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6.3.1.2 Some Thoughts on Ocean Chemistry

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The “acidification” of the ocean—or rather its potential progression toward less alkaline conditions—is postulated to result in serious consequences to marine life, including the dissolution of lime shells of various marine organisms. However, the foundation of the ocean acidification scare is disputed and challenged in the scientific literature as indicated in the multiple peer-reviewed studies referenced throughout Sections 6.3–6.5. The present section approaches and critiques the hypothesis from a geochemical perspective.

Water (H_2O) in the ocean is about one pH unit alkaline. Water protolyses as:

$H_2O \leftrightarrow H^+ + OH^-$ [1]

The ordinary hydrogen atom (H) has one proton and one electron. When the hydrogen’s electron is lost to the hydoxyl (OH^-), the remaining H^+ is just a proton. This dissociation of water is called protolysis: the formation of a proton from water.

The concentration of such protons in water determines its acidity or alkalinity. A high concentration is typical of acids, while a dominance of hydroxyl is typical of alkalies. Water is considered neutral (neither alkaline or acidic) when concentrations of H^+ and OH^- are equal. In thermodynamics the concentration is commonly expressed as activity—a thermodynamic concentration, denoted “a”.

pH (“power of hydrogen”) is a measure of the acidity of water, defined as the negative logarithm to the activity of H^+ (a_{H+}):

$pH \equiv - \log a_{H+}$ [2]

The protolysis constant for the chemical reaction for water protolysis, equation [1], has a value of ~10^{-14} at 25°C. At this temperature, the pH has a range up to 14 units, with a value of 14 representing the most alkaline waters, a value of 7 indicating neutral water, and values below 7 for acidic waters. The protolysis constant varies with temperature (and somewhat by pressure), so the value for neutral water changes with changing temperatures. Dissolved gases and solids also can change the pH of water.

6.3.1.2.1 The Assertion of Ocean Acidification

Oceanic pH varies naturally with latitude and ocean depth across Earth. Hence, no single value exists to define oceanic pH. For instance, the pH of surface waters in the western Pacific Ocean varies from around 7.8 to 8.5 between 60°N and 60°S. Although significant pH variations can occur both above and below this range, ocean water is generally characterized as alkaline. And because pH units of measure fall on a logarithmic scale (each pH unit change requires an order of magnitude change in the activity of H^+), large additions of gases and/or dissolved solids into water are needed to induce significant changes in pH.

Some researchers assert ocean waters have become less alkaline (by about 0.1 pH unit) since preindustrial times (e.g., Caldeira and Wickett, 2003). Ocean waters are projected to experience a further pH decline of 0.1–0.2 unit during the next decennia, and a reduction of 0.5–0.7 by the year 2100, caused by anthropogenic CO_2 (NIVA, 2008).

In its first assessment report, published in 1990, IPCC claimed anthropogenic CO_2 has a long lifetime in the atmosphere, of between 50 and 200 years. This long lifetime, according to IPCC, accounts for the modern rise in atmospheric CO_2, which they assert is caused by anthropogenic CO_2 emissions accumulating in the air year after year. Solomon *et al.* (2009) suggest an even longer residence time for anthropogenic CO_2 in the atmosphere, estimating it may be more than 1,000 years, where the CO_2 content flattens out asymptotically towards infinity in their model. Other researchers have provided contrasting findings. Many scientific papers, for example, contend the atmospheric CO_2 lifetime (halflife) is much shorter, at around five years (Bolin and Eriksson, 1959), that a similar lifetime is found for oceanic CO_2, and that natural processes play a far more significant role influencing the atmospheric content of CO_2 than previously thought (e.g., Segalstad, 1992; 1996; 1998; 2008; 2009; Starr, 1993; Rohde, 2000).

It is important to note the dissolution of CO_2 in water is governed by Henry's Law, evidenced by the fact there is approximately 50 times more CO_2 dissolved in the ocean than in the atmosphere at present. It is this vast mass of dissolved CO_2 in the ocean that holds the regulating power—not the relatively small amount of CO_2 contained in the air. Furthermore, the chemical reaction speeds involved in the dissolution of CO_2 are high, as is the ocean circulation speed in the upper parts of the ocean.

