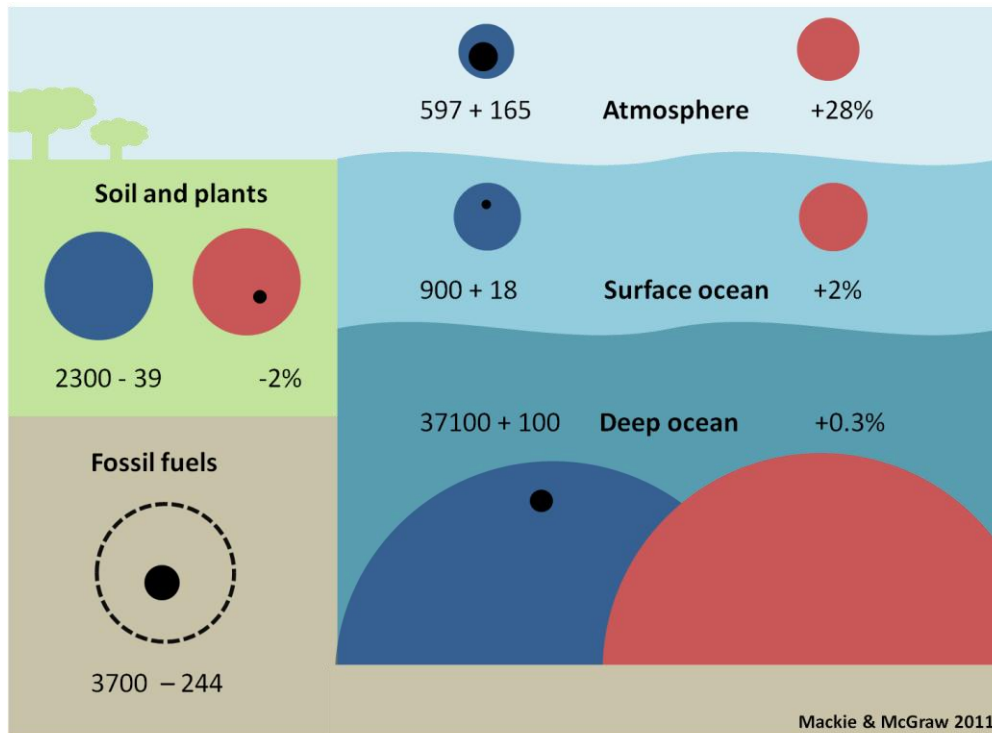


# OA not OK

An introduction to the chemistry of Ocean Acidification



The book of the "OA is not OK" series of blogs originally posted at [skepticalscience.org](http://skepticalscience.org) during July and August 2011.

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## Preface

In July and August 2011 we posted an 18-part series on ocean acidification at [scepticalscience.org](http://scepticalscience.org). You will be able to find the posts by searching there for "OA not OK". Here, lightly edited, are those posts in a single booklet. This booklet opens with the 18 blog posts, followed by a short summary of all the posts and appendices.

Our goal is to provide you with the background to understand the chemical and physical processes behind ocean acidification. This will allow you to evaluate the commentary on the web. We were motivated to write the series by the increasing number comments and posts in the blogosphere based on misconceptions about ocean acidification.

However, despite taking 18 posts and 18,000 words we have only scratched the surface of the chemistry. This is not surprising as the concepts we have introduced do not stand alone. Inevitably we have had to leave some things out and simplified others. For each concept we have explained a dozen more cry out for their 15 minutes. Here is a negligently incomplete list of a further 18 Quite Important concepts – each deserving of at least a post – that we didn't mention or skipped lightly over. There are hundreds more.

$\delta^{13}\text{C}$ ,  $\Psi$ , Activity coefficients and when and how to use them, Alkalinity: A really useful definition for alkalinity (i.e. one that is a measurable quantity), Buffer theory, Burial of  $\text{CaCO}_3$  sediments, Carbon vs. oxygen stoichiometry for combustion of different fossil fuels, Congruent/incongruent dissolution, Conservative ions and charge balance in seawater, Dissolution of  $\text{CaCO}_3$  above the lysocline, DOM, Fugacity, Inhibition of precipitation, Mass accumulation rate for  $\text{CaCO}_3$  sediments, Mixed carbonates (incorporation of other elements), Net global production of  $\text{CaCO}_3$ , different pH scales, Revelle Factor.

The posts require only high school science. However, this is deceptive, as some concepts and applications of 'simple' science can challenge 2<sup>nd</sup> and 3<sup>rd</sup> year university students. And that is probably why so much of the little that is written is based upon misconceptions.

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2. Ocean circulation:  $\text{CO}_2$  remains in surface waters until the slow circulation turns over.

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2.  $\text{CO}_2$  is increasing at >2 ppm per year – 100 times faster than the glacial-interglacial cycle.

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**Appendix 1: How long for weathering to remove all  $\text{CO}_2$  from the atmosphere** **Page 52**

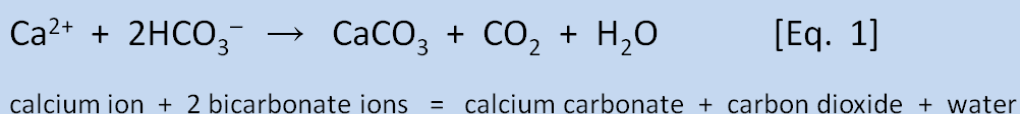
How long weathering would take to consume all atmospheric  $\text{CO}_2$  if Eq. 1 did not replace it

**Appendix 2: DIY Figure 3 speciation plot** **Page 53**

Instructions to construct your own speciation plot

Ocean acidification, OA, is the process of ocean pH decreasing (i.e. becoming more acidic) due to absorption of fossil fuel CO<sub>2</sub> from the atmosphere. Another effect of ocean acidification is to reduce the amount of carbonate in the water and this increases the dissolution of shells and skeletons.

The purpose of this section is to introduce a single chemical equation. We don't want to lapse into hyperbole but the equation is the E = mc<sup>2</sup> of ocean acidification. Having said that, knowing E=mc<sup>2</sup> does not confer knowledge about element formation during a supernova. Likewise, this equation will only be the start of our learning:



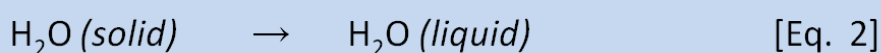
We need a few words about chemical equations before discuss what Equation 1 tells us. On the left side of the arrow is the calcium ion Ca<sup>2+</sup> (an **ion** is an atom or molecule that has an electrical charge, in this case 2+ meaning calcium has lost 2 negatively charged electrons to establish a +2 charge). Also on the left are 2 bicarbonate ions (HCO<sub>3</sub><sup>-</sup>, with the negative charge meaning it has gained an extra electron). The arrow indicates that the ions on the left of the arrow react to give the molecules on the right of the arrow: calcium carbonate (CaCO<sub>3</sub>), carbon dioxide (CO<sub>2</sub>), and water (H<sub>2</sub>O).

This equation describes the formation of calcium carbonate (i.e. shells) from calcium ions and bicarbonate ions. It shows that making 1 molecule of CaCO<sub>3</sub> from a calcium ion requires 2 molecules of bicarbonate (HCO<sub>3</sub><sup>-</sup>) and *releases* 1 molecule of H<sub>2</sub>O and 1 molecule of CO<sub>2</sub>. Yes, you read that right: The formation of calcium carbonate shells is a **source** of CO<sub>2</sub>, *not* a **sink** for CO<sub>2</sub>.

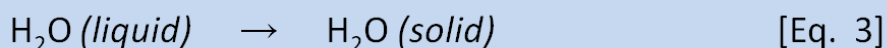
The formation of calcium carbonate shells is a **source** of CO<sub>2</sub>, *not* a **sink** for CO<sub>2</sub>

A basic principle is that chemical equations must be balanced. That is, they have the same number and types of atoms are on both sides. Counting up we see on both the left and the right are 1 calcium (Ca), 2 hydrogen (H), 2 carbon (C), and 6 oxygen (O) atoms.

However, not all balanced chemical equations are valid chemical equations. The trick of chemistry (Oh! there's *that* word again) is in knowing if a particular balanced equation is valid. For example, a simple balanced equation can be written for the melting of ice at room temperature and sea level pressure:



But we can also write a balanced equation for the reverse reaction:



The problem is that, despite being able to write a balanced equation, liquid water does not spontaneously freeze at room temperature, so the second equation must be wrong. Actually what is wrong is the direction of the arrow. Reverse the arrow and Equation 3 becomes Equation 2. The water example is familiar and we know the right answer from personal experience. But can we predict outcomes without doing the experiment? Yes – if we use thermodynamics.

## Part 2: Reactions are reversible

Page 5

In the first section we introduced Equation 1 for the formation of calcium carbonate and showed that the formation of calcium carbonate shells is a **source** of CO<sub>2</sub>, *not* a **sink** for CO<sub>2</sub>. We noted that most chemical reactions can go both forward or backwards and that we could use *thermodynamics* to predict the direction.

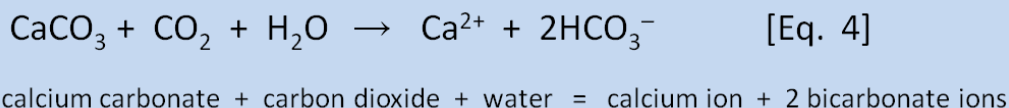
In fact, most reactions go in both directions at once but there is usually a *more favoured* direction. Consider a dinner party with 6 people. There are 5 people on one side of the table and 1 person on the other. Each side starts with a bowl of peanuts and they begin to throw them at each other. At any one time a few peanuts will be in flight, most of them coming from the side with 5 people. However, it is plain that very quickly almost all of the peanuts will end up on the side with 1 person. At this point, the side with 5 people can only throw peanuts as quickly as the lone peanut pitcher sends them over. An *equilibrium* has been reached. The number of peanuts on either side does not change even though a few individual peanuts swap sides.

Chemical reactions also proceed until equilibrium is reached. That is, the reaction proceeds until the forward reaction (the reaction on the left side of the equation) and the backwards reaction (the reaction on the right side of the equation) occur at the same rate. For most reactions, one side of an equation is vastly (by a factor of thousands or millions) more favoured than the other and for convenience chemists often write a single arrow to show the favoured direction.

Thermodynamics is based on energy differences and tells us if a reaction occurs under the given conditions. Chemists use the word *spontaneous* to describe a reaction that occurs without outside intervention. For example, ice melting at room temperature *is* spontaneous, while liquid water freezing at room temperature *is not* spontaneous.

Millions of experiments - like ice melting - have been done and the data has allowed chemists to calculate a change in energy content for every type of chemical reaction. It is, of course, complex and there are many considerations. Nevertheless these energy calculations show – and experiments confirm – that calcium and bicarbonate ions react according to Equation 1.

The reaction in equation 1 is spontaneous under the conditions in the surface oceans. That is, marine organisms like corals and shellfish *are* able to extract bicarbonate ions from seawater to make their shells or skeletons. However, as we will see, those conditions can be changed so that the reverse reaction happens, causing the calcium carbonate to dissolve:



Equation 4 is just Equation 1 running in the reverse direction. This is what takes place when limestone rocks are weathered by the action of rain and air. It is no surprise, therefore, that the most abundant ions in most river waters, calcium ( $\text{Ca}^{2+}$ ) and bicarbonate ( $\text{HCO}_3^-$ ), are derived from weathering. (Section 6 discusses weathering in detail).

Thus equations 1 and 4 explain the formation of carbonates and rock weathering. They also explain the time scales on which these reactions occur, oceanic control of atmospheric  $\text{CO}_2$ , and why acidification is happening in our ocean.

### Part 3: Wherever I lay my shell, that's my home

Page 6

In this section we will describe why making calcium carbonate shells via Eq. 1 is so easy.

Calcium carbonate,  $\text{CaCO}_3$ , is a salt. A salt is a substance containing an ion with a positive electric charge, (*cation* - like calcium  $\text{Ca}^{2+}$  or sodium  $\text{Na}^+$ ) and an ion with a negative electric charge (*anion* - like carbonate  $\text{CO}_3^{2-}$  or chloride  $\text{Cl}^-$ ). Thus, sodium chloride or table salt,  $\text{NaCl}$ , contains  $\text{Na}^+$  and  $\text{Cl}^-$ . While Equation 1 reminds us that while  $\text{CaCO}_3$  contains the ions calcium  $\text{Ca}^{2+}$  and carbonate  $\text{CO}_3^{2-}$ , the actual reaction to make it is more complicated than calcium + carbonate = calcium carbonate.



In chemistry *precipitation* is the process when a solid (often a salt) forms from a solution. One familiar example is the way crystals of sodium chloride,  $\text{NaCl}$ , form as seawater evaporates

**Figure 1.** Salt harvesting at Lake Grassmere, New Zealand. The pink colour comes from salt-loving (*halophile*) algae. [www.teara.govt.nz/en/salt](http://www.teara.govt.nz/en/salt)

What is happening? Does the seawater contain particles of sodium chloride (NaCl)? No. Seawater contains sodium ions ( $\text{Na}^+$ ) and chloride ions ( $\text{Cl}^-$ ), each surrounded by water molecules. The water molecules act as a shield, muffling the charges on the  $\text{Na}^+$  and  $\text{Cl}^-$  ions so they don't attract each other. As the seawater evaporates there is no longer enough water to keep the ions apart and their opposite electric charges allow them to get close and form solid sodium chloride.

What about the reverse process, dissolving sodium chloride in some water? It is obvious that we can't add salt indefinitely. Did you know that the amount that can dissolve differs from substance to substance? The maximum amount of a substance that can be dissolved in a given volume of water is called the *solubility* and is a fundamental property of the substance.

For sodium chloride a surprising 360 grams will dissolve per kg of freshwater at room temperature; for sodium fluoride, a close relative, the value is only 41 g. Calcium carbonate is even less soluble: only about 0.01 g (10 mg) will dissolve under the same conditions. (Spoiler alert: section 13 will discuss the different forms of calcium carbonate that have different solubilities and will go over the critical difference this will make under ocean acidification).

A solution that contains the maximum possible amount of a substance is described as being **saturated**. The corollary of this is that if you have a saturated solution and then add more of one or both of the component ions in the salt, (i.e. *if you exceed the solubility* and have too many ions in solution), then the substance will begin to precipitate until the excess has been removed and the solution is back to being saturated.

However, as well as being saturated, a solution can be **supersaturated**. This means the solution contains more ions that can combine to form a salt than is 'theoretically' possible. Plainly it *is* possible, since the surface seawater is supersaturated with  $\text{CaCO}_3$ .

The solubility of  $\text{CaCO}_3$  in freshwater is only 10 mg per kg. In comparison, the concentration of  $\text{Ca}^{2+}$  (the 3<sup>rd</sup> most abundant cation in seawater, after sodium and magnesium) is 412 mg (!) per kg of seawater and the surface concentration of bicarbonate  $\text{HCO}_3^-$  and carbonate  $\text{CO}_3^{2-}$  (section 5 will explain how bicarbonate and carbonate can interconvert) is 114 mg per kg of seawater. These concentrations are much higher than we would predict from simple solubility calculations alone. (In this case one of the reasons is that the presence of magnesium interferes with the formation of  $\text{CaCO}_3$  allowing  $\text{Ca}^{2+}$  to build up).

This supersaturation of  $\text{Ca}^{2+}$  means it takes very little effort to precipitate  $\text{CaCO}_3$  from seawater and the making of shells should be easy.



Confusion about pH is widespread, so we will use this section to remind readers about pH. Many people remember from school that pH is a measure of 'acidity' but not much more than that. The original definition of pH was that pH is the negative base 10 logarithm of the concentration of  $\text{H}^+$  ions (or, in a more accurate modern sense,  $\text{H}_3\text{O}^+$  ions) in a solution. But what does that mean?

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

[Eq. 5]

Coverage of the 2011 earthquakes in New Zealand and Japan has reminded us that many people have a weak understanding of logarithms. Both the Richter scale (and its variants) and the pH scale are logarithmic.

A base 10 logarithm (usually what people mean when they write 'log') is the number,  $x$ , so that  $10^x$  gives the number you want. For example, the log of 100 is 2. This means that  $\log(100) = \log(10 \times 10) = \log(10^2) = 2$ . Similarly, the log of a million is 6, meaning that  $\log(1,000,000) = \log(10 \times 10 \times 10 \times 10 \times 10 \times 10) = \log(10^6) = 6$ . The log of a number less than 1 is negative. For example,  $\log(0.01) = \log(1/100) = \log(1/10^2) = \log(10^{-2}) = -2$ , compared to 2 for the log of 100.

Before ready access to calculators and computers, logarithms offered a convenient way to multiply large numbers. Now they are mostly used to compare numbers that differ by a very large relative amount.

For example, if we take the population of New Zealand (4 million), China (1340 million), and India (1270 million) then it can be hard to make comparisons, since the *difference* between China and India (70 million) is almost 20 x the population of New Zealand. But if we take the logs of the populations, New Zealand = 6.6, China = 9.13, and India = 9.10. It is now obvious that, relatively speaking, the populations of India and China are the same while that of New Zealand is very much less.

Earthquakes can range from feeling like a truck driving past to having the ground shaken like a dog with a toy. So to group earthquakes we use the Richter scale. A force 5 earthquake is 1000 times weaker than a force 8 because a log difference of 3 means  $10^3 = 10 \times 10 \times 10 = 1000$  difference. (There are lots of complications with earthquakes like energy vs. ground movement but let's ignore that for now).

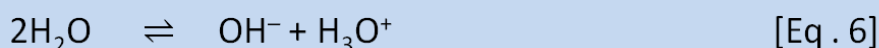
$\text{H}^+$  is never found by itself in a water based solution – it will always react with a  $\text{H}_2\text{O}$  to form  $\text{H}_3\text{O}^+$ . So these days when chemists talk about pH they refer to  $\text{H}_3\text{O}^+$  instead of  $\text{H}^+$  (which was in the original definition of pH and persists in some school text books). The definition of an acid (in aqueous chemistry) is thus a substance that gives (or *donates*) an  $\text{H}^+$  (proton) to water to form  $\text{H}_3\text{O}^+$ , while a base takes (or *accepts*) the proton. An acid is thus a source of  $\text{H}_3\text{O}^+$ .

The negative in the  $-\log$  part of the pH expression is an artefact of convention: Concentrations in pH calculations are much less than 1; so log values are negative. But, to avoid confusion by expressing a concentration as a negative number, the pH scale instead is multiplied by -1 to make all the numbers positive.

We are going to carry on pretending that it is this simple but, just for the record, the situation is, yet again, somewhat more complicated. (Chemists may wince, but we will avoid using 'activity'). However, we do need to introduce a chemical term: A **mole** is the SI ('metric') unit for *amount of substance*.

One mole of a substance is simply the molar mass in grams. For example, oxygen mass = 16 grams per mole, hydrogen mass = 1 gram per mole so the molar mass of water, H<sub>2</sub>O = 16 + 1 + 1 = 18 grams per mole. Therefore, 1 mole water = 18 g. Chemists use moles because the number of atoms or molecules in a mole is constant (1 mole = 6.022 x 10<sup>23</sup> atoms or molecules). Similarly, 1 mole of CO<sub>2</sub> = 44 g and thus contains the same number of molecules (6.022 x 10<sup>23</sup>) as 18 g water. This is useful for chemists because they can use moles to look at reactions as if they were recipes - to bake a cake you need to know how many eggs you have, not the weight of the eggs.

You may recall from school that a pH of 7 is *neutral*. If we do the calculation we find that neutral water has an H<sub>3</sub>O<sup>+</sup> concentration of 1 x 10<sup>-7</sup> moles per litre (mol L<sup>-1</sup>). It isn't much, but it is definitely greater than zero. Where does the H<sub>3</sub>O<sup>+</sup> come from? We mentioned the idea of equilibrium in section 1. The H<sub>3</sub>O<sup>+</sup> comes from the reaction (called a *dissociation*) between two molecules of water:



Water does this naturally to a small extent, so a water-based solution always contains a little H<sub>3</sub>O<sup>+</sup>. We define a neutral pH has the same concentration of H<sub>3</sub>O<sup>+</sup> as pure water.

