.

<sup>ii</sup> Lower, Stephen K: “Carbonate equilibria in natural waters”.

<http://www.chem1.com/acad/webtext/pdf/c3carb.pdf>.

[Caution: This often quoted, readily accessible reference does contain some errors in its derivations, eg eqtn 10, but its data are similar to other references.]

<sup>iii</sup> Newcomb LA, Milazzo M, Hall-Spencer JM, Carrington E. 2015 Ocean acidification bends the mermaid's wineglass. Biol. Lett. 11: 20141075. <http://dx.doi.org/10.1098/rsbl.2014.1075>

<sup>iv</sup> Fabricius, K.E. et al “Losers and winners in coral reefs acclimatized to elevated carbon dioxide concentrations.” Nature Climate Change Letters, May 2011. DOI: 10.1038/NCLIMATE1122