The ocean acidification hypothesis also ignores the presence of vast amounts of dissolved calcium in the ocean: the upper 200 m of ocean water contains enough dissolved calcium to bind all anthropogenic CO_2 as precipitated calcium carbonate (in the ocean) without affecting the ocean's pH (Jaworowski *et al.*, 1992a; Segalstad, 1996; 1998). The ocean acidification hypothesis also ignores or downplays other oceanic buffers (pH stabilizing reactions), the thermodynamic stability of solid calcium carbonate in ocean water, and photosynthesis by marine biological systems. Many assertions of ocean acidification are based on a methodology that has been called into serious question. For example, the Norwegian Institute for Water Research (NIVA, 2008) built its assertions of ocean acidification on a paper by Haugan and Drange (1996), who derived their claims from the work of Spivack *et al.* (1993). This latter group of authors presented a proxy history of the ocean's pH over the past 21 million years that used boron isotopes in foraminifera from only five dated boron isotope analyses. This methodology was challenged by Lemarchand *et al.* (2000), who found the boron isotopes in foraminifera represent changes in the marine boron isotope budget rather than changes in the ocean's pH. Claims that the oceans are presently "acidifying," if based on boron isotope measurements, are highly questionable, if not altogether invalid.

6.3.1.2.2 The Geochemistry of CO_2

Depending on physical conditions, CO_2 can both rapidly dissolve and de-gas in water. This is succinctly demonstrated in the making of carbonated sodas canned by breweries and the degassing of the dissolved CO_2 to the air with time upon opening the soda container.

The dissolved CO_2 first hydrolyzes with the water into carbonic acid, H_2CO_3. Next, the carbonic acid protolyzes in two steps, first producing H^+ and dissolved bicarbonate HCO_3^-, and next producing H^+ and dissolved carbonate CO_3^{2-}. With the presence of vast amounts of dissolved calcium Ca^{2+} in the ocean, calcium combines with dissolved carbonate or bicarbonate (the dominating dissolved carbon species in the ocean) to form solid calcium carbonate. In simple terms, this process explains how and why some marine organisms form solid calcium carbonate shells. And it further explains how and why the chemical sedimentation of precipitated calcium carbonate can occur to make limestone (or dolomite) on the ocean floor.

Budyko *et al*. (1987) has pointed out periods of maximum carbonate precipitation (as limestone and dolomite) tend to occur at times of intense volcanism (releasing vast amounts of CO_2 from Earth's interior). These periods also tend to correspond with periods of higher atmospheric CO_2, highlighting a geochemical path of CO_2 that initiates from Earth's interior, degasses from volcanoes to the atmosphere, dissolves into the oceans, and precipitates solid marine carbonate rocks on the ocean floor. The chemical reactions for these processes are illustrated below, where (g) = gas, (aq) = aqueous (dissolved in water), and (s) = solid. The protolysis of the water must be added to the system because the ocean water is alkaline, dominated by hydroxyl OH^-. By adding all the partial reactions in this system, the total net reaction for the marine precipitation of solid calcium carbonate from the air's CO_2 and dissolved calcium in ocean water can be obtained:

$CO_2\ (g) \leftrightarrow CO_2\ (aq)$	dissolution [3]
$CO_2\ (aq) + H_2O \leftrightarrow H_2CO_3\ (aq)$	hydrolysis [4]
$H_2CO_3\ (aq) \leftrightarrow H^+ + HCO_3^-\ (aq)$	1st protolysis [5]
$HCO_3^-\ (aq) \leftrightarrow H^+ + CO_3^{2-}\ (aq)$	2nd protolysis [6]
$Ca^{2+}\ (aq) + CO_3^{2-}\ (aq) \leftrightarrow CaCO_3\ (s)$	precipitation [7]
$2\ H^+ + 2\ OH^- \leftrightarrow 2\ H_2O$	protolysis [1]
$CO_2\ (g) + Ca^{2+}\ (aq) + 2\ OH^- \leftrightarrow CaCO_3\ (s) + H_2O$	total net reaction [8]

The Law of Mass Action ensures when all these chemical reactions have been accounted for in the total net reaction (and when increasing the amount of a gas, CO_2, in the air), calcium carbonate (solid) will be stabilized in the ocean, because the chemical reaction will be forced in the direction from left to right. This result is the opposite of what is commonly asserted (that solid calcium carbonate would be dissolved by the increasing amount of CO_2 in the air).

A simple example of this equation is seen in the oft-demonstrated school chemistry experiment of blowing one's exhaled breath (CO_2 gas) through a straw into a reaction tube with dissolved calcium hydroxide $Ca(OH)_2$ in water. Solid calcium carbonate precipitates out into the solution within seconds, providing a good visual of what happens in the ocean when gaseous CO_2 dissolves in the ocean, where there is an ample supply of dissolved calcium and hydroxyl.