A difference of 1 pH unit means a 10x difference in the concentration of H<sub>3</sub>O<sup>+</sup>. Measurements show **average ocean pH has decreased by 0.11 pH units (from 8.25 to 8.14) since the industrial revolution and is on track to decrease by a further 0.3 units** (0.4 units in total, to 7.8) by 2100. Is that so bad? Yes. A difference of 0.11 pH units corresponds to a 29% increase in the concentration of H<sub>3</sub>O<sup>+</sup>. A difference of 0.4 pH units corresponds to a 150% increase in H<sub>3</sub>O<sup>+</sup>.

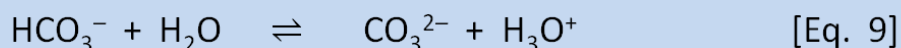
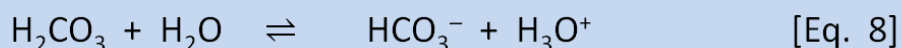
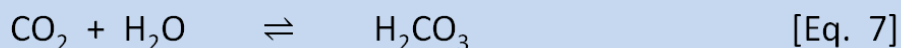
The concentration of H<sub>3</sub>O<sup>+</sup> in the ocean has increased by 29% since the industrial revolution. By 2100 the increase will be 150%.

Try these calculations yourself. On a spreadsheet enter =10<sup>-8.25</sup> to calculate the pre-industrial concentration of H<sub>3</sub>O<sup>+</sup> (on a calculator use the 10<sup>x</sup> button). In the next two cells enter =10<sup>-8.14</sup> and =10<sup>-7.8</sup>. You have now calculated the pre-industrial, current, and predicted end-of-century concentrations of H<sub>3</sub>O<sup>+</sup>. The 29% increase in H<sub>3</sub>O<sup>+</sup> can be verified by entering =100\*(10<sup>-8.14</sup> - 10<sup>-8.25</sup>)/(10<sup>-8.25</sup>). Replace 8.14 with 7.8 (=100\*(10<sup>-7.8</sup> - 10<sup>-8.25</sup>)/(10<sup>-8.25</sup>)) to check that the 0.4 pH unit difference (8.25 to 7.8) will lead to a 150% change.

In the last Sections, we introduced pH and solubility. We noted that the pH of the surface seawater has dropped from 8.2 to 8.1 since the pre-industrial revolution, leading to a 29% increase in  $\text{H}_3\text{O}^+$ . If  $\text{CO}_2$  emissions continue, a 150% increase in  $\text{H}_3\text{O}^+$  is predicted by 2100. Concerns about this increase in acidity are not limited to the decrease in pH (or increase in  $\text{H}_3\text{O}^+$ ), but include the resulting changes to carbon species in seawater.

Just as it is in biology, a **species** in chemistry is a classification. A chemical species describes different forms a substance can be found in. For example, the species of nitrogen in your garden soil and in stream water may be ammonium ( $\text{NH}_4^+$ ), ammonia ( $\text{NH}_3$ ), and nitrate ( $\text{NO}_3^-$ ). In the context of ocean acidification we refer to the different **species of inorganic carbon** – carbon dioxide ( $\text{CO}_2$ ), carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3^-$ ), and carbonate ( $\text{CO}_3^{2-}$ ) – and how it is possible to interconvert between them.

The equations below describe *overall* reactions (some are actually made up of several steps) of the inorganic carbon species in seawater. In equation 7,  $\text{CO}_2$  reacts with water to form carbonic acid ( $\text{H}_2\text{CO}_3$ ). In equation 8, carbonic acid dissociates in water to give bicarbonate ( $\text{HCO}_3^-$ ) and  $\text{H}_3\text{O}^+$ . In equation 9, bicarbonate dissociates to give carbonate ( $\text{CO}_3^{2-}$ ) and  $\text{H}_3\text{O}^+$ .

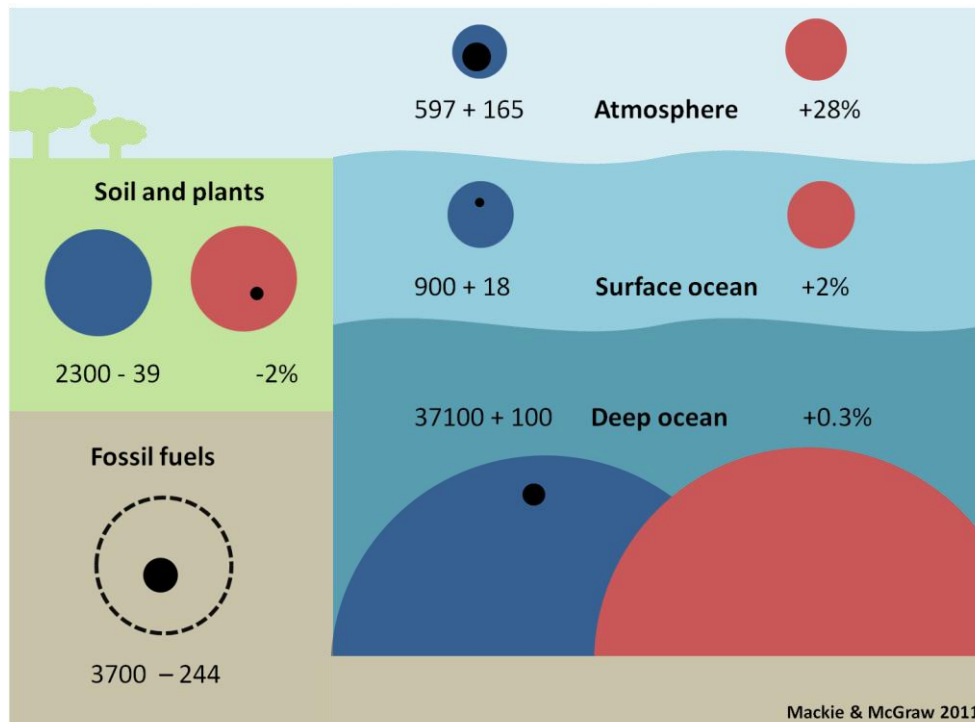


BUT, as we saw in Section 1, each equation is in equilibrium and can occur in the left-to-right direction (as written) or the right-to-left direction. That is, the equations **do not** tell us if a reaction is thermodynamically *spontaneous* (i.e. which direction is favoured) or about the *rate* of reaction. These things need to be determined experimentally.

The experiments have, of course, been done. For now we will just note that *at typical seawater pH values* the reactions in Eq. 7-9 are *spontaneous* as written from left to right.

Overall equations 7-9 mean that in the oceans 91% of 'carbonate' is in the form of bicarbonate ( $\text{HCO}_3^-$ ), 8% is in the form of carbonate ( $\text{CO}_3^{2-}$ ), and less than 1% is found as  $\text{CO}_2$  and  $\text{H}_2\text{CO}_3$ . (The way we calculate this distribution, is discussed in **Appendix One**).

There is a large amount of these inorganic carbon species being held in the ocean. **Figure 2** shows the size of each carbon reservoir on Earth.



**Figure 2.** Carbon reservoirs as preindustrial size (blue circles) and modern size (red circles) with change since the industrial revolution (black circles). Numbers give size of preindustrial with amount of change (+ or -) and also express the change as a %. Size in gigatons of carbon = Gt C. (1 Gt = 1,000 million tons, i.e. billion tons). Numbers are expressed here as gigatons of carbon (Gt C) because this is the unit used by the IPCC. Other publications may use gigatons of CO<sub>2</sub> (Gt CO<sub>2</sub>); multiply Gt C by 3.67 to convert to Gt CO<sub>2</sub> and divide Gt CO<sub>2</sub> by 3.67 to get Gt C. Another unit sometimes used is petagrams. 1 Pg = 1 Gt so 1 Pg C = 1 Gt C and 1 Pg CO<sub>2</sub> = 1 Gt CO<sub>2</sub>.

The first number in each box gives the size of the preindustrial reservoir in billions of tons (giga tons, Gt) of carbon. (Thus, the preindustrial surface ocean contained 900 billion tons of carbon). The second number is the change in the size of the reservoir from preindustrial to modern times in billions of tons of carbon. NOTE that here 'modern times' means the mid 1990's – the IPCC is very conservative – and the fossil fuel reservoir is an estimate for 'recoverable' fossil fuels.

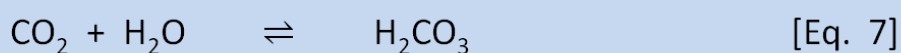
Thus, **the modern surface ocean contains an extra 18 billion tons of carbon**, which represents a +2% increase. In contrast, sea life and the surface sediment reservoirs have not changed appreciably in size.

The modern surface ocean contains an *extra* 18 billion tons of carbon

Where has so much inorganic carbon in the oceans come from? It has come from the weathering of rocks.

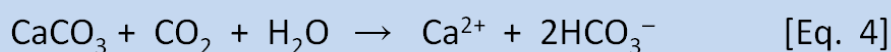
Carbonate rocks can be  $\text{CaCO}_3$  (calcium carbonate = limestone) or  $\text{MgCO}_3$  (magnesium carbonate) or mixed calcium-magnesium carbonate  $\text{CaMg}(\text{CO}_3)_2$  (=dolomite) and several other less common forms. We will discuss only calcium carbonate, but as calcium and magnesium are members of the same group (i.e. vertical column) on the periodic table you would just replace Ca with Mg in the equations.

Limestone weathering occurs when rainwater reacts with the carbonate rocks. Rainwater does not have a neutral pH, but this has nothing to do with industrial pollution. Rainwater is in equilibrium with atmospheric  $\text{CO}_2$ , so carbonic acid is formed via equation 7 from Section 5. This leads to mildly acidic rainwater with a pH of about 5.7.



(Note: acid rain refers to rain with a  $\text{pH} < 5.7$  due to equilibration of rain with sulphuric and nitric acids; the  $\text{SO}_2$  and  $\text{NO}_x$  are formed and released by burning fossil fuels and biomass.)

What happens when rain washes over limestone on its way to rivers? We need Equation 4, the reverse of calcification, which describes the weathering of carbonate rocks:



In Section 1 we said that Equation 1, calcification, was a source of  $\text{CO}_2$ . So it should come as no surprise to say that the weathering of carbonate rocks *consumes* atmospheric  $\text{CO}_2$ .

The weathering of carbonate rocks *consumes* atmospheric  $\text{CO}_2$

The result of weathering is that river water contains a lot of carbon species, in the form of bicarbonate and carbonate, compared to seawater.

River water also contains salts. Stephen Jay Gould wrote an engaging essay (republished in the book *Eight Little Piggies*) about Edmund Halley (he of the comet). Halley, like Gould, was a polymath and one of his ideas was to work out the age of the Earth from the amount of salts in the sea. It isn't clear if Halley knew about the other salts in the sea or if he just meant NaCl, but it doesn't matter as Halley's argument works just as well for carbonate species. Halley began with the observations that:

1) The oceans are not saturated with salts (NaCl and/or carbonate species etc). That is, you can add additional salt to seawater and it will dissolve.

2) River water contains salts.

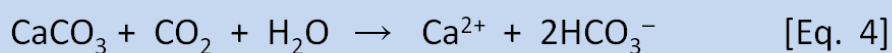
Halley knew the water was recycled and he knew the salts came from the rivers because of weathering. Halley assumed the salt content must be increasing with time as the rivers washed more salts in, but none ever left. So Halley concluded that if you measured the saltiness (*salinity*) at the time (1700ish for Halley) and again in a few hundred years then Halley expected that the salinity would have measurably increased and allow a *maximum* the age of the Earth to be calculated.

For example, current salinity is about 35 grams per kg of seawater. If it had been 34 g per kg of seawater 300 years ago, the salinity would have increased 1 g/kg over 300 years. Therefore, it would have taken 10,500 years to build up the current 35 g/kg - if we started from salt-free water. The *maximum* age part is because if the seas had *started* salty then the Earth would be younger than it seemed. Halley, a young-Earth creationist, expected an answer in the low thousands of years, but was wrong for several reasons.

Halley's biggest mistake was his assumption that it was a one way process, that salts never leave the ocean. But salts do leave the ocean and are part of a long slow cycle. Halley should have thought this one through as salt deposits (from ancient seas) have been mined by humans for thousands of years. Similarly, calcium carbonate (another salt delivered to the oceans by rivers) also leaves the ocean – as part of the **carbon cycle**. The most striking example of calcium carbonate leaving the ocean is the White Cliffs of Dover, which are made of the calcium carbonate skeletons of *coccolithophores*.

We are so familiar with the idea of a **carbon cycle** now that we don't recall how astonishing the idea would have been only a few hundred years ago that the weathering of carbon from rocks could possibly be part of such a cycle. But, as we shall see in later Sections, when atmospheric CO<sub>2</sub> is high then more acidic rain causes more weathering and that *consumes* CO<sub>2</sub> to lower the atmospheric CO<sub>2</sub>. Only problem is that this happens over a geological time scale.

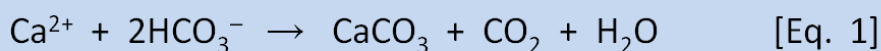
If we do the same thing that Halley did for salt with bicarbonate HCO<sub>3</sub><sup>-</sup> in rivers then we can get a good estimate of the amount of weathering that happens and thus how much bicarbonate added to the ocean by rivers. We know from Eq. 4 that weathering consumes CO<sub>2</sub>. So the amount of bicarbonate added to the ocean is equal to the amount of CO<sub>2</sub> consumed.



But remember that this CO<sub>2</sub> comes from the atmosphere. So it follows that given enough time then that the consumption of CO<sub>2</sub> by weathering will remove all the CO<sub>2</sub> from the atmosphere. It turns out that amount of weathering is sufficient to remove **all** CO<sub>2</sub> from the atmosphere in about 3500 years.

(**Appendix two** steps through this calculation).

Plainly this hasn't happened in the past. Something is returning CO<sub>2</sub> to the atmosphere. That something is our Eq. 1 for calcification:



Equation 1 explains the formation of CaCO<sub>3</sub> in the ocean from Ca<sup>2+</sup> and 2HCO<sub>3</sub><sup>-</sup> derived from weathering. When this CaCO<sub>3</sub> dissolves, by Eq. 4, it exactly reverses the original Ca<sup>2+</sup> and 2HCO<sub>3</sub><sup>-</sup> derived from weathering that was lost from the ocean by CaCO<sub>3</sub> formation, and also consumes the CO<sub>2</sub> formed at the same time. However, if CaCO<sub>3</sub> is buried in sediments, that Ca<sup>2+</sup> and 2HCO<sub>3</sub><sup>-</sup> must now be replaced by further weathering of terrestrial limestone. Fortunately, the CO<sub>2</sub> needed to do that has been returned to the atmosphere after CaCO<sub>3</sub> formation. Thus closure of the cycle!

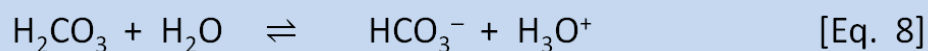
But what happens when the equilibrium of the oceans is disturbed?

#### Part 7: Le Chatelier not good enough

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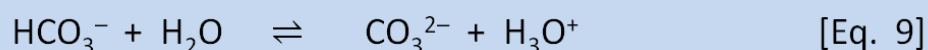
In this Section we shall expand on the speciation described in Section 5 and consider what happens when the equilibrium of the oceans is disturbed. We will show that naive application of Le Chatelier's principle is not good enough for complex chemistry.

As we noted in Section 4, the definition of an acid (in aqueous chemistry) is a substance that gives (or *donates*) an H<sup>+</sup> (proton) to water to form H<sub>3</sub>O<sup>+</sup>, while a base takes (or *accepts*) the proton. This means that each acid (or base) reacts with a base (or acid) to produce another acid-base pair. For example, consider the dissociation of carbonic acid given in Section 5's Equation 8.



Here the carbonic *acid* has, not surprisingly, acted as an acid and donated an H<sup>+</sup> to the H<sub>2</sub>O (becoming HCO<sub>3</sub><sup>-</sup>). The H<sub>2</sub>O has acted as a base by accepting the H<sup>+</sup> (becoming H<sub>3</sub>O<sup>+</sup>). In the reverse reaction HCO<sub>3</sub><sup>-</sup> acts as a base by accepting H<sup>+</sup> from H<sub>3</sub>O<sup>+</sup> (becoming H<sub>2</sub>CO<sub>3</sub>) and the H<sub>3</sub>O<sup>+</sup> acts as an acid by donating H<sup>+</sup> (becoming H<sub>2</sub>O). The strength of an acid is a measure of how effectively an acid donates its proton.

We can also consider Equation 9 for the dissociation of bicarbonate to carbonate:





With our definition of acids we can see that bicarbonate is now acting as an acid by donating an  $\text{H}^+$ . That is, bicarbonate can act as both an acid and as a base.

Chemical equilibria can be considered to be a self-balancing seesaw, pivoting around the equilibrium arrow. If one side becomes unbalanced there is a 'drive' to restore equilibrium. BUT equilibrium seldom means a 50:50 even distribution of molecules on both sides; natural equilibrium might mean a million-to-one balance.

Chemists describe the ratio of one side of a reaction equation to the other by using an **equilibrium constant (K)**. This is the balance that a reaction will eventually reach if left undisturbed. K is calculated by using the reaction equation.

For example in the case of Equation 8 the expression is given by Equation 10:

$$K = \frac{\text{conc. HCO}_3^- \text{ at equilibrium} \times \text{conc. of H}_3\text{O}^+ \text{ at equilibrium}}{\text{conc. of H}_2\text{CO}_3 \text{ at equilibrium}} \quad [\text{Eq. 10}]$$

To describe this balance the expression takes the concentrations of the products ( $\text{HCO}_3^-$  and  $\text{H}_3\text{O}^+$ ) and divides by the concentrations of the reactants ( $\text{H}_2\text{CO}_3$ ). Note that we do **not** include the concentration of water ( $\text{H}_2\text{O}$ ) when we divide by the products. This is because the expression uses concentrations of each substance *in water* and the concentration of water in water is always 1 litre of water per litre of water (or whatever unit you are using).

The reason why the concentrations are *multiplied* is really outside the scope of a blog post. (And, in fact, for more complex salts the concentrations must sometimes be squared or cubed). At the risk of hand waving, we note that these relationships were discovered **experimentally** and theory caught up many years later.

However, as we have noted, such a balance is not necessarily achieved instantly. Many reactions are quite slow and so quite often a reaction system is **not** at equilibrium. Chemists describe the *actual* balance between the sides of an equation by using a **reaction quotient (Q)** (Equation 11).

$$Q = \frac{\text{conc. HCO}_3^- \text{ now} \times \text{conc. of H}_3\text{O}^+ \text{ now}}{\text{conc. of H}_2\text{CO}_3 \text{ now}} \quad [\text{Eq. 11}]$$

For now we will just state that **K** gives the ratio of products to reactants that exists when a system is at equilibrium and **Q** gives the ratio of products to reactants that is present at a given time before equilibrium has been reached.



Many readers may be familiar with *Le Chatelier's Principle* as a way to predict how a see-saw like equilibrium reaction responds when it is disturbed. It is a useful way to consider **simple** reactions. However, Le Chatelier's principle only applies to single-step chemical reactions. It can't be applied in a simple way to coupled or sequential reactions.

Recall our peanut analogy for equilibrium from Section 2:

*Consider a dinner party with 6 people. There are 5 people on one side of the table and 1 person on the other. Each side starts with a bowl of peanuts and they begin to throw them at each other. At any one time a few peanuts will be in flight, most of them coming from the side with 5 people. However, it is plain that very quickly almost all of the peanuts will end up on the side with 1 person. At this point, the side with 5 people can only throw peanuts as quickly as the lone peanut pitcher sends them over. An equilibrium has been reached. The number of peanuts on either side does not change even though a few individual peanuts swap sides.*

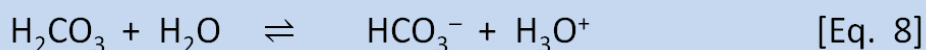
Now imagine that instead there is a long table. The lone peanut thrower is in the middle and there is a group at each end of the table. And, just to complicate things, at the top of the table a waiter keeps bringing in bowls of peanuts and at the foot of the table peanuts can only be thrown back if they land on the table (those landing on the floor stay there). What additional things do we need to know before we can decide how the equilibrium would change?

In our case Equations 7-9 are a coupled set of equations where the reactants (things on the left hand side) of one equation are the products (things on the right hand side) of the previous equation and both reactions are happening at the **same time**. For this reason Le Chatelier's Principle does not apply. Instead we need to consider the equilibrium balances for each equation.

If we look at equation 9 in isolation, Le Chatelier predicts that if a little  $\text{H}_3\text{O}^+$  (i.e. acid) is added then it will force the reaction to the left side, **producing** bicarbonate. However other reactions are occurring *at the same time* and (for example) we also need to consider equation 8. If we consider equation 8 in isolation Le Chatelier predicts that if a little acid  $\text{H}_3\text{O}^+$  is added then this should force the reaction to the left side, **consuming** bicarbonate.

That is, Le Chatelier predicts that adding acid both produces **and** consumes bicarbonate. To resolve this apparent paradox, we need to consider the **equilibrium constants** for the reactions.

In the last section we introduced the concept of **reaction quotient** to describe the state of a reaction relative to the **equilibrium constant**. For equation 8 we have the following expressions:



$$K = \frac{\text{conc. HCO}_3^- \text{ at equilibrium} \times \text{conc. of H}_3\text{O}^+ \text{ at equilibrium}}{\text{conc. of H}_2\text{CO}_3 \text{ at equilibrium}} \quad [\text{Eq. 10}]$$

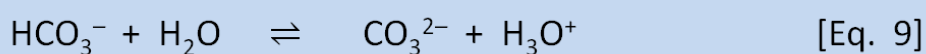
$$Q = \frac{\text{conc. HCO}_3^- \text{ now} \times \text{conc. of H}_3\text{O}^+ \text{ now}}{\text{conc. of H}_2\text{CO}_3 \text{ now}} \quad [\text{Eq. 11}]$$

The direction in which a reaction responds to a disturbance is given by comparing  $Q$  to  $K$ . If  $Q < K$  then the reaction system is 'not yet at' equilibrium and favours the right side (products) to reach equilibrium. If  $Q > K$  then the reaction system has 'gone past' equilibrium and favours the left side (reactants) to return equilibrium. (If  $Q = K$  the system is *at* equilibrium).  $K$  values cover a wide range and  $\text{p}K$ , analogous to  $\text{pH}$ , is more commonly used:  $\text{p}K = -\log(K)$  and  $K = 10^{(-\text{p}K)}$ .

Consider Equation 8 at equilibrium (i.e.  $Q = K$ ) and ask what happens if we add some acid  $\text{H}_3\text{O}^+$  to the system. By adding  $\text{H}_3\text{O}^+$  we increase the products, thus increasing the denominator and therefore increasing  $Q$  so that now  $Q > K$ . The reaction system therefore favours the left side (reactants) and  $\text{H}_2\text{CO}_3$  is produced.

So far this sounds like Le Chatelier, but now we consider what happens with equation 8 and equation 9 occurring simultaneously.

For Eq. 8, in seawater at  $10^\circ\text{C}$ ,  $\text{p}K = 6.00$ . At the preindustrial ocean  $\text{pH}$  of 8.25, the equilibrium ratio of the left side, carbonic acid, to the right side, bicarbonate, is about 1:170 (depending on salinity). The calculation is  $10^{-6.00} / 10^{-8.25}$ . For Eq. 9, in seawater at  $10^\circ\text{C}$ ,  $\text{p}K = 9.19$ . At the preindustrial ocean  $\text{pH}$ , the equilibrium ratio of the left side, bicarbonate, to the right side, carbonate, is about 9:1 (the calculation is  $10^{-9.19} / 10^{-8.25}$ ).

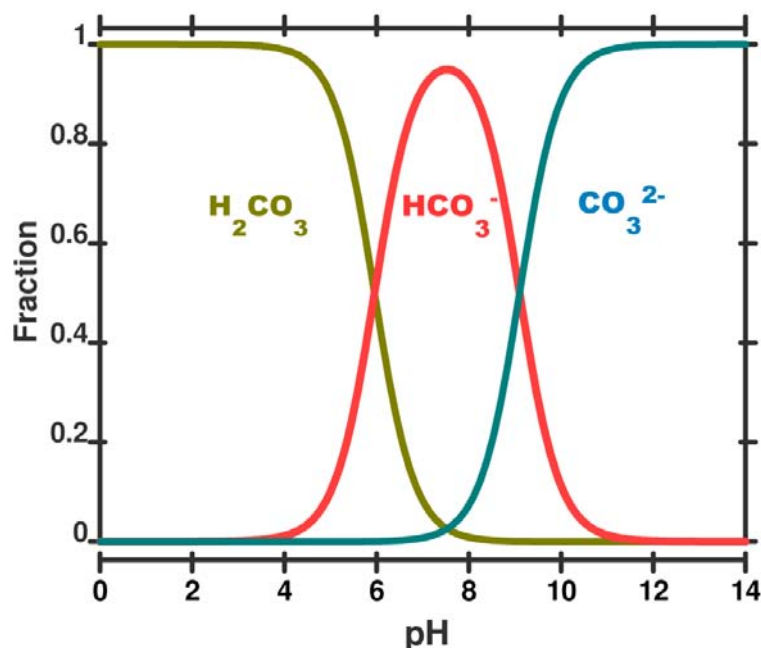


If we couple these reactions, we see that at typical ocean pH equation 8 produces a ratio of carbonic acid to bicarbonate (and carbonic acid to  $\text{H}_3\text{O}^+$ ) of 1:170. If we do add a little acid ( $\text{H}_3\text{O}^+$ ), then 170 parts of the acid stay as acid ( $\text{H}_3\text{O}^+$ ) and only 1 part reacts to form carbonic acid and water. But equation 9 tells us that if acid is added then 1 part of the acid remains as  $\text{H}_3\text{O}^+$  but 9 parts of the acid, **and** therefore some of the carbonate, are consumed to produce bicarbonate. At typical seawater pH, the response of the system to the addition of acid is dominated by the consumption of carbonate shown in Equation 9.

Now we can see that adding acid to the system does indeed push equation 9 to the left. Though a naive application of Le Chatelier's Principle to seawater chemistry gets the 'right' answer, this is only because of a fortuitous combination of the values for the equilibrium constants. (Seawater is in fact even more complex and there are many other competing reactions going on at the same time).

Thus, adding acid to the seawater- $\text{CO}_2$  system massively changes the proportion of carbonate since it is consumed in the reaction. However, it hardly changes the proportion of bicarbonate since most of the carbon is already in the form of bicarbonate.

Calculations based on these concepts can be used to produce a speciation plot like **Figure 3** which expresses the concentration of each species (expressed as a fraction of the whole) as a function of pH. In this figure the total sum of species containing carbon atoms is constant. What changes is the relative proportion of each species. We hasten to add that by adding  $\text{CO}_2$  to the ocean this is no longer true and the calculations become more difficult.



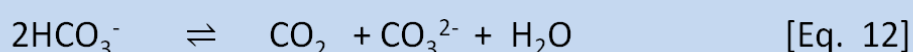
**Figure 3.** A speciation diagram for the carbonic acid system in seawater as a function of pH. The y-axis gives the fraction of each species present. A vertical line drawn at any pH value gives the relative proportion of each species. This plot is simplified to illustrate the concept; in real seawater several other factors like salinity, temperature and pressure are important.

We can run through some example calculations. Concentrations are given as moles per kg of seawater. For prior to the industrial revolution we have taken a pH of 8.25. Other input parameters are a total dissolved inorganic carbon concentration of  $2100 \times 10^{-6} \text{ mol kg}^{-1}$  (total dissolved inorganic carbon is the sum of the species described in Section 5, temperature = 15 deg C, and the salinity = 35. Under these conditions, which are typical for the ocean, the concentration of  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  would have been  $10 \times 10^{-6} \text{ mol kg}^{-1}$ ,  $1830 \times 10^{-6} \text{ mol kg}^{-1}$  and  $260 \times 10^{-6} \text{ mol kg}^{-1}$  of seawater, respectively (Roy constants used – see below).

The calculated values add to give the total dissolved inorganic carbon of  $2100 \times 10^{-6} \text{ mol kg}^{-1}$  and  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  are roughly in a 7:1 ratio (the carbonic acid does not really contribute, because, as expected it is 170 times less than the  $\text{HCO}_3^-$ ). Today, after a decrease in pH to 8.14 – and an increase of 29% in the concentration of  $\text{H}_3\text{O}^+$  – typical calculated concentrations of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  are about  $1880 \times 10^{-6} \text{ mol kg}^{-1}$  and  $210 \times 10^{-6} \text{ mol kg}^{-1}$ , respectively. You can see that  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  are now roughly in 9:1 ratio. The concentration of carbonate  $\text{CO}_3^{2-}$  has changed by  $-25\%$  ( $(260-210)/210 \times 100$ ), but the concentration of bicarbonate  $\text{HCO}_3^-$  has only changed by  $3\%$  ( $(1880-1830)/1830 \times 100$ ).

We have made several simplifications as the calculations are complex and are not encountered before postgraduate study. However, if you would like to try it yourself, you can download a program, written by one of us (KH) called **SWCO2** available from [http://neon.otago.ac.nz/research/mfc/people/keith\\_hunter/software/swco2/](http://neon.otago.ac.nz/research/mfc/people/keith_hunter/software/swco2/). You will need to take some care – actual realistic values for the various entry parameters fall within a relatively narrow range.

If you do have a go yourself you will discover yet another layer of complexity: There are several sets of equilibrium constant,  $K$ , values to choose from. The reasons are complex and rest on the way that these values are determined **experimentally** and, though each set of values is internally consistent, each set uses a slightly different set of initial assumptions. Now, just to further complicate things, we will introduce another equation:



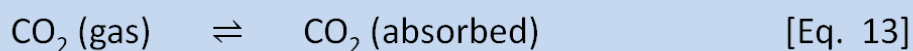
$K$  for this reaction is about  $10^{-4}$ . That is, the ratio of left to right is about 10,000:1. This means that, to a first approximation, seawater (dominated by  $\text{HCO}_3^-$ ), has only a little bit of  $\text{CO}_2$  and  $\text{CO}_3^{2-}$ . More importantly, it also shows that if we add  $\text{CO}_2$  to seawater,  $\text{CO}_2$  will spontaneously react with  $\text{CO}_3^{2-}$  to form  $2\text{HCO}_3^-$  because  $K$  for the reverse reaction is  $10^4$ .

Ocean acidification is caused by absorbance of atmospheric  $\text{CO}_2$  by seawater. We now see that this acidification of surface seawater is causing the removal of  $\text{CO}_3^{2-}$ :

Adding  $\text{H}_3\text{O}^+$  to seawater causes the removal of  $\text{CO}_3^{2-}$

But why should this be a problem? We know from Equation 1 that calcification uses bicarbonate  $\text{HCO}_3^-$ , not carbonate  $\text{CO}_3^{2-}$ . Why does it matter if some carbonate from the oceans is converted to bicarbonate? Won't that actually help the shellfish?

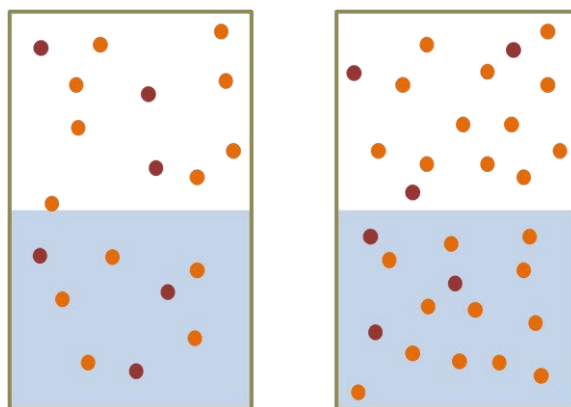
How does CO<sub>2</sub> get into the ocean? We saw in Section 5 that the oceans contain **50** times more carbon than the atmosphere. Is it possible that instead the oceans are actually the source of CO<sub>2</sub> in the atmosphere, not fossil fuels? The relevant equation (below) is the equilibrium of CO<sub>2</sub> in the atmosphere (or *gas* phase) and CO<sub>2</sub> absorbed by the ocean:



Equations 7-9 show what can happen once CO<sub>2</sub> is absorbed, but Eq. 13 (in the left to right direction) is the process of getting the CO<sub>2</sub> into the seawater in the first place. The reverse process (right to left) is called **degassing**. Familiar examples of degassing are carbonated beverages, like beer and fizzy drinks, going flat as they release CO<sub>2</sub> to the atmosphere. To follow and predict what happens we need to know some gas laws.

The first is Dalton's Law of partial pressures. Dalton's Law is that the total pressure exerted by a gas mixture is the sum of the pressure exerted by each component. For example the pressure exerted by a container of compressed air is the sum of the pressure exerted by the oxygen + the pressure exerted by the nitrogen + the pressure exerted by the argon + the pressure exerted by the carbon dioxide + all the other components. The pressure exerted by a given component is called its **partial pressure**.

The other gas law we need to know is **Henry's Law of gas solubility**. Henry's Law is sort of an extension of Dalton's and says that if you have a liquid **in equilibrium** with the gas above it, then the amount of gas that is absorbed in the liquid is directly proportional to the partial pressure of the gas. That is, if you take a vessel half full of water and double the amount of air by pressurising the air space, then twice as much of each component in the air is absorbed.



**Figure 4.** Henry's Law. The more molecules of a gas (i.e., the greater the partial pressure) then the more of that gas that dissolves in the water. In the headspace above the water the number of orange dots has increased from left to right. Henry's Law tells us that therefore the number of orange dots in the water also increases from left to right.

A Henry's Law coefficient,  $K_H$  expresses the *equilibrium* ratio between the two sides of Eq. 13. However, a critical point to note is that the ocean is **NOT** in such equilibrium with the atmosphere. (We will return to this in a later Section). Calculations are complicated because of biological activity and because; as we have seen in Section 5, as soon as  $\text{CO}_2$  is absorbed then it forms carbonic acid. However these gas laws tell us that the concentration (really we should say *partial pressure*) of  $\text{CO}_2$  in both the atmosphere and the oceans are directly related. (Yes, it is correct to refer to a partial pressure of  $\text{CO}_2$  gas in the ocean). That is, a  $\text{CO}_2$  increase in the atmosphere causes a  $\text{CO}_2$  increase in the ocean.

Henry's Law is temperature dependent and warmer liquids hold less gas than colder liquids. This temperature dependence explains why a warm soda is much more likely to fizz out of the bottle than a cold soda and has large implications for regional differences in ocean acidification.

There is a huge range in temperature (and consequently  $\text{CO}_2$  partial pressure) throughout the ocean. For example, deep ocean water that has recently been in contact with the atmosphere contains more  $\text{CO}_2$  than surface water for two reasons. Firstly, it is colder so it can hold more  $\text{CO}_2$ . Secondly, falling organic matter – fish poo and the like – gets eaten by bacteria (thus releasing  $\text{CO}_2$  by respiration) as it falls to the bottom. Exchange of cold,  $\text{CO}_2$ -rich deep ocean water and surface water happens through upwelling and downwelling. This can result in some ocean regions being sources of  $\text{CO}_2$  as deep water comes to the surface, warms up and degasses. Other regions are sinks of  $\text{CO}_2$  as warm water with low  $\text{CO}_2$  cools down, sucks up extra  $\text{CO}_2$  and sinks.

How can we be sure that ocean acidification is caused by  $\text{CO}_2$  in the atmosphere? That is, how do we now that the extra  $\text{CO}_2$  in the atmosphere is not coming from a natural warming of the ocean?

\*This was to have been the 8<sup>th</sup> in the series but we intercalated one post and lost the original title: "Henry the 8<sup>th</sup> I am".

## Part 10: Is the ocean blowing bubbles?

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In the last section we asked "how can we be sure that atmospheric  $\text{CO}_2$  is entering the oceans to cause acidification?" That is, how can we be certain that the oceans are not a net *source* of the increased  $\text{CO}_2$  in the atmosphere? Our answer to this question is a modification of an earlier 2010 post by one of us at Sceptical Science.

We can use four key observations to be confident the extra  $\text{CO}_2$  in the atmosphere has come from the combustion of fossil fuels and *not* from outgassing of  $\text{CO}_2$  from the ocean or from soil or land sources: (1) the decrease in atmospheric oxygen corresponds to the usage of fossil fuels, (2) the carbon isotope ratio in the atmosphere indicates that the excess  $\text{CO}_2$  comes from fossil fuels, (3) not enough warming of the ocean has occurred, and (4) known emission of  $\text{CO}_2$  from fossil fuel usage. First, a quick word about 'ppm': Scientists use *parts per million* ppm for concentrations that are much lower than percent (parts per hundred) or (parts per thousand). 1 ppm = 0.0001%.

## 1. Oxygen decrease

Atmospheric oxygen (O<sub>2</sub>) is going down by the same amount atmospheric CO<sub>2</sub> is going up.

We have seen in previous sections that carbon in the ocean is always bound to oxygen in some way – as H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, or CO<sub>3</sub><sup>2-</sup>. So if the oceans were the source of the extra CO<sub>2</sub> in the atmosphere there would be no change in atmospheric oxygen as the carbon is already bonded to oxygen. On the other hand, we know that the burning of any sort of fuel (including non fossil fuels like wood) requires oxygen and produces CO<sub>2</sub>. This suggests that the burning of some sort of carbon containing fuel is responsible for both the CO<sub>2</sub> increase and the oxygen decrease.

Atmospheric Oxygen is so abundant at about 21% (209,500 parts per million or ppm) that we are in no danger of running out. However, the measured *decrease in oxygen* corresponds to the amount of oxygen required to burn the amount of fossil fuels *known* to have been burned. See the IPCC 3<sup>rd</sup> Assessment Report (2001) section 3.5.1, especially Figure 3-4 and the IPCC 4<sup>th</sup> Assessment Report (2007) Figure 2-3. But how do we know that *fossil* fuels are the source of added carbon that is causing the decrease in oxygen?

## 2. Isotope ratios

Isotopes are different forms of the same element that differ in the mass of the nucleus. You may have heard of uranium-235 and uranium-238. These are two (of the many) forms of uranium. The nucleus contains particles with a positive electric charge (protons) and particles with no electric charge (neutrons). Isotopes have the same number of protons but different numbers of neutrons. Mostly the properties of isotopes are the similar except for properties that depend on the mass of the atoms. For example, diffusion of a gas: A heavier gas diffuses more slowly than a lighter gas. This principle was used to separate uranium isotopes during the Second World War's atomic bomb programme, the Manhattan project.

Not all isotopes are radioactive. Isotopes that do not undergo radioactive decay are called **stable isotopes**. There are two common stable isotopes of carbon, <sup>12</sup>C and <sup>13</sup>C, and one common radioactive isotope, <sup>14</sup>C. The carbon in all living things is a mixture of all three of these isotopes of carbon. <sup>14</sup>C is very rare; only about 0.000000001% (1 part per trillion) of the carbon in the atmosphere is <sup>14</sup>C, 98.9% is <sup>12</sup>C, and 1.1% is <sup>13</sup>C. Such a relative ratio of <sup>12</sup>C to <sup>13</sup>C is usually different for each type of carbon source.