<u>6.3.1.2.3 pH Stabilizing Reactions in the Ocean</u>

A "buffer" can be defined as a reaction system that modifies or controls the magnitude of an intensive (mass independent) thermodynamic variable, such as pressure, temperature, concentration, pH (acidity), etc. The ocean's carbonate system acts as a pH buffer through the presence of a weak acid (H_2CO_3 and its protolysis products) and a salt of the acid ($CaCO_3$). The pH of the water can be calculated as:

$$\mathrm{pH} \approx [\log K + a(CO_2,g) + a(Ca^{2+},aq)] / -2 \qquad [9]$$

where K is the chemical equilibrium constant, and a the activity (thermodynamic concentration). At the ocean surface the $a(Ca^{2+},aq)$ is much larger than the $a(CO_2,g)$. Therefore the alkalinity is the determining factor for the pH, and not the activity (or the fugacity or the partial pressure) of atmospheric CO_2 (Charlson and Emerson, 2000).

In his book on geochemical thermodynamic calculations, Bethke (1996) shows that in a system with only water and CO_2, without mineral buffers present, more than a doubling of the amount of CO_2 in the air above the water surface will lead to a pH decrease of less than 0.4 pH unit. He further demonstrates this is within the natural variation, and thus nothing to worry about.

The ocean is not chemically uniform. Colder water will have a naturally lower pH, because the protolysis constant for water changes with temperature. An upwelling ocean current with colder water, or movement of water from higher latitudes, may lead to a somewhat lower pH within the natural variation—without an anthropogenic influence.

It is also important to note when solid calcium carbonate is brought into the system, a change in the amount of CO_2 gas alone cannot change the pH, because of the buffer action of the calcium carbonate. Thermodynamic calculations on an ocean water composition in equilibrium with calcium carbonate at 25°C show the pH would have to be lowered by 2 units in order to dissolve the calcium carbonate at this temperature. This means the H^+ concentration would have to be increased by 2 logarithm units, i.e. 100 times (see Figure 6.3.1.2.1).

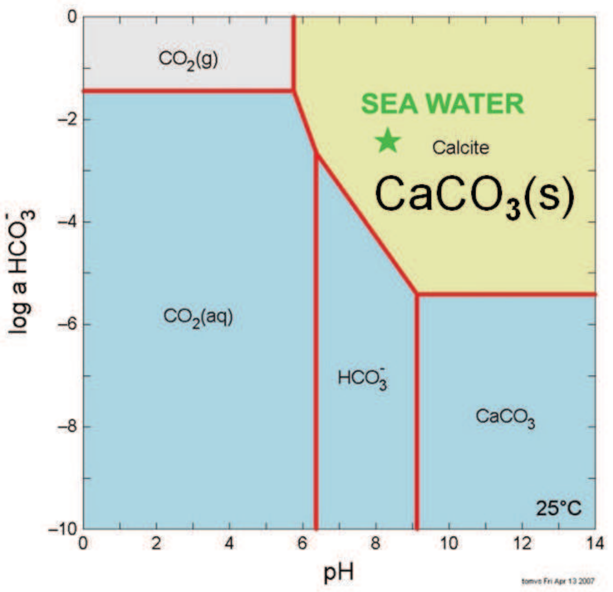

Figure 6.3.1.2.1. A phase diagram for the system CO_2—H_2O—$CaCO_3$ at 25°C and water composition of average sea water. The blue stability fields show the stability of different aqueous species for given pH and log activity of bicarbonate. The green star indicates the sea water position, within the $CaCO_3$ stability field. The diagram was constructed using the program package "The Geochemist's Workbench," by Craig Bethke.

When adding more CO_2 (g), more bicarbonate will be produced. Yet as the phase diagram illustrates (Figure 6.3.1.2.1), such a CO_2 addition will only stabilize $CaCO_3$ even more—the star in the figure (denoting the sea water composition) would move upward. Furthermore, the star would have to be moved out of the $CaCO_3$ (s) stability field in order for calcium carbonate (calcite) to be dissolved. This is impossible to do by adding CO_2 (g) when calcium carbonate is present (Segalstad, 2008). Hence, the pH of ocean water appears to be well buffered with respect to adding more CO_2 to the atmosphere. At 0°C the pH would have to be lowered 1.5 pH units for solid calcium carbonate (calcite) to be dissolved.