For example, photosynthesis favours <sup>12</sup>CO<sub>2</sub> for several reasons (including poor diffusion of <sup>13</sup>CO<sub>2</sub> into cells because it is heavier). This means that living plants and fossil fuels (which are derived from plants) have a relatively low proportion of <sup>13</sup>CO<sub>2</sub> – chemists say fossil fuels are **depleted** in <sup>13</sup>C. Also, because they are so old, fossil fuels contain no <sup>14</sup>C. The half life of <sup>14</sup>C is 5730 years so after a few million years of halving in number every 5730 years there is no <sup>14</sup>C left. Compared to fossil fuels, seawater water is **enriched** in <sup>13</sup>C and <sup>14</sup>C.

Isotope ratios can be determined with great precision and have been monitored in the atmosphere and ocean for decades. Observations show that the isotope ratios of carbon in the atmosphere are changing due to an influx of CO<sub>2</sub> depleted in <sup>13</sup>C. That is, the new isotope ratios of carbon contained in atmospheric CO<sub>2</sub> tells us that the additional carbon must be coming from <sup>13</sup>C-depleted fossil fuels, not the <sup>13</sup>C-rich oceans. ([www.esrl.noaa.gov/gmd/outreach/isotopes/c13tellsus.html](http://www.esrl.noaa.gov/gmd/outreach/isotopes/c13tellsus.html)).

### 3. Not enough warming

Warm water can hold less CO<sub>2</sub> than cold water. Our knowledge of Henry's Law and the CO<sub>2</sub> equilibria allow us to calculate the increase in seawater temperature that would be needed to cause the observed increase in *p*CO<sub>2</sub> in the atmosphere (i.e. the partial pressure of CO<sub>2</sub>). To explain the 100 ppm of additional CO<sub>2</sub> added to the atmosphere since preindustrial times by ocean warming, the average temperature of the surface ocean would have had to increased by about 10° C, much larger than has occurred.

As noted in Section 9, the Henry's Law coefficient, *K<sub>H</sub>*, is dependent on temperature (and salinity to a lesser extent). However, there is no exact expression as seawater is sufficiently complex that the values for *K<sub>H</sub>* in seawater have been **experimentally** determined. For constant salinity, the *p*CO<sub>2</sub> in the atmosphere doubles (i.e. =200% the initial concentration) for every 16° C increase in seawater temperature\*. Atmospheric CO<sub>2</sub> is now 140% of the preindustrial value (it increased by 110 ppm from 280 to 390 ppm). Thus the temperature change required to sufficiently change the Henry's Law coefficient is 140/200 × 16 = 11° C.\*\*

This calculation shows that the *surface* ocean would *on average* have to have warmed by about 10° C *since* about 1750 if the oceans had been the source of the CO<sub>2</sub>. Plainly the ocean does not have a uniform temperature, so the changes would actually need to be even more extreme in some places. Of course, no such warming has occurred.

\* For the interested this is explained in Takahashi et al. "Seasonal variation of CO<sub>2</sub> and nutrients in the high-latitude surface oceans: A comparative study" *Global Biogeochemical Cycles*, **7**(4), 843-878. <http://www.agu.org/pubs/crossref/1993/93GB02263.shtml>

\*\* This is a simplification; the actual relationship is expressed in terms of a partial derivative.

$$\frac{\partial \ln p\text{CO}_2}{\partial T} = 0.0423^\circ\text{C}^{-1}$$

### 4. Known fossil fuel CO<sub>2</sub> emissions

Most obviously, any alternative explanation for the source of the CO<sub>2</sub> in the atmosphere must also come up with where the 30 billion tonnes of CO<sub>2</sub> released yearly by fossil fuel burning goes.

We have a very good idea of the total amount of fossil fuel burned in the last 150 years. But, if we want to stick to really solid data we can limit our discussion to the last 30 odd years. The US Dept Energy publication, *The International Energy Annual*, (available at <http://eia.doe.gov/iea/carbon.htm>) shows that since 1980 to 2006 (the most recent year they have data for) a world total of 603 billion metric tons of CO<sub>2</sub> have been **released** into the atmosphere from the 'consumption and flaring of fossil fuels'.

This amount of **released** fossil fuel CO<sub>2</sub> is **less** than the amount of extra CO<sub>2</sub> that is currently **in** the atmosphere. That is, not only have humans released a lot of CO<sub>2</sub> to the atmosphere over the last 30 years, but not all of it is still in the atmosphere. Where is this 'missing' CO<sub>2</sub>?



This section steps through the calculation for how much CO<sub>2</sub> is 'missing' from the atmosphere. That is, how do we work out how much CO<sub>2</sub> that we know was released to the atmosphere is just not there?

The International Energy Annual reports that globally, 603 billion tons of CO<sub>2</sub> were released from the 'consumption and flaring of fossil fuels' between 1980 and 2006 (the most recent available data). Over the same time atmospheric CO<sub>2</sub> increased by 43 ppm from 339 ppm to 382 ppm (i.e. 2006 = 13% more than 1980).

For historical reasons atmospheric concentrations of gases are expressed as parts per million (ppm). So we need to convert the *tons of CO<sub>2</sub>* to *ppm*. To do this we need to know the mass of the atmosphere. Calculations by Trenberth give  $5.148 \times 10^{18}$  kg, (see <http://www.cgd.ucar.edu/cas/Trenberth/trenberth.papers/massERA40JC.pdf>) which we will round to  $5.1 \times 10^{18}$  kg. (You can roughly check this by taking sea level air pressure and multiplying by the area of the Earth).

1 part per million (ppm) of this atmospheric mass is  $5.1 \times 10^{12}$  kg (5.1 billion tons), but this does not take into account the fact that CO<sub>2</sub> molecules are heavier than other molecules in the atmosphere. Most of the atmosphere is nitrogen (78%) and oxygen (21%). Nitrogen (N<sub>2</sub>) has an atomic mass of 28 and oxygen (O<sub>2</sub>) has a mass of 32. Thus, we can say the 'average' molecule in air has a relative mass of about 29. CO<sub>2</sub> however has a mass of 44.

So, 1 ppm of CO<sub>2</sub> thus has a mass of  $(44/29) \times (5.1 \times 10^{12})$  kg =  $7.7 \times 10^{12}$  kg = 7.7 billion tons. If the calculation is done more carefully then the answer is 7.8 billion tons of CO<sub>2</sub>. (Some sources will give 1 ppm CO<sub>2</sub> = 2.13 Gt C, but we recall from Section 5 that we can convert that to Gt CO<sub>2</sub> by multiplying by 3.67:  $2.13 \times 3.67 = 7.8$ )

Using the more accurate value, we can see that the 603 billion tons of fossil fuel CO<sub>2</sub> released in the last 30 years gives an **expected** change of 77 ppm (=  $603/7.8$ ) CO<sub>2</sub> in the atmosphere. But, CO<sub>2</sub> has increased by only **43 ppm**. That is, about half (44%) of the fossil fuel CO<sub>2</sub> released over the last 30 years by humans – some 270 billion tons! – is missing.

Almost half the fossil fuel CO<sub>2</sub> released into the atmosphere over the last 25 years by humans – over 270 billion tons – is 'missing'. It is not in the atmosphere.

Where has it gone? Could it have been taken up by soils and plants? No, not all of it. The total global masses of carbon in land plants and soil are about 500 billion and 1500 billion tons, respectively (see Table 3-2 from the IPCC 3<sup>rd</sup> Assessment Report of 2001). That is, the collective 'standing crop' of soils and plants is 6 to 7 times the mass of the missing CO<sub>2</sub>. If soil and plants had taken up all or most of the fossil fuel CO<sub>2</sub> it means they must have increased by about 1/6<sup>th</sup> (15-20%) since 1980. There is simply no evidence to support the idea that soils and/or plant mass has increased by this amount. So where *has* the CO<sub>2</sub> gone?

We know from Henry's Law that there is a strong drive for the CO<sub>2</sub> to be absorbed by water. If the CO<sub>2</sub> has been absorbed then we would expect to have seen a decrease in ocean pH. Has this happened?

If CO<sub>2</sub> has been absorbed by the ocean, we would expect to see a decrease in ocean pH. Has this happened? Anyone who has taken high school chemistry knows that measuring pH the concentration of H<sub>3</sub>O<sup>+</sup>, is easy. Just pop in a pH electrode and read the number of the display. Right? Well, not quite.

To cut a long story short, a pH electrode is just one example of a whole class of electrodes – called *ion selective electrodes* (ISEs) – that indirectly measures concentration of H<sub>3</sub>O<sup>+</sup> by measuring the potential difference between *two* electrodes. For simple solutions this difference is directly related to the concentration of ions in the solution between the electrodes. (You may recall this as the Nernst Equation). The trick (there's that word again) is in having a barrier that is *selective* for a given ion (e.g. H<sub>3</sub>O<sup>+</sup>) so that the electrode is only in contact with the ion of choice. However, no barrier is perfectly selective and seawater is not a simple solution. Other ions that are present in seawater – as well as carbonate species, which can interconvert – interfere and make measurement of pH quite difficult.

Marine chemists have developed easier ways to measure the pH of seawater than the pH electrode. You may recall acid-base indicators from school. These are substances that change their colour as a function of pH. Red cabbage juice works quite well. The cabbage juice starts purple, turns red under acid conditions (e.g. if you add vinegar), and goes yellowy-green under basic conditions (e.g. if you add household ammonia or baking soda). Indicator dyes used by marine chemists are more sensitive, but operate on the same principle. A spectrophotometer can then be used to measure subtle colour changes of the dye, giving more precise pH measurements than electrode-based systems.

But there is another way to measure pH – **calculate it**. There are 4 parameters to describe what chemists call the marine CO<sub>2</sub> system:

1. Total dissolved inorganic carbon (CO<sub>2</sub>, H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>)
2. Total alkalinity
3. pH
4. CO<sub>2</sub> partial pressure

We should be familiar now with 1, 3, and 4. The other parameter in the list is **alkalinity**. A definition of alkalinity is surprisingly complex, but an approximation is to say that it is not quite the opposite of 'acidity measured by pH' and is a way to quantify the difference between the things in solution that act as bases (i.e. accept H<sup>+</sup>) and the things that act as acids (i.e. donate H<sup>+</sup>) in addition to HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. Another useful way to describe alkalinity is that it is the equivalent concentration of bases like CaCO<sub>3</sub> and silicates that have been dissolved by weathering.

In the case of fresh water really only HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, OH<sup>-</sup> and H<sup>+</sup> need be considered. In the case of seawater two additional groups of components are significant. Bases stronger than HCO<sub>3</sub><sup>-</sup> (i.e. B(OH)<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, and SiO(OH)<sub>3</sub><sup>-</sup>) and acids stronger than H<sub>2</sub>CO<sub>3</sub> (i.e. HSO<sub>4</sub><sup>-</sup>, HF, and H<sub>3</sub>PO<sub>4</sub>). The utility of alkalinity is that it is straight forward to measure, even if we have no idea of concentration values for each of the contributing components.

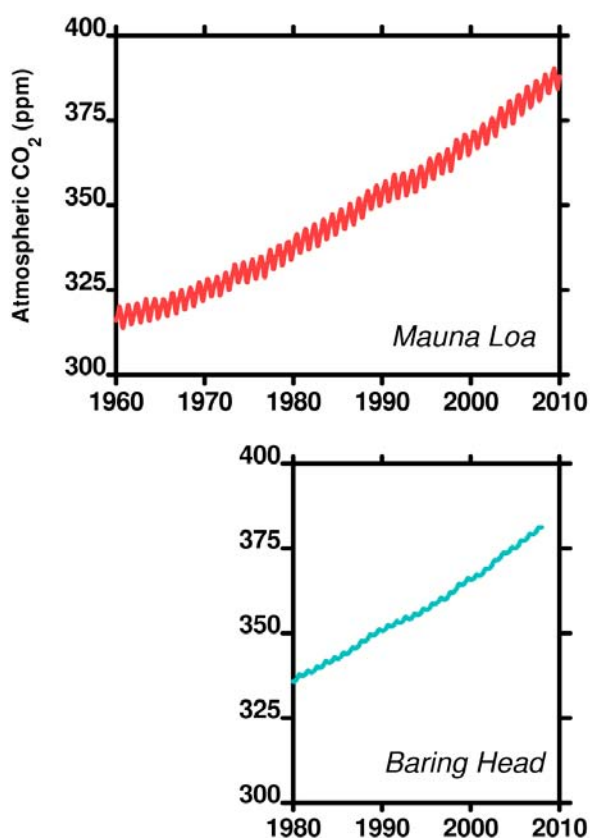
If you have been paying close attention, you may be struck as how similar some of the items on the list of marine CO<sub>2</sub> system parameters are. All these parameters are related through well-known equilibrium relationships. In fact if you know any 2 of the items on the list it is possible to calculate the other 2 parameters. There seems to be some confusion about the way any 2 parameters can be used to derive the other parameters (limited only by goodness of the *K* values). And this perhaps creates the impression that 'calculated' values are simply fitted to a linear decrease equation.

At some data collection buoys moored in the open ocean, pH and pCO<sub>2</sub> are the most frequently measured parameters but if for some reason pH is not measured at a given time, then it is calculated from other parameters like alkalinity or dissolved inorganic carbon. As we explained, pH electrodes are a proxy technique in any event. So, while pH at ocean moorings is not always *measured* directly with a pH electrode, the calculated values are nearly as accurate as measured values. (Slight discrepancies can arise because the equilibrium constants have uncertainties in what is essentially the 2<sup>nd</sup> decimal place).

Number 4 in the list, the partial pressure or concentration of CO<sub>2</sub> in the atmosphere, has been measured in many places for many years. There are seasonal changes as the amount of atmospheric CO<sub>2</sub> changes as plants photosynthesize.

Take a close look at this plot of data for CO<sub>2</sub> from Mauna Loa and Baring Head (New Zealand). Both data sets available at CDIAC, the US government Carbon Dioxide Information Analysis Centre. <http://cdiac.ornl.gov/trends/co2/sio-keel.html>

**Figure 5.** Atmospheric CO<sub>2</sub> at Mauna Loa (March 1958 to May 2011) and Baring Head (Jan 1978 to Dec 2007).

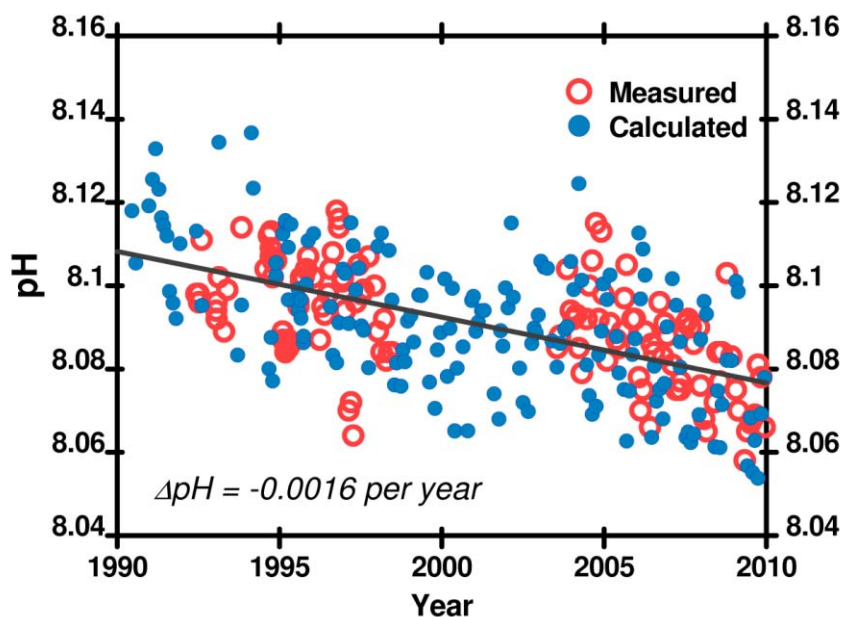


Both graph lines have regular oscillations each year – described by some as 'saw-toothing'. In the Northern Hemisphere spring, the plants grow new leaves, taking up CO<sub>2</sub> and slightly decreasing the atmospheric CO<sub>2</sub> level. In the winter, a lot of plants die off or drop their leaves over winter and CO<sub>2</sub> increases as the leaves decay. The same effect occurs in the Southern Hemisphere – though offset by 6 months.

However, the Northern hemisphere has a greater land mass and therefore more plants (especially at higher latitudes where the Southern Hemisphere is empty) so the oscillations are dominated by the Northern Hemisphere. These fluctuations alter the partial pressure of CO<sub>2</sub> in the atmosphere and thus in the ocean on a seasonal basis.

Since pH is influenced by the partial pressure of CO<sub>2</sub>, the pH of seawater also shows seasonal fluctuations. There are seasonal fluctuations due to water temperature changes (see Section 9 about Henry's Law). There are also small scale local changes induced when phytoplankton (small ocean plants) take up CO<sub>2</sub> from the water for photosynthesis. We have also discussed upwelling and downwelling hot spots as sources and sinks of CO<sub>2</sub> on a local scale.

All these fluctuations are large compared to the expected annual changes. Nevertheless we have good quality data for many places. Though the rate of change is not even around the world, all the data agree: **ocean pH is decreasing**. The example below is from the Hawaii Ocean Time Series (HOTS) and covers 1989 – 2009. The drop in pH is 0.035 pH units in 20 years – an 8% change in the concentration of H<sub>3</sub>O<sup>+</sup>.



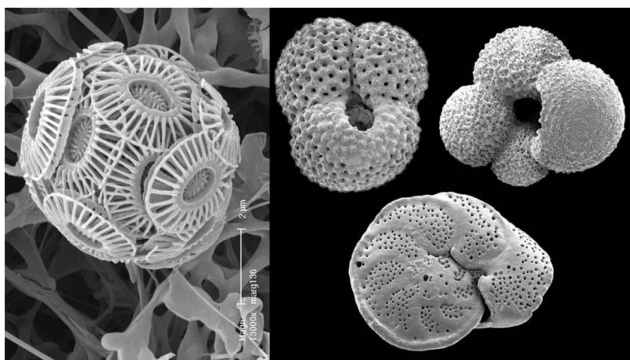
**Figure 6.** pH recorded at the Hawaii Ocean Time Series (HOTS) station. Note the good agreement between measured pH and pH calculated from other CO<sub>2</sub> system parameters. Measured pH data and carbonate parameter data (used to calculate pH) at <http://hahana.soest.hawaii.edu/hot/trends/trends.html>

The drop in pH is 0.035 pH units in 20 years – an 8% change in H<sub>3</sub>O<sup>+</sup> concentration

In this section we describe the types of calcium carbonate used in by marine organisms to make their shells. Why calcium carbonate for shells? If truth be told, it isn't always calcium carbonate; other bio-minerals are also used. Radiolaria (single cell protozoan zooplankton that sometimes host symbiotic zooxanthellae algae in the same way as corals) and diatoms (single-celled photosynthetic algae) have skeletons made of **silica**, as do most sponges. Vertebrates, on the other hand, favour various **phosphates**.

But calcium carbonate is the most common marine biomineral. Why? In a single sentence, calcium carbonate is hard, (mostly) insoluble, and cheap. Actually, there are several forms of calcium carbonate and we may as well get the distinctions clear now.

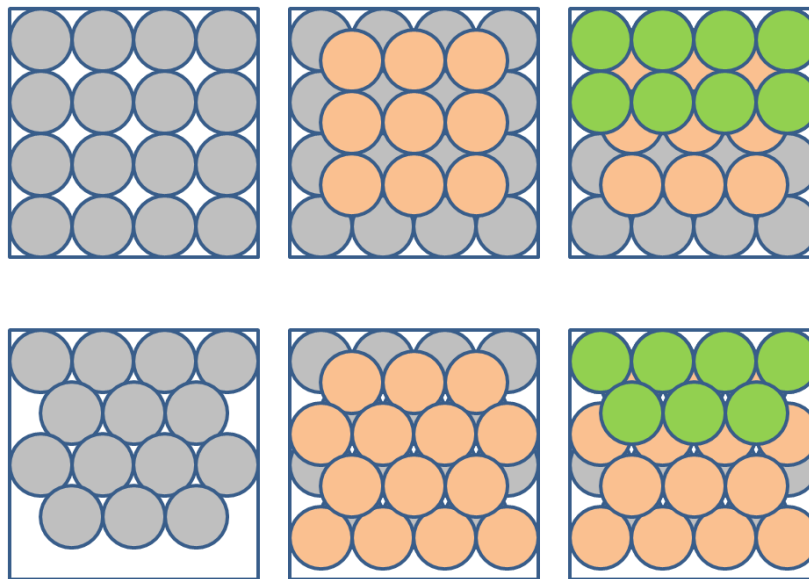
Biological calcium carbonate comes in two main forms, or *polymorphs* (poly = many, morph = form): aragonite and calcite. A third form, *vaterite*, is quite soluble and is rare in biology. Aragonite is found, for example, in thecosomata pteropods (small free swimming sea snails) and corals. Calcite is found, for example, in coccolithophores and foraminifera. Molluscs can use either or both polymorphs.



**Figure 7.**

(L) *Emiliana huxleyi* a common coccolithophore about 5 microns across, ([http://public.ornl.gov/hgmis/gallery/originals/Emiliana\\_huxleyi\\_orig.jpg](http://public.ornl.gov/hgmis/gallery/originals/Emiliana_huxleyi_orig.jpg))  
 (R) assorted fossil foraminifera from New Zealand about 500 microns across, (<http://www.teara.govt.nz/en/fossils/7/1>).

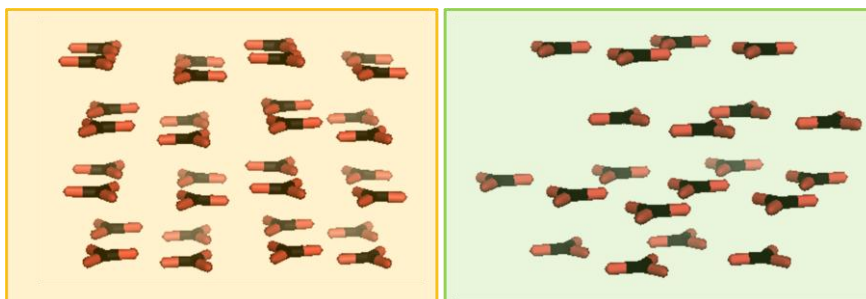
Without going into great detail (fascinating though it is) we will say that the polymorphs differ in the way the molecules stack when they form crystals. As an analogy, think of stacking balls in a box. **Figure 8** shows two of the several (230) ways to stack spheres. The left panels show 2 ways to lay the bottom layer and the right panels show 2 ways to lay the top layer. In the top row of boxes, each ball not on an edge touches 4 neighbours in a given layer (plus 4 in each layer above and below). In the second row of boxes each ball not on an edge touches 6 neighbours in a given layer (plus 3 in each layer above and below). That is balls in both ways of stacking have the same number of neighbours – though the neighbourhood makeup is different.



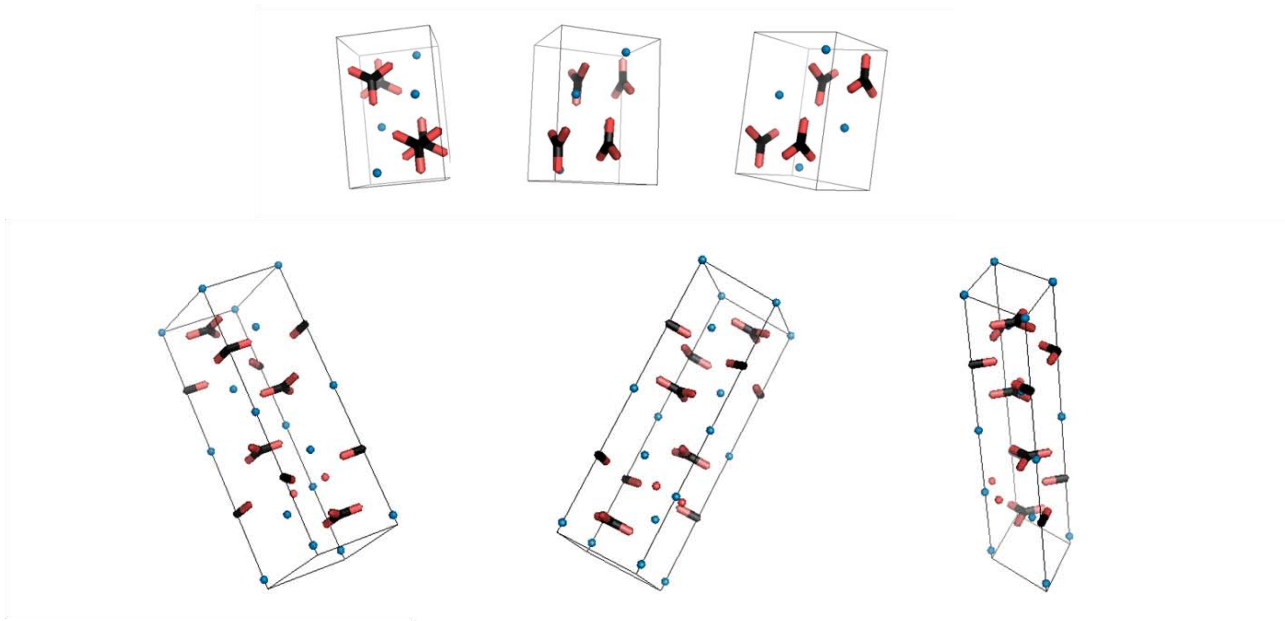
**Figure 8.** Some ways to pack spheres. Left panels give two ways to lay the first layer. Middle gives second layer and right gives the third layer. These are NOT representations of aragonite and calcite. (For the curious the top row is a body centred cubic, bcc, and the bottom row is hexagonal closest packing, hcp; the packing efficiencies are 68 and 74%, respectively)

Note that these figures do NOT represent aragonite or calcite. It would take a lot of subtle technical terms to adequately explain their actual crystal structure, but the basic principles exemplified in the figures holds. You can see that the spheres in the bottom boxes are packed more tightly than the spheres in the top boxes. This sort of packing difference explains why aragonite is denser (2.95 grams per cubic centimetre) than calcite (2.71). The packing arrangement (including things like the length of bonds between molecules and the makeup of the neighbours) also controls the attributes like solubility. In the case of  $\text{CaCO}_3$  aragonite is always more soluble than calcite.

Aragonite is always more soluble than calcite



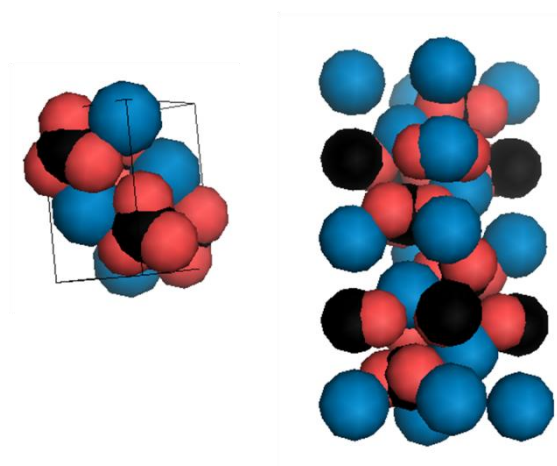
**Figure 9.** Crystal structures of carbonate molecules in aragonite (L) and calcite (R). Black = carbon, red = oxygen. The differences are primarily in the way the  $\text{CO}_3^{2-}$  molecules align or are staggered so calcium atoms omitted for clarity.



**Figure 10.** Frames taken from animations (see original blog post) of the unit cells for crystal structures of aragonite (top) and calcite (bottom). Carbonates shown as 'Y' shape sticks. Black = carbon, red = oxygen, blue = calcium. The black boxes outline the unit cell.

The unit cell is the repeating unit of the crystal. This is the same principle as wallpaper pattern groups. A simple repeating unit is used to build up the pattern. Sometimes a simple pattern is reproduced within a short space, other times it takes much longer before the pattern repeats. It turns out that the calcite unit cell is 3x longer than the aragonite unit cell and that the calcite unit cell contains partial  $\text{CO}_3^{2-}$  (hence the funny looking non Y shapes at the edges).

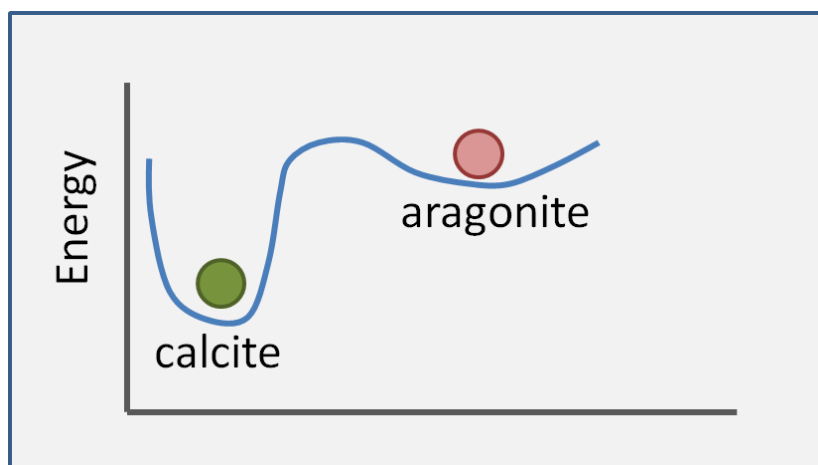
Don't think that the molecules are mostly empty space. The 'stick' form structures are given because they highlight spatial relationships between the  $\text{CO}_3^{2-}$  molecules. Space-fill representations show the electrical sphere of influence of each atom (Figure 11) but obscure the molecule to molecule positioning.



**Figure 11.** Space filling sphere representations of unit cell for calcite (L) and aragonite (R).



How is the stability of calcium carbonate shells affected by the packing arrangement? In Section 2 we mentioned that lower energy reaction products are favoured by thermodynamics. For 2 or more polymorphs we can illustrate this graphically. The thick blue line in **Figure 12** shows the relative energy of calcium carbonate with respect to packing conditions. The two dips in the line correspond to two states where a compound is stable. Imagine placing a ball in each dip - aragonite (pink ball) and calcite (green ball). The green ball (calcite) is well and truly sunk in its pocket and is thus stable. Aragonite is formally described as *metastable*: the pink ball mostly stays put, but a gentle push could get it roll down to calcite.



**Figure 12.** Stability of polymorphs of calcium carbonate. (The schematic illustrates the generic concept of polymorphs but is not accurate for aragonite vs. calcite. For one thing, the relative stabilities depend on temperature, pH etc).

Ever since Rutherford became *malleus atomic*\* chemists have had a funny idea about what 'gentle' is and in this case a 'gentle push' means heating to a couple of hundred of degrees and/or sitting around for a few million years. So in the real world, under most conditions, aragonite shells are as stable as calcite shells. \*Yes of course I know he didn't; it is a joke.

In previous sections we have talked about the carbon chemistry of calcium carbonate but we haven't really discussed the main processes that shift and transform carbon in the ocean: photosynthesis and respiration.

Seaweeds like kelp are pretty, but they are not significant in terms of total photosynthesis. Most photosynthesis in the oceans is by the single celled phytoplankton like diatoms and coccolithophores. Photosynthesis in the ocean is confined to the upper 200 m or so where sunlight reaches. Below that depth life is powered solely by respiration – i.e. eating (or 'burning') organic matter. Back in Section 8 link we noted that: *falling organic matter – fish poo and the like – gets eaten by bacteria (producing CO<sub>2</sub>) as it falls to the bottom.*

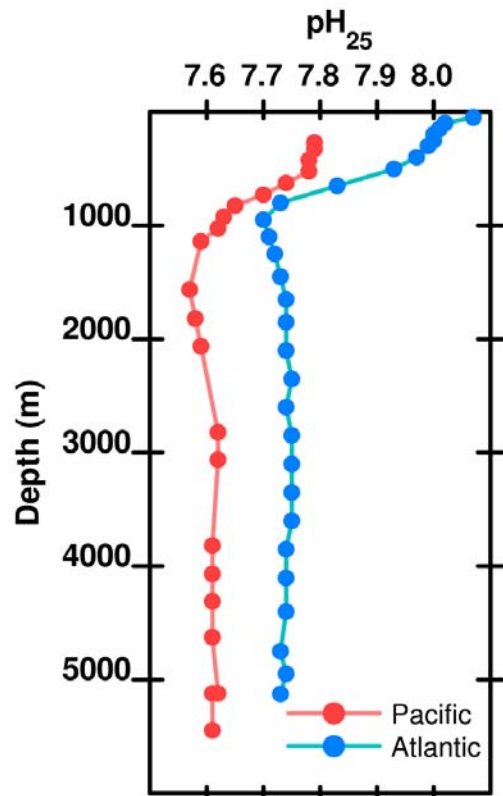
That is, respiration in the deep ocean produces CO<sub>2</sub>. We know enough about the equilibrium in Eq. 7 from Section 5 to say that making CO<sub>2</sub> pushes Eq. 7 to the right, making H<sub>2</sub>CO<sub>3</sub> (carbonic acid). In turn the carbonic acid produces H<sub>3</sub>O<sup>+</sup> via Eq. 8.



$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$	[Eq. 7]
$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+$	[Eq. 8]

Thus, we predict that the deeper you go the lower the pH (i.e. the more  $\text{H}_3\text{O}^+$ ). And, this is just what happens *for the first kilometre or so*.

**Figure 13.** pH (at 25 deg C) as a function of depth in the Atlantic and Pacific oceans. Data are for representative stations from the 1990-1998 World Ocean Circulation Experiment; WOCE <http://cdiac.ornl.gov/oceans/CDIACmap.html>. Note that there are several scales for pH and several ways of expressing a pH value. Values for pH measured at 25 deg C and surface pressure differ somewhat from the in situ pH at the ambient pressure and temperature.



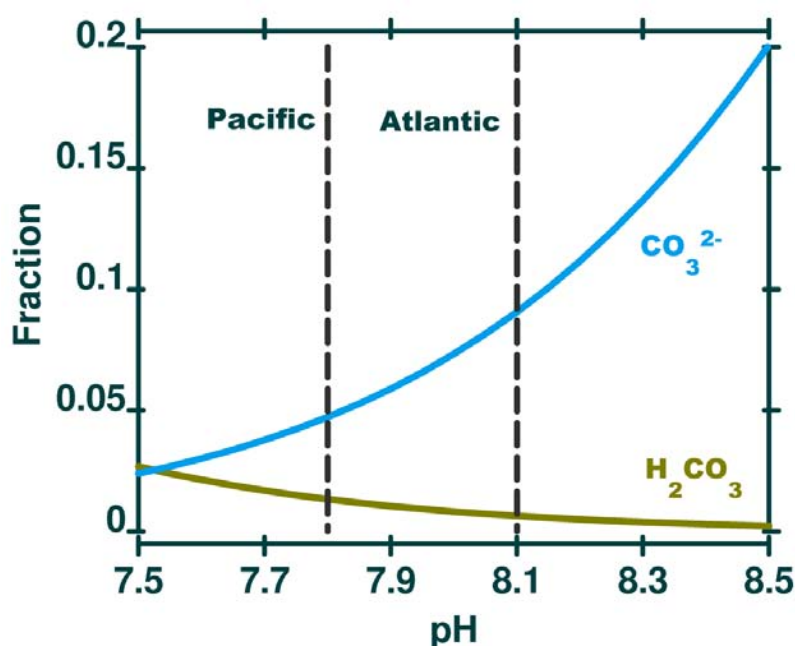
But below 1 km, we begin to see that the pH does not continue to drop. In fact pH increases a little between 1 and 2 km depth and then more or less stabilises. What is going on?

The pH in the deep Atlantic is around 7.7-7.8, while for the Pacific at depth the pH is around 7.6-7.7. In Section 5 we said that by 2100 the pH of the ocean might approach 7.8 and that this was a cause for concern. But, here we have a deep ocean pH of that (or even less) already. If ocean acidification is so bad shouldn't this low pH have some sort of effect?

It does. The low pH water, which was made more acidic by the release of  $\text{CO}_2$  during respiration, dissolves, or **weathers**, the sinking calcium carbonate shells of organisms like foraminifera and coccolithophores.

As we saw in Section 6, weathering or dissolution of calcium carbonate consumes  $\text{CO}_2$  (effectively an acid as it readily reacts via Eq. 7 to make carbonic acid). That is, dissolution of calcium carbonate increases the pH slightly (by removing an acid). As depth increases, the pH does not recover to the surface value and this tells us that there must be more respiration (producing acid) than shell dissolution (consuming acid). This makes sense because *everything* in the deep ocean respire but *not everything* produces a shell that can be dissolved. Note that temperature, salinity and pressure also have a lesser effect on all these equilibrium, but we will ignore them to focus on the impact of  $\text{CO}_2$ .

If we return to the speciation plot from Section 8, enlarged below, we can see that as pH decreases with depth, the amount of carbonic acid increases but the amount of carbonate decreases. (Bicarbonate increases slightly as it approaches the 'hump' in the profile).



**Figure 14.** Enlarged portion of Figure 3 from Section 8, a speciation plot for the carbonic acid system in seawater. Shown here for the range of **realistic** pH in seawater. Typical pH for surface Pacific and surface Atlantic noted for comparison. As pH decreases carbonate decreases and carbonic acid increases (bicarbonate also increases over this pH range but is off the scale of this plot).

Thus, even though *total dissolved carbon* increases with depth (due mainly to respiration) the amount of carbonate decreases with depth because it is a function of pH which decreases with depth.

The reason that the Pacific and Atlantic are different is a result of the **thermohaline ocean circulation**. The deep water circulation starts in the North Atlantic Ocean, where atmospheric cooling near Greenland and Scandinavia generates a downward-moving deep water current. This current flows south through to the Antarctic polar regions where further cold water is added by the same atmospheric cooling process. From there, the current flows into the Indian and Pacific Oceans.

This ocean current sets up a **conveyor belt** for chemical materials generated by the biological pump. Thus, as biological debris containing both organic tissue and CaCO<sub>3</sub> that will soon be dissolved sinks into deep water, it hitches a ride on a current system flowing in the general direction Atlantic to Pacific. As a result, the products of dissolution build up at the end of the conveyor, in the North Pacific Ocean.

We can see that there is increased dissolution of calcium carbonate with depth but that because there is so much respiration at depth the overall carbonate concentration decreases with depth. The saturation depth isn't like an on/off switch. Instead, for sediments (i.e. sinking dead shells), there is a zone, like a snow line. The top of the zone is called the **lysocline** (lysis, literally to separate, refers to breaking something down). Here there is a little dissolution of calcium carbonate. At the bottom of the saturation zone is the **carbonate compensation depth**. Here there is no net accumulation of carbonates because the rate of sediment deposition is matched by the rate of dissolution.

Some background theory in this section including a walk through a calculation that troubles many students.

Solubility expressions (Section 3) are written and calculated in terms of the simplest equation for the reaction. In the case of calcium carbonate this equation is:



Eq. 14 is the baseline dissolution of calcium carbonate. (If we consider external influences like the weathering of limestone by rain containing carbonic acid then the dissolution also involves the release of bicarbonate  $\text{HCO}_3^-$  and consumption of  $\text{CO}_2$  i.e. Eq. 4).