The carbonate buffer is not the only pH buffer acting in the ocean. The ocean has a set of other mineral-buffer-reactions, such as the buffer:

$$CaAl_2Si_2O_8\ (s) + 2H^+ + H_2O \leftrightarrow Al_2Si_2O_5(OH)_4\ (s) + Ca^{2+}\ (aq) \qquad [10]$$

This anorthite feldspar ↔ kaolinite buffer has a buffering capacity 1,000 times larger than the ocean's carbonate buffer (Stumm and Morgan, 1970). There are also clay mineral buffers, plus a calcium silicate ↔ calcium carbonate CO_2 buffer (MacIntyre, 1970; Krauskopf, 1979) [for simplicity]:

$$CaSiO_3\ (s) + CO_2\ (g) \leftrightarrow CaCO_3\ (s) + SiO_2\ (s) \qquad [11]$$

All these buffers act as a "security net" under the CO_2 (g) ↔ $CaCO_3$ (s) buffer. Together they constitute an almost infinite buffer capacity (Stumm and Morgan, 1970; Segalstad and Jaworowski, 1991).

The last two buffers mentioned are slower than the CO_2 (g) ↔ $CaCO_3$ (s) buffer at low temperatures. But their reactions are fast at the hot mid-ocean ridges, where temperatures can reach several hundred degrees C. There is no shortage of dissolved calcium in the ocean water, because this element is constantly being added from weathered surface rocks to the ocean by rivers, and by water-rock interactions at hot mid-ocean ridges.

Rainwater has a pH of about 5.7 (Krauskopf, 1979), because of the acidity caused by dissolution and protolysis of atmospheric CO_2. All the acidic rain supplied to the ocean water through the millennia have not changed the ocean's pH of near 8, which also supports the notion of strong pH buffering in ocean water (Pytkowicz, 1972).

6.3.1.2.4 Carbon Isotopes and Mass Balance Calculations

Stable $^{13}C/^{12}C$ isotope ratios, expressed as $\delta^{13}C$ vs. PDB, provide the only way to determine unequivocally the fraction of anthropogenic CO_2 in the atmosphere. The natural atmospheric CO_2 reservoir has $\delta^{13}C \approx -7‰$ when in isotopic equilibrium with marine HCO_3^- (aq) and $CaCO_3$ (s). CO_2 gas from burning of fossil-fuel and biogenic materials has $\delta^{13}C \approx -26‰$ (Ohmoto and Rye, 1979; Deines, 1980).

IPCC identifies 280 ppmv (ppm by volume) as the preindustrial CO_2 value, but that may be arbitrarily influenced by the selection of low-value

CO_2 data from ice cores (where measured values up to 7,400 ppmv were omitted), as well as from the mismatching of contemporary measurements with different ages (Jaworowski *et al*., 1992a; 1992b). IPCC claims the rise in CO_2 to 353 ppmv in 1990, and 379 ppmv in 2005, is due only to anthropogenic CO_2 (IPCC, 1990; 2007).

The $\delta^{13}C$ value reported for atmospheric CO_2 was -7.489‰ in December 1978, decreasing 10 years later to -7.807‰ in December 1988 (Keeling *et al*., 1989). If the resultant decrease were solely the product of mixing natural CO_2 with CO_2 produced from the burning of fossil fuels or plants (~79% / ~21% CO_2 mix; lifetime 50–200 years; IPCC, 1990), the current atmospheric CO_2 $\delta^{13}C$ value should be -11, much lower than reported (Segalstad, 1992; 2008).

The December 1988 atmospheric CO_2 composition has been computed for its 748 Gt C (Gt = 10^{15} g) total mass and $\delta^{13}C$ value of -7.807‰ for three components: (1) natural fraction remaining from the preindustrial atmosphere, (2) cumulative fraction remaining from all annual fossil-fuel CO_2 emissions, and (3) carbon isotope mass-balanced natural fraction. The masses of component (1) and (2) were computed for different atmospheric lifetimes of CO_2 (Segalstad, 1992).

The result fits a lifetime of about five years, in agreement with ^{14}C studies (see Sundquist, 1985; Segalstad, 1998; 2009; for further references). The mass of all past fossil-fuel and biogenic emissions remaining in the current atmosphere was -30 Gt C or less; i.e. a maximum of around 4% of the total, corresponding to an atmospheric concentration of approximately 14 ppmv. The implication of the five-year lifetime is that approximately 135 Gt C (18%) of the atmospheric CO_2 is dynamically exchanged each year (Segalstad, 1992; 1996; 1998; 2008).

The above calculations also demonstrate that over this 10-year period (1978–1988), at least 96% of the atmospheric CO_2 is attributed to non-fossil-fuel sources, and this percentage has not likely varied much in the years since. Hence, it is clear marine degassing and juvenile degassing from sources such as volcanoes must be much more important for the atmospheric CO_2 budget than the burning of fossil-fuels and biogenic materials. IPCC has failed to recognize this conclusion.