In Section 3 we wrote of doing calculations about dissolution or precipitation in comparison to *solubility*. But, as we now know, the dissolution reaction depends on the concentration of **both** parts of an ionic salt (e.g. the  $\text{Ca}^{2+}$  and the  $\text{CO}_3^{2-}$ ). For this reason solubility varies, depending on the concentration of ions in the solvent. So chemists prefer to use an expression that is derived from the equilibrium constant. We might think that we could write an equilibrium constant for the reaction in Eq. 14 as:

$$K = \frac{\text{conc. Ca}^{2+} \text{ at equilibrium} \times \text{conc. of CO}_3^{2-} \text{ at equilibrium}}{\text{conc. of CaCO}_3 \text{ at equilibrium}} \quad [\text{Eq. 15}]$$

But Eq. 15 is **wrong**. Dissolutions are *heterogeneous*. That is, they involve different *phases* or states of matter (e.g. solid, liquid, gas). Because the  $\text{CaCO}_3$  is a solid it doesn't have a *dissolved* concentration in water. So we leave it out and instead write an expression called a **solubility product** or  $K_{\text{sp}}$  as:

$$K_{\text{sp}} (\text{CaCO}_3) = \text{equilibrium conc. Ca}^{2+} \times \text{equilibrium conc. CO}_3^{2-} \quad [\text{Eq. 16}]$$

In this series we have done our best to avoid jargon and too much symbolic representation but now we think it will help if we say that chemists write concentration expressions using square brackets and (often but with some variance) use a subscript e to mean the concentration at equilibrium so we now have:

$$K_{\text{sp}} (\text{CaCO}_3) = [\text{Ca}^{2+}]_e \times [\text{CO}_3^{2-}]_e \quad [\text{Eq. 17}]$$

The solubility product is exactly what we need to decide whether or not something will precipitate or dissolve. Very often this is all the answer that is required. But it is also possible to use the solubility product to derive the solubility,  $s$ , which tells us *how much* of a substance dissolves.

For a simple substance like  $\text{CaCO}_3$  this is easy. We imagine placing a lump of  $\text{CaCO}_3$  in **pure water** and waiting until the system has reached equilibrium. Though, as we have noted several times, just because a reaction is thermodynamically favoured does not mean it will happen quickly.

Diamond is the canonical example of thermodynamics vs. rate of reaction used in undergraduate text books. Diamond is formed under conditions of high temperature and pressure and at room temperature and pressure diamond has more energy than graphite – recall Figure 12 describing the relative energies of aragonite and calcite. So, over time diamond is thermodynamically unstable and spontaneously converts to graphite. The reaction is, however, slow. (Note: diamond is usually described in texts as an **allotrope** of carbon. The terms have become somewhat blurred in the last few decades but in general usage an allotrope is a polymorph of an **element** with the more general term polymorph referring to **compounds**).

Thus, to dissolve the  $\text{CaCO}_3$  we could add powdered limestone to a known volume of water in a beaker and stir until it had dissolved. Finally we would reach a point where the limestone would no longer dissolve no matter how much stirring and would start to pile up on the bottom of the beaker. (One of us has a friend who comes close to achieving this with sugar in their coffee). When as much  $\text{CaCO}_3$  has dissolved as is ever going to, we imagine measuring the concentration of  $\text{Ca}^{2+}$  dissolved in what is now a solution of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ . We call this value the **solubility**,  $s$ . Since  $\text{CaCO}_3$  contains 1  $\text{Ca}^{2+}$  for each  $\text{CO}_3^{2-}$  we **assume** that the concentration of  $\text{CO}_3^{2-}$  is also  $s$ . Thus we can say that:

$$K_{\text{sp}}(\text{CaCO}_3) = s \times s = s^2 \quad [\text{Eq. 18}]$$

$$s = \sqrt{K_{\text{sp}}} \quad [\text{Eq. 19}]$$

As we should expect, the calcium carbonate polymorphs calcite and aragonite have different solubility products. We will get to seawater in a moment but in a simple freshwater system at  $25^\circ\text{C}$  (see caveats in the next section)  $K_{\text{sp}}$  (calcite) =  $4.5 \times 10^{-9}$  and  $K_{\text{sp}}$  (aragonite) =  $6.0 \times 10^{-9}$  (the units here,  $\text{mol}^2 \text{L}^{-2}$ , are not vital for our purposes and as they can be confusing we won't use them). We can calculate that in freshwater the solubility of calcite =  $(4.5 \times 10^{-9})^{1/2} \approx 7 \times 10^{-5} \text{ mol L}^{-1}$  and for aragonite  $\approx 8 \times 10^{-5} \text{ mol L}^{-1}$ .

**Note 1:**  $x^{1/2}$  is another way of writing  $\sqrt{x}$ , the square root of  $x$ .

**Note 2:** We have been a little sloppy in about concentration units. The volume of water changes a function of temperature (and pressure) so it is actually better practice to use mass (kg) instead of volume (L) but most laypeople are more used to seeing concentration as a mass per volume so we have mostly used  $\text{mol L}^{-1}$ ).

The **assumption** that the concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  are equal is valid if the only source of each ion is the dissolution process; that is if  $\text{CaCO}_3$  is the only source of both  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ . But what happens when there is another supply source for one of the ions? This is called the **common ion effect**. You may remember this from high school chemistry but if not here is a quick refresher.

Imagine, for example, that our beaker of water already had some calcium chloride dissolved into it and that we are adding calcite. That is, it contains a solution of  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ . Let's say that the concentration of  $\text{Ca}^{2+}$  already in the beaker before we begin to try dissolving any calcite is  $1 \times 10^{-3} \text{ mol L}^{-1}$ . The solution in the beaker and the calcite have calcium ions in **common**.

When the calcite dissolves it produces both  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  and the concentration of both ions increases by  $s$ , the solubility of calcite. So can we use Eq. 17? Not yet; recall that the concentration of calcium was already  $1 \times 10^{-3}$  while the concentration of carbonate was initially zero). The easiest way to visualise the system is to set up a concentration table to describe the system before, during and after the addition of the calcite.

	$\text{Ca}^{2+}$	$\text{CO}_3^{2-}$
Initial concentration	$1 \times 10^{-3}$	9.3
Change in concentration	+ $s$	+ $s$
Equilibrium concentration	$1 \times 10^{-3} + s$	$s$

Using the equilibrium values we can calculate a numerical value for  $s$ :

$$\begin{aligned}
 K_{\text{sp}(\text{calcite})} &= 4.5 \times 10^{-9} = [\text{Ca}^{2+}]_e \times [\text{CO}_3^{2-}]_e \\
 &= (1 \times 10^{-3} + s) \times s \\
 &= 1 \times 10^{-3} s + s^2 \qquad \qquad \qquad [\text{Eq. 20}]
 \end{aligned}$$

We can solve for  $s$  in two ways. First, we can rearrange and solve as a quadratic.

$$\begin{aligned}
 s^2 + 1 \times 10^{-3} s - 4.5 \times 10^{-9} &= 0 \\
 s(\text{calcite}) &= 4.48 \times 10^{-6} \text{ mol L}^{-1} \qquad \qquad \qquad [\text{Eq. 21}]
 \end{aligned}$$

**Or**, if it has been a long time since high school maths and you don't remember if the quadratic equation uses  $4ac$  or  $4AD$  (a record label) then we can take a shortcut. We know that  $s = 7 \times 10^{-5}$  when we do this in freshwater without the extra calcium present before we start. So we have a pretty fair idea that the new  $s$  will be of a similar order of magnitude. We can see that the initial concentration of calcium,  $1 \times 10^{-3}$ , is very much bigger than  $7 \times 10^{-5}$ . This lets us make the assumption that  $1 \times 10^{-3} + s \approx 1 \times 10^{-3}$ . In this case we have:

$$\begin{aligned}
 K_{sp(\text{calcite})} &= 4.5 \times 10^{-9} = [\text{Ca}^{2+}]_e \times [\text{CO}_3^{2-}]_e \\
 &\approx (1 \times 10^{-3}) \times s \\
 &\approx 1 \times 10^{-3} s
 \end{aligned}
 \tag{Eq. 22}$$

$$\begin{aligned}
 s(\text{calcite}) &\approx 4.5 \times 10^{-9} / 1 \times 10^{-3} \\
 &\approx 4.5 \times 10^{-6} \text{ mol L}^{-1}
 \end{aligned}
 \tag{Eq. 23}$$

This shortcut answer is less than 1% different from the quadratic solution and there is something of an art in knowing when you can get away with it and when the full solution is needed. Both answers show that if some calcium ( $1 \times 10^{-3} \text{ mol L}^{-1}$ ) is already present then the solubility of calcite changes by about a factor of 15 from  $7 \times 10^{-5}$  to  $4.5 \times 10^{-6} \text{ mol L}^{-1}$ . Similar calculations help us predict what will happen when the concentration of one of the ions, say carbonate, has been **removed** by an external factor.

These sorts of interactions (and some other complex interactions that await you if you take a university chemistry course) explain why seawater chemistry is so very different to freshwater chemistry. In surface seawater at  $25^\circ\text{C}$  and 35 salinity the  $K_{sp}(\text{calcite}) = 4.4 \times 10^{-7}$  and  $K_{sp}(\text{aragonite}) = 6.5 \times 10^{-7}$ . We can now calculate that the solubilities are  $6.6 \times 10^{-4}$  and  $8.1 \times 10^{-4} \text{ mol L}^{-1}$ , respectively. That is, both calcium carbonate polymorphs are about 10 times more soluble in seawater than in freshwater.

**Part 16: Omega: when shells dissolve**

In the last section we introduced the **solubility product**,  $K_{sp}$ .  $K_{sp}$  describes the state of dissolution at *equilibrium*. By analogy with  $K$  and  $Q$  we can also describe a  $Q_{sp}$  that describes the state of dissolution when system is not at equilibrium.

To formalise this relationship and predict what will happen in a given situation we can write this as a ratio of the concentration of dissolved ions *currently present* in a given solution to the concentration of dissolved ions in a *saturated* solution. We call this ratio **omega**,  $\Omega$ .

$$\Omega = \frac{\text{concentration of } \textit{currently present} \text{ dissolved ions}}{\text{concentration of dissolved ions in a } \textit{saturated} \text{ solution}}
 \tag{Eq. 24}$$

If  $\Omega < 1$  then the solution is *undersaturated* and dissolution occurs. If  $\Omega > 1$  then the solution is *supersaturated* and dissolution does not occur (i.e. precipitation can occur). If  $\Omega = 1$  the solution is exactly saturated and nothing happens. In the next section we explore  $\Omega$  in more detail.

We now know that the amount of ions present is given by the *solubility product* so we can rewrite the expression for  $\Omega$  as Equations 25:

$$\Omega = \frac{\text{solubility product of dissolved ions currently present}}{\text{solubility product of dissolved ions in a } \textit{saturated} \text{ solution}} \quad [\text{Eq. 25}]$$

And we can, in turn, replace this with an expression specific for calcium carbonate as Eq. 26:

$$\Omega = \frac{\text{concentration Ca}^{2+} \textit{ present} \times \text{concentration CO}_3^{2-} \textit{ present}}{\text{concentration Ca}^{2+} \textit{ saturated} \times \text{concentration CO}_3^{2-} \textit{ saturated}} \quad [\text{Eq. 26}]$$

Now we see that the bottom line of Eq. 26 for  $\Omega$  is the same as the expression for  $K_{sp}(\text{CaCO}_3)$  (Eq. 17) and the top line is  $Q_{sp}$  for a system that is not at equilibrium:

$$\Omega = \frac{Q_{sp}}{K_{sp}} \quad [\text{Eq. 27}]$$

Recall that the 2 main polymorphs of calcium carbonate have different solubilities; so there is an  $\Omega$  for calcite and an  $\Omega$  for aragonite. That is, the values for the *saturated* concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  in the denominator of Eq. 15 are different for aragonite and calcite.

In surface seawater at 25°C and 35 salinity the  $K_{sp}$  (calcite) =  $4.4 \times 10^{-7}$  and  $K_{sp}$  (aragonite) =  $6.5 \times 10^{-7}$ . And, as we have come to expect, each of those conditions – pressure, temperature, and salinity influence the solubility product.

The solubility of calcium carbonate *increases* at lower temperatures ; for surface water at constant salinity a temperature change from 25°C to 5°C corresponds to a change in  $K_{sp}$  of ~1% for calcite and ~5% for aragonite. If you take a heap of salt and dissolve it in a cup of water you will find the water gets noticeably colder. This happens because it takes energy to shake the ions out of their stacked array. The source of the energy is heat energy from the water. The hot water has more energy that can be stolen by the salt for the dissolution process. A reaction that takes in energy is called *endothermic*.

Similarly, a reaction that gives out energy is called *exothermic* and, unlike most minerals, the dissolution of calcium carbonates is exothermic it means that solid calcium carbonate is favoured at higher temperatures i.e. the solubility is greater at lower temperatures.

The effect of salinity is not so noticeable because in deep water there is little variation in salinity (though in surface waters local variation in salinity can have an impact on  $K_{sp}$  (including, tautologically, because "salinity" includes  $\text{Ca}^{2+}$  and dissolved inorganic carbon species).



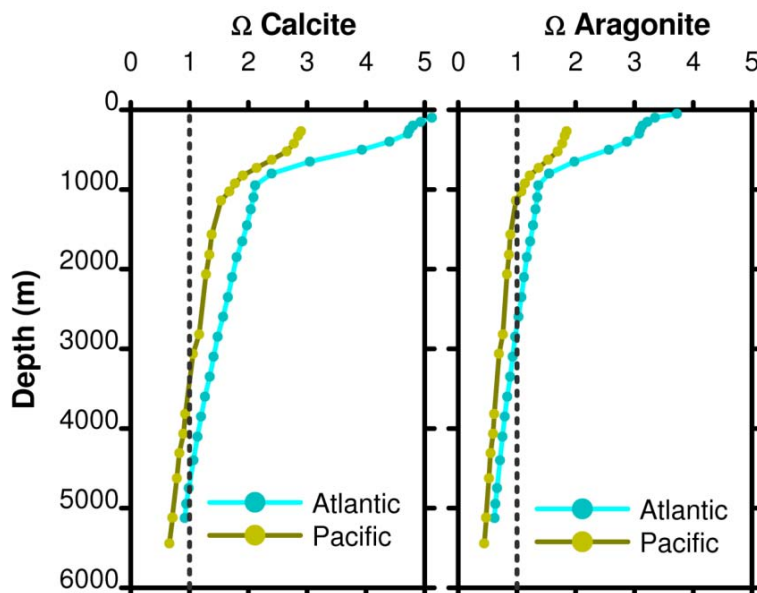
Pressure also has an effect; solubility decreases with pressure. The theory behind this is way beyond a simple blog post but mostly comes down to the change in volume with pressure (this is the reason why we said earlier that it is better to use moles per kg for concentration than moles per L). So we'll simply give some values for 3000 m (at 25°C and 35 S) to demonstrate the extent of the effect. The  $K_{sp}$  for calcite at 3000 m is the same as the  $K_{sp}$  for aragonite at the surface.

	Surface	3000 m
$K_{sp}$ calcite	$4.0 \times 10^{-7}$	$6.5 \times 10^{-7}$
$K_{sp}$ aragonite	$6.5 \times 10^{-7}$	$9.6 \times 10^{-7}$

The concentration of calcium in seawater doesn't change much with depth or location. This is because it has only one main source (the weathering of carbonate and silicate rocks) and, because weathering is slow, the ocean is well mixed in terms of the time scale for supply of calcium by weathering. (Removal of Ca  $\sim$ 1 million years, mixing time  $\sim$ 1600 years). But, as we have said, the relative concentration of carbonate species *and* the concentration of total carbonate species **does** change with depth. This is true even without a human influence.

Since the concentration of carbonate  $\text{CO}_3^{2-}$  that is *present* decreases with depth, we can see that the **ratio** of present concentrations to the theoretical saturation values,  $\Omega$ , *decreases*. Thus, we expect that  $\Omega$  will decrease with depth in the **deep** ocean. And, so it does.

We can calculate  $\Omega$  using the same deep ocean profiles we presented in Figure 13. If we draw a line at  $\Omega = 1$  then the depth at which this line crosses the actual  $\Omega$  gives the depth below which aragonite and calcite dissolve. This is called the **saturation depth** or **saturation horizon**.



**Figure 15.** Depth profile of  $\Omega$  for calcite and aragonite as a function of ocean basin. Data from the same WOCE stations as the pH profile in Figure 13.

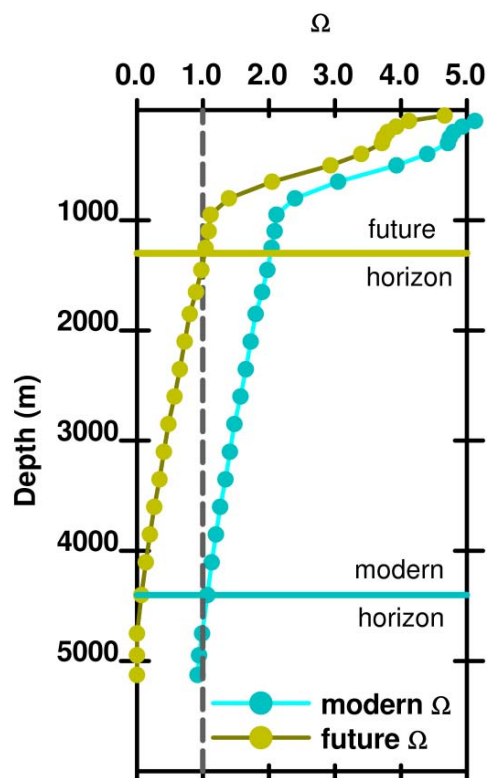
$\Omega = 1$  for calcite at about 3000 m and 4500 m in the Pacific and Atlantic oceans, respectively.  $\Omega = 1$  for aragonite at about 1000 m and 2500 m in the Pacific and Atlantic oceans, respectively. A poetic image

used is to compare  $\Omega$  to a mountain snow line; in the oceans any parts shallower than the saturation horizon will have white sediments containing calcium carbonate while the lower slopes are covered with brownish clay sediments. The real world is not quite so simple but the image is vivid and let it not be said that we will let reality get in the way of poetry.



What happens when  $\text{CO}_2$  is **added** to the atmosphere? Although the total amount of carbon species increases, we now know from Henry's law and equations 7-9 that the net effect is to reduce the concentration of carbonate  $\text{CO}_3^{2-}$  present in surface water and to leave the concentration of  $\text{Ca}^{2+}$  unchanged. We also know that if  $\text{CO}_3^{2-}$  decreases, then  $\Omega$  also decreases. That is, adding  $\text{CO}_2$  to the surface ocean will cause overall carbon to increase, but also causes the relative fraction of carbonate to decrease. In turn this decreases  $\Omega$  so the profiles in Figure 15 to move to the **left** and the saturation horizon thus moves towards the surface, sketched in **Figure 16**. (Note that the future plot is *not* a prediction for a particular future time – we will go over such predictions in detail in a second series of posts).

**Figure 16.** Conceptual plot of the saturation horizon moving towards the surface as  $\text{CO}_2$  is added to the surface ocean.



Adding  $\text{CO}_2$  to the atmosphere causes the ocean depth at which calcium carbonate shells dissolve to become shallower.

Two processes move  $\text{CO}_2$  from the air-sea boundary into deep waters: the biological pump and ocean circulation.

### 1. Biological pump

We have already discussed the biological pathway where photosynthesis transforms the  $\text{CO}_2$  into big organic particles (like fish poo) that sink rapidly. As the particles fall to the bottom, they get eaten by bacteria, producing  $\text{CO}_2$  in deep waters. Collectively this pathway is called the **biological pump**. Full details of the impact of increased  $\text{CO}_2$  on the biological pump are the subject of current research by many scientists, but we can give a brief overview here.

In most areas of the ocean the activity of the biological pump is **not** limited by lack of carbon. If you are a gardener you will know that the plants in your garden do not have unlimited growth. Something stops them. It can be lack of sunlight, water, or a soil nutrient, such as cobalt. If you can figure out what is limiting the growth of your plants, you can add whatever you are missing. But, you can only do this *until the next thing runs out*. For example, adding phosphate to a garden might help initially, but once phosphate levels are sufficiently high, plant growth will be limited by something else, such as nitrogen.

Similarly, since ocean biological pump activity is not limited by a lack of carbon, adding CO<sub>2</sub> to surface waters does not substantially change the amount of photosynthesis in surface waters. This means that the amount of carbon transported to deep waters (i.e. **exported** from surface waters) by the biological pump does also not change substantially when CO<sub>2</sub> is absorbed by the ocean.

Extra carbon might increase the efficiency of the biological pump in some areas, but the effect would likely be transitory. (You may have heard of **Ocean Iron Fertilisation**. In about 20% of the world, ocean photosynthesis is limited by a lack of iron. If iron is added, the water practically turns green with growth overnight. BUT, the effect is transitory and involves major changes to the species makeup of the ecosystem.

## **2. Ocean circulation**

The other pathway to transport CO<sub>2</sub> into deep water is ocean circulation. There are several systems that move water in the oceans. Here we will discuss the high volume but slow (100s-1000s of years) **thermohaline ocean circulation** which eventually swaps surface water with deep water. Briefly, the deep water circulation starts in the North Atlantic Ocean, where atmospheric cooling near Greenland and Scandinavia generates a downward-moving deep water current. This current flows south through to the Antarctic polar regions where further cold water is added by the same atmospheric cooling process. From there, the current flows into the Indian and Pacific Ocean. The details vary from ocean basin to ocean basin, but thermohaline circulation causes surface water to exchange with deep water over a period of to a few centuries to a thousand years.

The high altitude atomic bomb tests of the 1950s and 60s produced a radioactive isotope of hydrogen called **tritium**. Deep water profiles [including those of the WOCE project that we used to make the figures for pH (Figure 13) and  $\Omega$  (Figure 15)] show that tritium *penetrates* into deep water over about 1600 years. CFCs shows the same pattern, so we expect that CO<sub>2</sub> will be similar. For this reason, most added CO<sub>2</sub> remains in surface waters until the slow ocean circulation turns the surface waters over. This means the surface ocean is undergoing acidification to a much greater extent than the deep ocean.

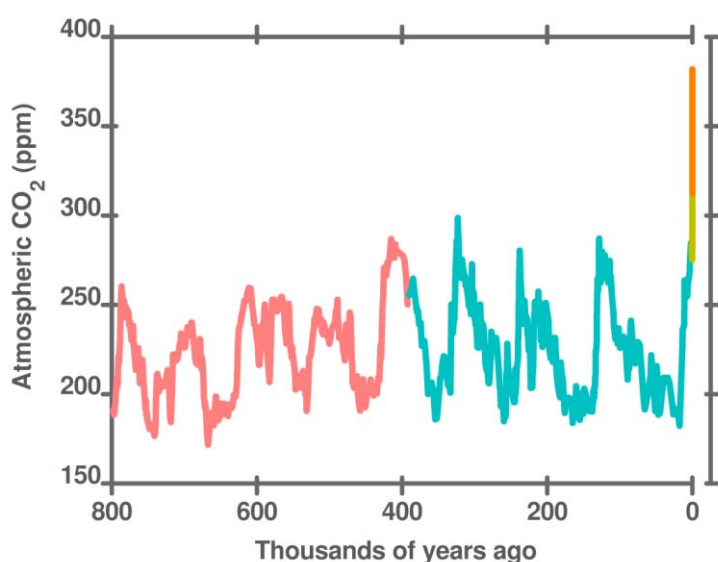
However, if increased CO<sub>2</sub> in surface waters causes an increase in the efficiency of the biological pump (exporting organic matter to deep water) then an unexpected side effect could be transporting CO<sub>2</sub> to deep water more quickly than the purely physical processes that move tritium and CFCs – thus leading to an increased acidification of deep water.

Slow ocean circulation means the surface ocean is currently undergoing acidification to a much greater extent than the deep ocean. But an unexpected side effect of increased CO<sub>2</sub> in surface water might lead to increased efficiency of the biological pump and more acidification of deep water.

Over the next few hundred years, surface waters will continue to undergo acidification. However, as surface water is slowly exchanged with deep water this will help slow the acidification of surface water. These next few hundred years will be a trying time.

CO<sub>2</sub> has high in the past and the pH of the ocean has changed before and life survived. What makes this time different? Same answer as for air temperature: *rate of change*.

There are proxies for past conditions (alkalinity, pH, temperature etc) in the ocean (especially various isotope fractionation processes) but the temporal resolution is not as fine as recent ice core data for atmospheric CO<sub>2</sub>. However, as we now understand the link between atmospheric and oceanic CO<sub>2</sub> we are going to discuss atmospheric CO<sub>2</sub>.



**Figure 17.** Atmospheric CO<sub>2</sub> over the last 8 glacial cycles to modern times. EPICA Dome C (800,000-393,000 y) Vostok (393,000-2400 y) Law Dome (1000 – 50 y) Mauna Loa (50 y – present).

<http://doi.pangaea.de/10.1594/PANGAEA.472488>  
<http://cdiac.ornl.gov/trends/co2/vostok.html>  
<http://cdiac.ornl.gov/trends/co2/lawdome.html>  
<http://cdiac.ornl.gov/trends/co2/sio-mlo.html>

### 1. We are outside normal CO<sub>2</sub> levels

The concentration of CO<sub>2</sub> in the atmosphere undergoes quite large fluctuations with each ice age to interglacial period. During an ice age, CO<sub>2</sub> is about 180 ppm; during an interglacial warm period CO<sub>2</sub> increases to about 280 ppm. Atmospheric CO<sub>2</sub> was 280 ppm 200 years ago. It is currently (August 2011) 394 ppm. This is well over **100 ppm above the normal maximum during the last million years.**

We know that when atmospheric CO<sub>2</sub> is high then Henry's law results in the transfer of CO<sub>2</sub> from the atmosphere into the ocean. The transfer is not instantaneous and various physical and biological processes we have mentioned in this series mean there is usually a *disequilibrium* between atmosphere and ocean. Nevertheless, the oceans will continue to take up CO<sub>2</sub>. The rate of uptake may slow as the oceans warm and/or circulation patterns change but those changes to temperature and circulation will bring their own problems.

### 2. Changes are happening faster than normal.

Hollywood notwithstanding, changes in temperature and CO<sub>2</sub> at the start or end of ice ages is slow. Each ice age is different, but on average an ice age lasts for a few tens of thousands of years. At the end of an ice age, the 10 deg C temperature change and the 100 ppm CO<sub>2</sub> change occurs over 10,000-15,000 years. CO<sub>2</sub> is currently increasing at over 2 ppm per year – over 100 times faster than the glacial-interglacial cycle. Henry's law tells us that CO<sub>2</sub> in the ocean is changing at almost the same rate. (Variations in the transfer processes discussed in the previous section account for the disequilibrium).

That is, changes in atmospheric CO<sub>2</sub> during glacial cycles are slow and occur on the same timescale as the exchange of surface and deepwater. So, CO<sub>2</sub> is transported to deep water about as fast as it enters the ocean. However, we are currently adding CO<sub>2</sub> to the surface seawater much faster than it can be transported to the deepwater.

Of course, once the CO<sub>2</sub> does get into the deepwater then dissolution of CaCO<sub>3</sub> sediments will replace some of the lost CO<sub>3</sub><sup>2-</sup> but will also increase Total Alkalinity.

The ocean carbonate buffer system will **not** restore the ocean to a preindustrial state. Instead the ocean, and the climate of the Earth as a whole, will converge towards a new stable state. We still don't know precisely what that state will be.

Gentle reader, the idea that humans can have such an effect on our environment seems almost science fiction. At <http://www.youtube.com/watch?v=LO0sCs8jI4k> you can see and hear **Isaac Asimov** - science fiction author and science populariser - in 1989 reminding us that he had been talking about the greenhouse effect for over 20 years. Ocean acidification isn't science fiction. It is happening now.



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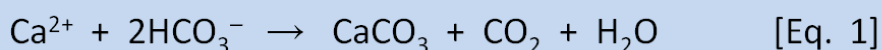


## SUMMARY

### Part 1: OA not OK

Page 4

Ocean acidification, OA, is the process of ocean pH decreasing (i.e. becoming more acidic) due to absorption of fossil fuel CO<sub>2</sub> from the atmosphere. Another effect of ocean acidification is to reduce the amount of carbonate in the water and this increases the dissolution of shells and skeletons.

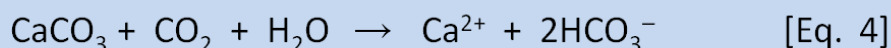


The formation of calcium carbonate shells is a **source** of CO<sub>2</sub>, *not* a **sink** for CO<sub>2</sub>

### Part 2: Reactions are reversible

Page 5

Equation 1 is spontaneous in the surface ocean and shellfish etc extract bicarbonate ions from seawater to make their skeletons and shells. However, those conditions can be changed so that the reverse reaction happens, causing the calcium carbonate to dissolve via Equation 4. This is what takes place when limestone rocks are weathered by the action of rain and air.



### Part 3: Wherever I lay my shell, that's my home

Page 6

A solution that contains the maximum possible dissolved amount of a salt (like CaCO<sub>3</sub>) is saturated. If you add more, the salt will precipitate until the excess has been removed. A solution can be *supersaturated* and contain more ions in solution than is 'theoretically' possible. Surface seawater is supersaturated with CaCO<sub>3</sub>. This means it takes very little effort to precipitate CaCO<sub>3</sub> from seawater.

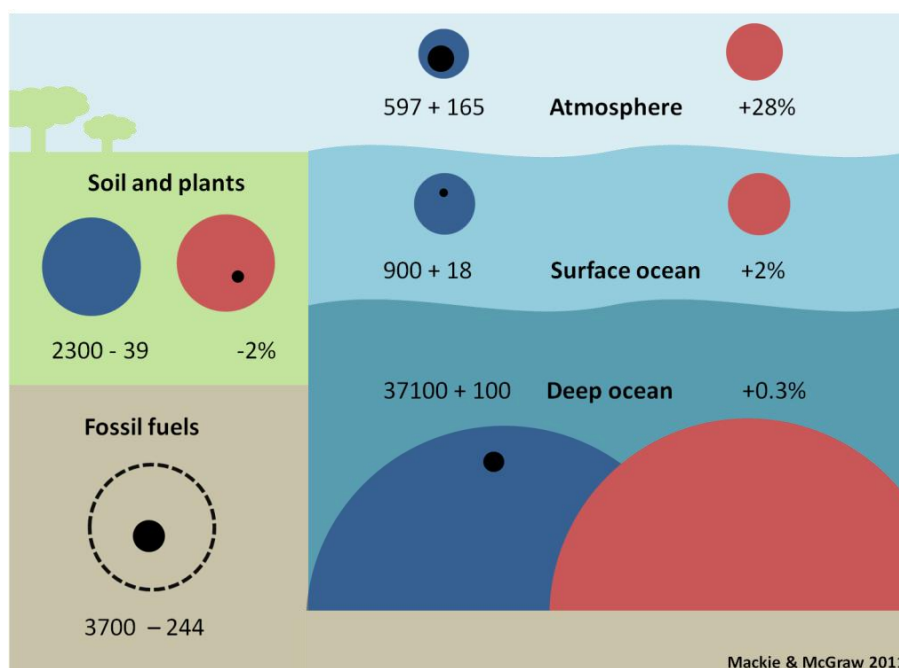
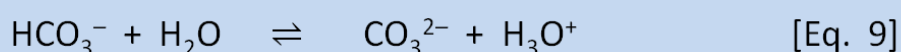
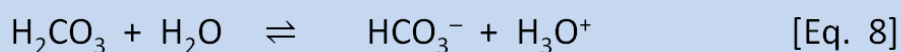
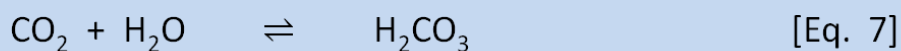
### Part 4: The f-word: pH

Page 8

Average ocean pH has decreased by 0.11 pH units (from 8.25 to 8.14) since the industrial revolution and will decrease a *further* 0.3 units to 7.8 by 2100. A difference of 0.11 pH units corresponds to a 29% increase in the concentration of H<sub>3</sub>O<sup>+</sup>. A difference of 0.4 pH units corresponds to a 150% increase in H<sub>3</sub>O<sup>+</sup>.

The concentration of H<sub>3</sub>O<sup>+</sup> in the ocean has increased by 29% since the industrial revolution. By 2100 the increase will be 150%.

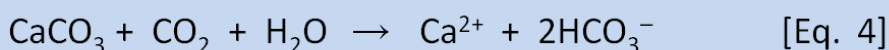
Equations 7-9 describe reactions of inorganic carbon in seawater. The balances between these equations mean 91% of carbon is in the form of bicarbonate ( $\text{HCO}_3^-$ ), 8% is carbonate ( $\text{CO}_3^{2-}$ ), and less than 1% is found as  $\text{CO}_2$  and  $\text{H}_2\text{CO}_3$ .



**Figure 2.** Carbon reservoirs as preindustrial size (blue circles) and modern size (red circles) with change since the industrial revolution (black circles). Numbers give size of preindustrial with amount of change (+ or -) and also express the change as a %. Size in gigatons of carbon = Gt C. (1 Gt = 1,000 million tons, i.e. billion tons).

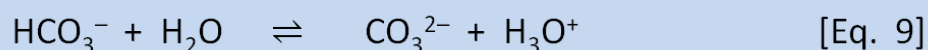
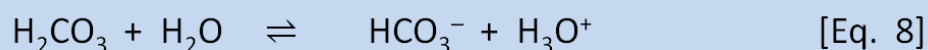
The modern surface ocean contains an extra 18 billion tons of carbon

Weathering occurs when rainwater reacts with carbonate rocks. Rainwater is in equilibrium with atmospheric  $\text{CO}_2$ , so carbonic acid is formed via Eq. 7. This leads to mildly acidic rainwater (pH 5.7). Weathering consumes  $\text{CO}_2$  and means that river water contains a lot of bicarbonate. The amount of bicarbonate added to the ocean by rivers is equal to the amount of  $\text{CO}_2$  consumed and is sufficient to remove all  $\text{CO}_2$  from the atmosphere in 3500 years. Plainly this hasn't happened in the past. Something is returning  $\text{CO}_2$  to the atmosphere. That *something* is Eq. 1 for calcification.



The weathering of carbonate rocks *consumes* atmospheric  $\text{CO}_2$

You may be familiar *Le Chatelier's Principle* as a way to predict how an equilibrium reaction responds when it is disturbed. However, it only applies to single-step chemical reactions and cannot be applied to coupled or sequential reactions. For Eq. 9, Le Chatelier predicts if  $\text{H}_3\text{O}^+$  (i.e. acid) is added then it will force the reaction to the left side, **producing** bicarbonate. However, for Eq. 8 **that is occurring at the same time**, Le Chatelier predicts that if acid is added then the reaction should be forced to the left side, **consuming** bicarbonate.



For Eq. 8, in seawater at the preindustrial ocean pH of 8.25, the equilibrium ratio of the left side, carbonic acid, to the right side, bicarbonate, is about 1:170. For Eq. 9 the ratio of the left side, bicarbonate, to the right side, carbonate, is about 9:1.

Eq. 8 says that if we add a little acid ( $\text{H}_3\text{O}^+$ ), then 170 parts of the acid stay as acid ( $\text{H}_3\text{O}^+$ ) and only 1 part reacts to form carbonic acid and water. But Eq. 9 tells us that if acid is added then 1 part of the acid remains as  $\text{H}_3\text{O}^+$  but 9 parts of the acid, **and** therefore some of the carbonate, are consumed to produce bicarbonate. At typical seawater pH, the response of the system to the addition of acid is dominated by the consumption of carbonate in Eq. 9.

Adding acid to the seawater- $\text{CO}_2$  system massively changes the proportion of carbonate but hardly changes the proportion of bicarbonate since most of the carbon is already in the form of bicarbonate. Since preindustrial times the concentration of carbonate has changed by  $-25\%$  but the concentration of bicarbonate  $\text{HCO}_3^-$  has only changed by  $3\%$ .

Adding  $\text{H}_3\text{O}^+$  to seawater causes the removal of  $\text{CO}_3^{2-}$



Henry's Law of gas solubility says that for a liquid **in equilibrium** with the gas above it, the amount of gas absorbed in the liquid is directly proportional to the partial pressure of the gas. Calculations are complicated because of biological activity and because absorbed CO<sub>2</sub> forms carbonic acid. However the concentration of CO<sub>2</sub> in the atmosphere and the oceans are directly related.

Four observations show the extra CO<sub>2</sub> in the atmosphere has come from the combustion of fossil fuels and *not* from outgassing of CO<sub>2</sub> from the ocean:

### 1. Oxygen decrease

Atmospheric oxygen (O<sub>2</sub>) is going down by the same amount that atmospheric CO<sub>2</sub> is going up. See AR4 Figure 2-3.

### 2. Isotope ratios

Observations (<http://www.esrl.noaa.gov/gmd/outreach/isotopes/c13tellsus.html>) show that the isotope ratios of carbon in the atmosphere are changing due to an influx of CO<sub>2</sub> depleted in <sup>13</sup>C – as occurs in fossil fuels.

### 3. Not enough warming

Warm water can hold less CO<sub>2</sub> than cold water. To explain the 100 ppm of additional CO<sub>2</sub> added to the atmosphere since preindustrial times, the average temperature **rise** of the surface ocean needs to be about 10° C, much larger than has occurred.

### 4. Known fossil fuel CO<sub>2</sub> emissions

Any alternative explanation for the source of the CO<sub>2</sub> in the atmosphere must explain where the 30 billion tonnes of CO<sub>2</sub> released yearly by fossil fuel burning goes. However, the amount of **released** fossil fuel CO<sub>2</sub> is **less** than the amount of extra CO<sub>2</sub> that is currently **in** the atmosphere.

The International Energy Annual (<http://eia.doe.gov/iea/carbon.html>) reports that globally, 603 billion tons of CO<sub>2</sub> were released from 'consumption and flaring of fossil fuels' between 1980 and 2006 giving an **expected** change of 77 ppm CO<sub>2</sub> in the atmosphere. BUT atmospheric CO<sub>2</sub> increased by only 43 ppm. 270 billion tons of CO<sub>2</sub> is missing.

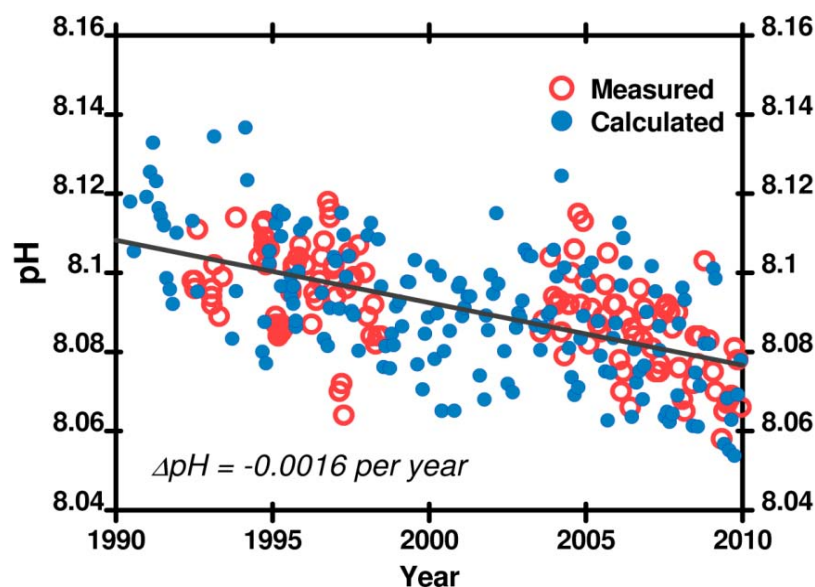
Almost half the fossil fuel CO<sub>2</sub> released into the atmosphere over the last 25 years by humans – over 270 billion tons – is 'missing'. It is not in the atmosphere.



Four parameters describe the marine CO<sub>2</sub> system. If you know any 2 you can **calculate** the other 2.

1. Total dissolved inorganic carbon (CO<sub>2</sub>, H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>)
2. Total alkalinity
3. pH
4. CO<sub>2</sub> partial pressure

The partial pressure of CO<sub>2</sub> in the atmosphere changes seasonally as plants photosynthesize. Since pH is influenced by the partial pressure of CO<sub>2</sub>, the pH of seawater also shows seasonal fluctuations. Though the rate of change is not even around the world, all the data agree: **ocean pH is decreasing**.