6.3.1.2.5 Can Anthropogenic Carbon Double the Atmospheric CO_2 Content?

Many models suggest there is enough fossil carbon on Earth that, if burned, would raise the atmospheric CO_2 concentration to two or more times its preindustrial value. There are reasons to conclude such an increase may never occur.

The equilibrium partition coefficient for the CO_2 distribution between the atmosphere and ocean is approximately 1:50 (Revelle and Suess, 1957; Skirrow, 1975), given by Henry's Law and the Henry's Law Constant. This partition coefficient can be used to set an upper limit for how much the CO_2 concentration will rise in the atmosphere if all available fossil carbon fuel (coal, petroleum, gas) were burned.

To permanently double the current level of CO_2 in the atmosphere under chemical equilibrium conditions, the atmosphere would have to be supplied with approximately *51 times* the present amount of CO_2 if equilibrium should be attained, in order to keep the partition coefficient (air:sea = 1:50) constant according to Henry's Law. At the double amount of CO_2 in the air, the new ratio would have to be 2:100. In other words, an increase of one unit CO_2 in air leads to an increase of 50 units CO_2 in the sea; thus a total of 51 units has to be supplied. All available fossil fuel carbon amounts to 11 times the amount of carbon in today's atmospheric CO_2 (Jaworowski *et al*., 1992a). Therefore, mankind does not have enough fossil fuel to double the current level of atmospheric CO_2 under equilibrium conditions, all other factors held constant.

If the total fossil fuel reservoir of 7,200 Gt C were burned during the next 300 years, only the dissolved organics (carbon pool of about 1,000 Gt C) would consume all manmade CO_2 by their photosynthesis, because this period covers 6 to 15 turnovers of the upper-ocean pool of dissolved organic carbon, based on radiocarbon (^{14}C) studies. However, the vast oceanic dissolved inorganic carbon reservoir of 38,000 Gt C indicates the sea is a much more powerful sink for atmospheric CO_2. Hence, it is unlikely a permanent doubling of the amount of atmospheric CO_2 is attainable by human activities. See Jaworowski *et al*. (1992a) for further details and references.

6.3.1.2.6 Conclusion

Brian Mason (1966) wrote in his textbook, *Geochemistry* (3rd edition), "The ocean may thereby act as a self-balancing mechanism in which most of the elements have reached an equilibrium concentration."

That statement remains valid, as seen through a considerable constancy of sedimentation and pH over many past hundreds of millions of years. The circulation of CO_2 among the atmosphere, ocean, and biosphere is a fast exchange, with an average measured lifetime (half-life) for one atmospheric CO_2 molecule of about five years (Bolin and Eriksson, 1959; Segalstad, 1992; 1996; 1998; 2008; 2009; Starr, 1993; Rohde, 2000).

According to Mason, "it is apparent that the oceans, by controlling the amount of atmospheric CO_2, play a vital part in maintaining stable conditions suitable for organic life on the Earth." As the material above demonstrates, physical chemistry and thermodynamics provide strong reasons for questioning the validity of the so-called ocean "acidification" hypothesis, especially when considering the vast buffering capacity of the ocean's many buffering mechanisms.

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6.3.2 Effects on Marine Plants

6.3.2.1 Phytoplankton

6.3.2.1.1 Coccolithophores

Coccolithophores are single-celled algae and protists found throughout the surface euphotic zones of the world's oceans. They contain chlorophyll, conduct photosynthesis, and possess special plates or scales known as coccoliths, which they create through calcification. This section reviews the results of studies that address how they may be affected by a possible decline in ocean pH levels in a CO_2-enriched world of the future. Several of the findings challenge the alarming negative projections of IPCC, as noted in the bullet points below and further discussed in the main portion of the section.

- Shifts in dominance among species of coccolithophores or clones within a species have been found to occur as the air's CO_2 content rises, which may enable the species to function much as they do today—if not better—in a high-CO_2 world of the future.
- Contemporary evolution likely will help to maintain the functionality of microbial processes at the base of marine food webs in the face of projected lower pH levels.
- Various coccolithophore species appear able to track the environmental value of ocean pH in real time.
- There is evidence the coccolithophore *Calcidiscus leptoporus* has adjusted successfully to the 80 ppm CO_2 difference between preindustrial and the present, as well as the 180 ppm CO_2 difference between glacial times and the present.

Riebesell (2004) notes a doubling of present-day atmospheric CO_2 concentrations "is predicted to cause