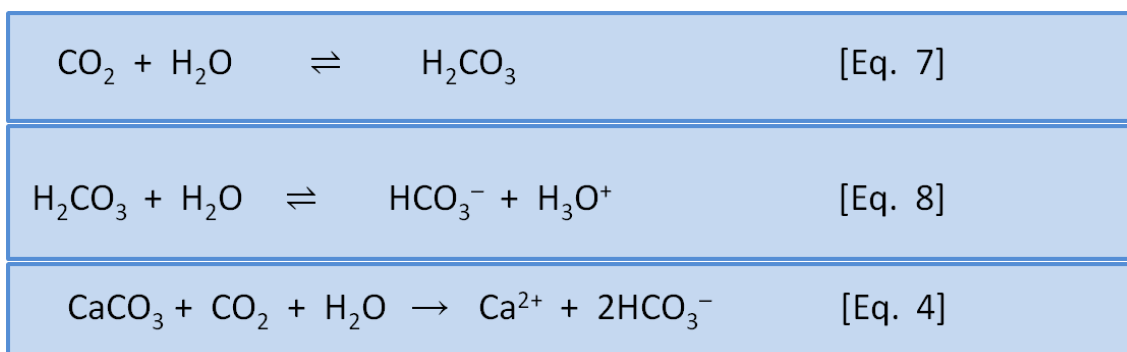
**Figure 6.** pH recorded at the Hawaii Ocean Time Series (HOTS) station. (<http://hahana.soest.hawaii.edu/hot/trends/trends.html>)

The drop in pH is 0.035 pH units in 20 years – an 8% change in H<sub>3</sub>O<sup>+</sup> concentration

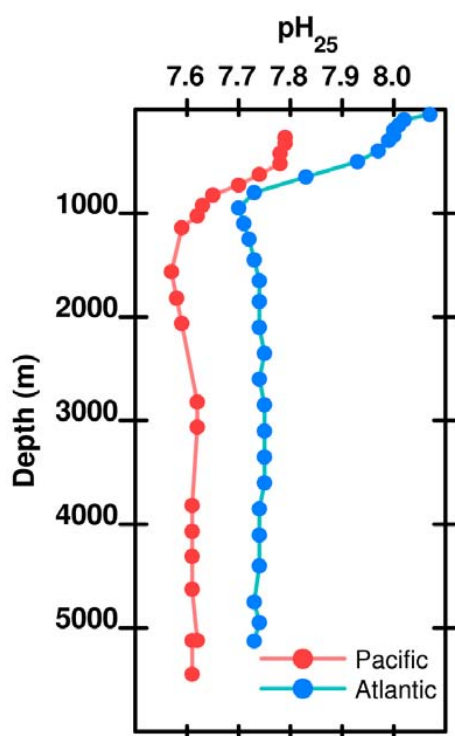
Biological calcium carbonate comes in two main forms, or *polymorphs*: aragonite and calcite. Aragonite is found in pteropods (small free swimming snails) and corals. Calcite is found in coccolithophores and foraminifera. Molluscs can use either or both polymorphs.

Aragonite is always more soluble than calcite

Photosynthesis in the ocean is confined to the upper 200 m or so where sunlight reaches. Below that depth falling organic matter gets eaten by bacteria (producing  $\text{CO}_2$ ). Making  $\text{CO}_2$  produces  $\text{H}_3\text{O}^+$  via Eq. 7 & 8. Dissolution of calcium carbonate via Eq. 4 increases the pH slightly (by removing this acid).



As depth increases, the pH does not recover to the surface value because there is more respiration (producing acid) than shell dissolution (consuming acid). Thus, *total dissolved carbon* increases with depth (due to respiration) but carbonate decreases with depth because it is a function of pH (which decreases with depth).



**Figure 13.** pH (at 25 deg C) as a function of depth in the Atlantic and Pacific oceans.

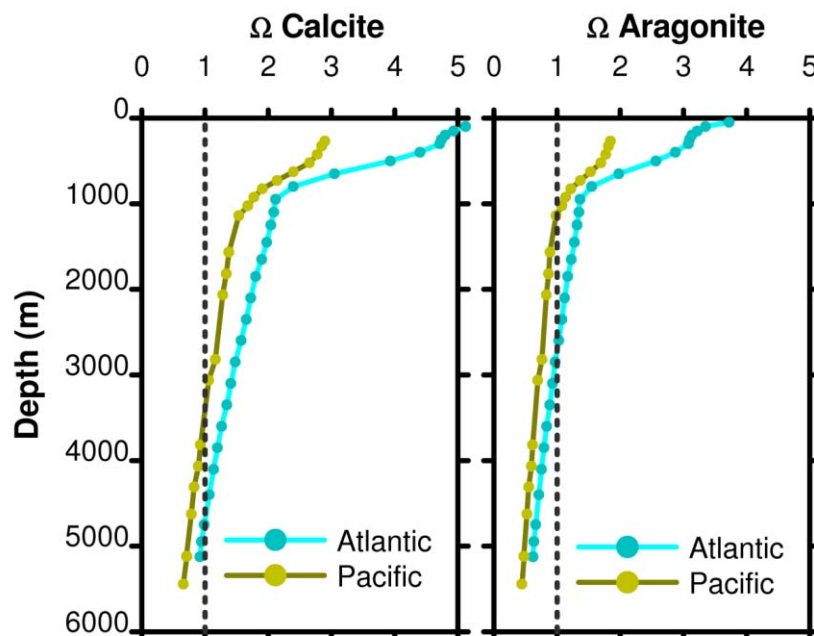
Data: <http://cdiac.ornl.gov/oceans/CDIACmap.html>

The **common ion effect** describes the way the dissolution of a salt is inhibited if the solvent already contains an ion in common with the salt (e.g. the solubility of  $\text{CaCO}_3$  decreases in water containing lots of  $\text{Ca}^{2+}$  ions). Similarly, dissolution is enhanced if the concentration of one of the ions, say carbonate, is low (e.g. the dissolution of  $\text{CaCO}_3$  increases in water if  $\text{CO}_3^{2-}$  has been **removed** by an external factor).

[Eq. 26]

$$\Omega = \frac{\text{concentration Ca}^{2+} \text{ present} \times \text{concentration CO}_3^{2-} \text{ present}}{\text{concentration Ca}^{2+} \text{ saturated} \times \text{concentration CO}_3^{2-} \text{ saturated}}$$

If  $\Omega < 1$  the solution is *undersaturated* and dissolution occurs. If  $\Omega > 1$  the solution is *supersaturated* and dissolution does not occur. For a line at  $\Omega = 1$ , the depth at which this line crosses the actual  $\Omega$  gives the depth below which aragonite and calcite dissolve. This is the **saturation depth**. A poetic image used is to compare  $\Omega$  to a mountain snow line.



**Figure 15.** Depth profile of  $\Omega$  for calcite and aragonite as a function of ocean basin.

Adding  $\text{CO}_2$  to the surface ocean will cause overall carbon to increase, but also causes the relative fraction of carbonate to decrease. In turn this decreases  $\Omega$  so the profiles in Figure 15 to move to the **left** and the saturation horizon moves towards the surface.

Adding  $\text{CO}_2$  to the atmosphere causes the ocean depth at which calcium carbonate shells dissolve to become shallower.

Two processes move CO<sub>2</sub> from the air-sea boundary into deep waters:

### 1. Biological pump

Photosynthesis transforms the CO<sub>2</sub> into big organic particles that sink rapidly. As the particles fall to the bottom, they get eaten by bacteria, producing CO<sub>2</sub> in deep waters.

### 2. Ocean circulation

The high volume but slow (100s-1000s of years) circulation called the thermohaline ocean circulation swaps surface water with deep water. Added CO<sub>2</sub> remains in surface waters until the slow ocean circulation turns the surface waters over. This means the surface ocean is undergoing acidification to a much greater extent than the deep ocean.

We know CO<sub>2</sub> levels have been high in the past. What makes this time different?

### 1. We are outside normal CO<sub>2</sub> levels

During an ice age, CO<sub>2</sub> is about 180 ppm; during an interglacial CO<sub>2</sub> is about 280 ppm. Atmospheric CO<sub>2</sub> is currently 394 ppm - **100 ppm above the normal recent maximum.**

### 2. Changes are happening faster than normal.

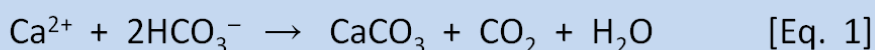
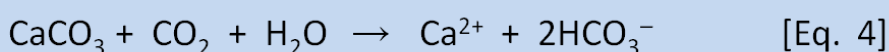
At the end of an ice age, the 10°C temperature change and the 100 ppm CO<sub>2</sub> change occur over 10,000-15,000 years. CO<sub>2</sub> is currently increasing at >2 ppm per year – over 100 times faster than the glacial-interglacial cycle.

The ocean carbonate buffer system will **not** restore the ocean to a preindustrial state. Instead the ocean, and the climate of the Earth as a whole, will converge towards a new stable state. We still don't know precisely what that state will be.

## Appendix 1: How long for weathering to remove all CO<sub>2</sub> from the atmosphere.

In Section 6 we presented an argument to show that Equation 1 (the formation of calcium carbonate as a source of CO<sub>2</sub>) is correct. We pointed out that the reverse process – weathering – requires the consumption of CO<sub>2</sub>. In this calculation we are rounding to avoid giving an overly precise number with a semblance of authority.

- Rain becomes mildly acidic by absorbing atmospheric CO<sub>2</sub>.
- Weathering (Eq. 4) by rain dissolves carbonate rocks (& silicates) forming bicarbonate.
- Bicarbonate is the most abundant anion in river water.
- The amount of bicarbonate released from rocks equals the CO<sub>2</sub> consumed by the rain.
- CO<sub>2</sub> consumption by weathering is sufficient to rapidly consume **all** atmospheric CO<sub>2</sub>.
- Because atmospheric CO<sub>2</sub> has not been used up, some process replaces it: Equation 1.



NOTE: In this calculation we ignore silicate weathering for simplicity but it is considerably slower than carbonate weathering and is complicated because it is mostly *incongruent*.

- Bicarbonate concentration in average river water:

A well accepted value for average river water [HCO<sub>3</sub><sup>-</sup>] = 59.8 ppm with global total river flow of 37,700 km<sup>3</sup>. [Kempe, S. (1979) Carbon in the freshwater cycle. In: Bolin, B., Degens, E. T., Kempe, S. and Ketner, P. (Eds) *The Global Carbon Cycle*. SCOPE Rep. 13, Wiley, Chichester, pp. 317-42].

59.8 ppm means 59.8 mg per litre, where 1 mg = 1 × 10<sup>-3</sup> g. The mass of HCO<sub>3</sub><sup>-</sup> is 61 so 59.8 mg = (59.8 × 10<sup>-3</sup>) / 61 = 9.8 × 10<sup>-4</sup> moles per litre.

1 km<sup>3</sup> = 1 × 10<sup>12</sup> L so 37,700 km<sup>3</sup> per year = 3.8 × 10<sup>16</sup> L per year.

Total HCO<sub>3</sub><sup>-</sup> = (9.8 × 10<sup>-4</sup> moles per litre × 3.8 × 10<sup>16</sup> L per year) = 3.7 × 10<sup>13</sup> moles per year.

- Equation 4 tells us that 1 CO<sub>2</sub> produces 2 HCO<sub>3</sub><sup>-</sup>. Therefore the annual consumption of CO<sub>2</sub> is thus (3.7 × 10<sup>13</sup> / 2) moles per year = 1.9 × 10<sup>13</sup> moles per year.

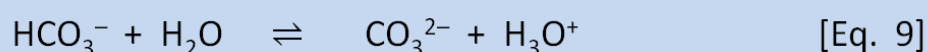
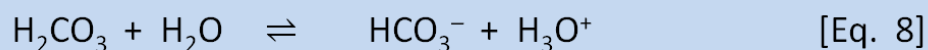
- 1 ppm CO<sub>2</sub> in the atmosphere is (from Section 11) = 7.8 × 10<sup>12</sup> kg = 7.8 × 10<sup>15</sup> g

For 395 ppm CO<sub>2</sub> the total mass of CO<sub>2</sub> is (395 × 7.8 × 10<sup>15</sup> g) = 3.1 × 10<sup>18</sup> g.  
Mass CO<sub>2</sub> = 44 so moles CO<sub>2</sub> = (3.1 × 10<sup>18</sup> g / 44 g per mole) = 7.0 × 10<sup>16</sup> moles

To use up 7.0 × 10<sup>16</sup> moles at 1.9 × 10<sup>13</sup> moles per year takes (7.0 × 10<sup>16</sup> / 1.9 × 10<sup>13</sup>) = 3700 years. (But given the uncertainties, anything between 3,000 and 5,000 is plausible).

## APPENDIX 2 DIY Figure 3

Here are step by step instructions on how to derive your own version of Figure 3. We begin with equations 8 and 9 that describe the dissociation of carbonic acid  $\text{H}_2\text{CO}_3$ . These equations show how the 3  $\text{CO}_2$  species are related.



We call equation 8 the *first dissociation* of carbonic acid and equation 9 the *second dissociation*. We can write  $K$  expressions for each equation:

$$K_1 = \frac{[\text{HCO}_3^-] \times [\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]} \quad [\text{Eq. A1}]$$

$$K_2 = \frac{[\text{CO}_3^{2-}] \times [\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]} \quad [\text{Eq. A2}]$$

Rearranging we can get expressions for each component in terms of  $[\text{HCO}_3^-]$ , because  $\text{HCO}_3^-$  occurs in both Eq. 8 and Eq. 9.

$$[\text{H}_2\text{CO}_3] = \frac{[\text{H}_3\text{O}^+] \times [\text{HCO}_3^-]}{K_1} \quad [\text{Eq. A3}]$$

$$[\text{CO}_3^{2-}] = \frac{K_2 \times [\text{HCO}_3^-]}{[\text{H}_3\text{O}^+]} \quad [\text{Eq. A4}]$$

The sum of the 3 CO<sub>2</sub> species,  $C_{total}$  is:

$$C_{total} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad [Eq. A5]$$

And we can rewrite this in terms of the expressions in Eq A3 and A4:

$$C_{total} = \frac{[H_3O^+] \times [HCO_3^-]}{K_1} + [HCO_3^-] + \frac{K_2 \times [HCO_3^-]}{[H_3O^+]} \quad [Eq. A6]$$

Taking out the common term [HCO<sub>3</sub><sup>-</sup>] we get:

$$C_{total} = [HCO_3^-] \left[ \frac{[H_3O^+]}{K_1} + 1 + \frac{K_2}{[H_3O^+]} \right] \quad [Eq. A7]$$

If we consider the concentration of each component as a *fraction* of the total we can make use of the fact that the fractions add to give 1. So we need expressions for each fraction:

$$Fraction\ H_2CO_3 = a_0 = \frac{[H_2CO_3]}{C_{total}} \quad [Eq. A8]$$

$$Fraction\ HCO_3^- = a_1 = \frac{[HCO_3^-]}{C_{total}} \quad [Eq. A9]$$

$$Fraction\ CO_3^{2-} = a_2 = \frac{[CO_3^{2-}]}{C_{total}} \quad [Eq. A10]$$

We can substitute in Eq. A7, the expression for  $C_{total}$ . Because we chose to define concentrations in terms of  $[HCO_3^-]$ , we will do that one first in full:

$$\begin{aligned}
 \text{Fraction } HCO_3^- = a_1 &= \frac{[HCO_3^-]}{C_{total}} \\
 &= \frac{[HCO_3^-]}{[HCO_3^-] \left[ \frac{[H_3O^+]}{K_1} + 1 + \frac{K_2}{[H_3O^+]} \right]}
 \end{aligned}
 \tag{Eq. A11}$$

Simplifying by multiplying both sides by  $[HCO_3^-]$  we get:

$$a_1 [HCO_3^-] = \frac{[HCO_3^-]}{\left[ \frac{[H_3O^+]}{K_1} + 1 + \frac{K_2}{[H_3O^+]} \right]}
 \tag{Eq. A12}$$

Again, we want to simplify so we multiply both sides by  $(K_1 \times [H_3O^+])$  because it is on the bottom of the bottom on the right side. We now get Eq. A13 and can simplify to Eq. A14:

$$a_1 [HCO_3^-] K_1 [H_3O^+] = \frac{[HCO_3^-]}{[H_3O^+]^2 + [H_3O^+] K_1 + K_1 K_2}
 \tag{Eq. A13}$$

$$a_1 K_1 [H_3O^+] = \frac{1}{[H_3O^+]^2 + [H_3O^+] K_1 + K_1 K_2}
 \tag{Eq. A14}$$



Finally, we solve in terms of  $a_1$  to get:

$$a_1 = \frac{K_1 [\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]^2 + [\text{H}_3\text{O}^+] K_1 + (K_1 K_2)} \quad [\text{Eq. A15}]$$

If we do similar manipulations for the other components we get:

$$\begin{aligned} \text{Fraction H}_2\text{CO}_3 = a_0 &= \frac{[\text{H}_2\text{CO}_3]}{C_{total}} \quad [\text{Eq. A16}] \\ &= \frac{[\text{H}^+]^2}{[\text{H}_3\text{O}^+]^2 + [\text{H}_3\text{O}^+] K_1 + K_1 K_2} \end{aligned}$$

$$\begin{aligned} \text{Fraction CO}_3^{2-} = a_0 &= \frac{[\text{CO}_3^{2-}]}{C_{total}} \quad [\text{Eq. A17}] \\ &= \frac{K_1 K_2}{[\text{H}_3\text{O}^+]^2 + [\text{H}_3\text{O}^+] K_1 + K_1 K_2} \end{aligned}$$

Thus the relative fraction of each species can be defined solely in terms of  $[\text{H}_3\text{O}^+]$  (i.e. pH) and the equilibrium constants  $K_1$  and  $K_2$ .

Here, then, are the instructions to draw your version of Figure 3 using excel or Open Office:

- [1] In two cells on the top row enter the first and second dissociation constants for carbonic acid in seawater or freshwater (as you please), at your preferred temperature. Standard data tables will give this at 298 K (25°C). In fact, most tables will give pK values. We know from the section on pH that we can easily convert.  $K = 10^{-\text{p}K}$  and  $\text{p}K = -\log K$ . (Where log is log base 10).

[2] In seawater, as we have noted, there are several sets of internally consistent  $pK$  values that differ mostly in what is essentially the 2<sup>nd</sup> decimal place. Useful values at 15°C in seawater are  $pK_1 = 5.94$  and  $pK_2 = 9.13$ . Values at other temperatures:

Temp (°C)	$pK_1$	$pK_2$
5	6.05	9.30
10	5.99	9.21
15	5.94	9.13
20	5.89	9.05
25	5.85	8.97
30	5.81	8.89

[3] In column A below the row containing the dissociation constants enter pH values from 0-14 using a suitable increment (e.g. you could go up in 1's or 0.5's; you will get only a marginal improvement to plot smoothness by using a very small increment).

[4] In column B calculate  $[H_3O^+] = 10^{-pH}$ .

[5] In column C calculate the bottom line of equations 15-17:  
(i.e.  $[H_3O^+]^2 + [H_3O^+] K_1 + K_1 K_2$ )

[6] In column D calculate fraction  $[CO_3^{2-}]$  as  $K_1 K_2 /$  column C

[7] In column E calculate fraction  $[HCO_3^-]$  as  $K_1 [H_3O^+] /$  column C

[8] In column F calculate fraction  $[H_2CO_3]$  as  $[H_3O^+]^2 /$  column C

[9] Plot the values in columns D, E and F against pH.

$H_2CO_3$  is a **diprotic** acid because it can donate 2 protons. For acids that can donate more protons (e.g. a triprotic acid like  $H_3PO_4$ ) the same process is followed. Such calculations and plots are used extensively in biology to determine the speciation of amino acids as a function of pH.

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