Ocean Health –
Is there an "Acidification" problem?

CO2 COALITION

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Executive Summary

Ocean “acidification” from carbon dioxide emissions would require a virtually impossible ten-fold decrease in the alkalinity of surface waters, so using that term is misleading. Even if atmospheric CO_2 concentrations triple from today’s four percent of one percent, which would take about 600 years, today’s surface pH of 8.2 would plateau at 7.8, still well above neutral 7.

In fact, ocean health is improved rather than damaged by additional CO_2, because it is a phytoplankton food that stimulates food webs. Converted CO_2 allows phytoplankton such as algae, bacteria, and seaweed to feed the rest of the open ocean food web. As carbon moves through this food web, much of it sinks or is transported away from the surface. This “biological pump” maintains a high surface pH and allows the ocean to store 50 times more CO_2 than the atmosphere. Digestion of carbon at lower depths maintains the lower pH in the deeper ocean. Carbon is then stored for up to millennia.

Upwelling recycles carbon and nutrients from deep ocean waters to sunlit surface waters. Upwelling injects far more ancient CO_2 into the surface than diffuses there from atmospheric CO_2. Upwelling at first lowers surface pH, but then stimulates photosynthesis, which raises surface pH. It is a necessary process to generate bursts of life that sustain ocean food webs.

When CO_2 enters ocean water, it creates a bicarbonate ion plus a hydrogen ion, resulting in a slight decrease in pH. But photosynthesis requires CO_2. So marine organisms convert bicarbonate and hydrogen ions into usable CO_2, and pH rises again. Contrary to popular claims that rising CO_2 leads to shell disintegration, slightly lower pH does not stop marine organisms from using carbonate ions in building their shells.

The amount of organic carbon created and transported in the oceans is a subject of much scientific uncertainty. Measuring global trends of ocean pH only began in the 1990s. This field is still in its infancy and the factors affecting surface pH are still being debated. More research is needed.

The principal researcher for this White Paper is biologist Jim Steele, a CO2 Coalition member who for 25 years was a researcher and director of San Francisco State University’s Sierra Nevada Field Campus. He was assisted in editing by Genesis Torres, an aquatic ecologist who serves as the CO2 Coalition’s science associate and congressional educator, and Caleb Stewart Rossiter, a climate statistician who serves as the Coalition’s executive director.

I. The Ocean's Carbon Cycle

The oceans absorb, use, sequester, and ventilate 50 times more CO_2 than is in the atmosphere

The Carbon Cycle Before Fossil Fuels

Carbon dioxide plays an important role in determining the ocean's health, both by stimulating the food web and through its effect on pH level. The acidity or alkalinity of sea water is described by a number, the pH. At a representative ocean surface temperature of 25 C, water is acidic if pH is less than 7 and basic, or alkaline, if pH is greater than 7. Pure water is neutral at 7. Rainwater is slightly acidic (5.6) and seawater is slightly alkaline (8.2). pH is a logarithmic measure of the concentration of hydrogen ions, so a one-unit change represents a tenfold change in hydrogen ions.

During the last glacial maximum, 20,000 years ago, the mass storage of CO_2 made the ocean's average pH lower than today. However, there is no evidence that it fell to "acidic" levels. In any event, it is no easy task to measure surface pH precisely. Estimating the ocean's surface pH is complicated by varying ocean dynamics, which affect regions differently.

To understand how rising concentrations of atmospheric CO_2 affect ocean life, we must first understand the carbon cycle before the industrial era. During the pre-industrial period 250 years ago, the atmosphere's CO_2 concentration hovered around 280 parts per million (ppm). However, when the earth's long-standing natural 100,000-year temperature cycle brought us the last glacial maximum, atmospheric CO2 fell from 280 ppm to about 180 ppm. Where did the missing CO_2 go?

The concentration of atmospheric CO_2 was governed by the balance between stored carbon and CO_2 released back to the atmosphere. On land, carbon is continuously stored as organic material in living and dead organisms, with some carbon eventually buried in sediments. During the last major glaciation, expanding glaciers destroyed much of the northern hemisphere's forests and reduced the earth's ability to store terrestrial carbon. Just as deforestation does today, that loss of forests should have increased atmospheric CO_2. Instead, atmospheric CO_2 decreased! The only possible explanation for this paradox is that the glacial maximum's missing atmospheric CO_2 was increasingly stored in the ocean.

Various mechanisms enable the oceans to store 50 times more CO_2 than exists in the atmosphere. There is a balance between how much CO_2 is absorbed and transported to sequestration depths versus how much carbon is upwelled to the oceans' surface and ventilated back to the atmosphere. During pre-industrial times, the UN IPCC suggests 60 billion tons of carbon were absorbed through ocean surfaces each year, while 60.7 billion tons ventilated back to the atmosphere. That surplus of ventilated CO_2 could then be utilized by land plants for photosynthesis. The great importance of CO_2 ventilation is often under-appreciated. If all other climate dynamics remained unchanged, but ventilation of ocean CO_2 completely stopped, our atmosphere would become devoid of CO_2 within four or five decades. Land photosynthesis would come to a devastating halt. This would be true with or without industrial emissions.

It has now been estimated that during the last glacial maximum the oceans stored 850 billion tons *more* carbon than the oceans store today.[1,2] That amount accounts for both the decrease in atmospheric

CO_2 and the lost storage from glacier-covered forests. A growing consensus holds that in addition to cooler temperatures, reduced ocean upwelling was a factor in the glacial maximum accumulation of ocean carbon.[3]

Counter-intuitively, the total amount of CO_2 stored in the ocean does not correlate with the surface pH. Proxy evidence from the glacial maximum shows that despite the ocean's much greater amount of stored CO_2 relative to today, the surface pH hovered around 8.3,[4] paradoxically *higher* than today. At the end of the glacial maximum, when increased warmth and wind-driven upwelling ventilated stored carbon[5], surface pH fell as low as pH 8.1[6] and concentrations of atmospheric CO_2 rose. This surface pH was much lower than physics would predict if the ocean surface was in equilibrium with atmospheric CO_2. Thus, ocean surface pH appears to have been affected by the upwelling from ocean depths of stored CO_2.

How Added Fossil Fuels Affect the Carbon Cycle

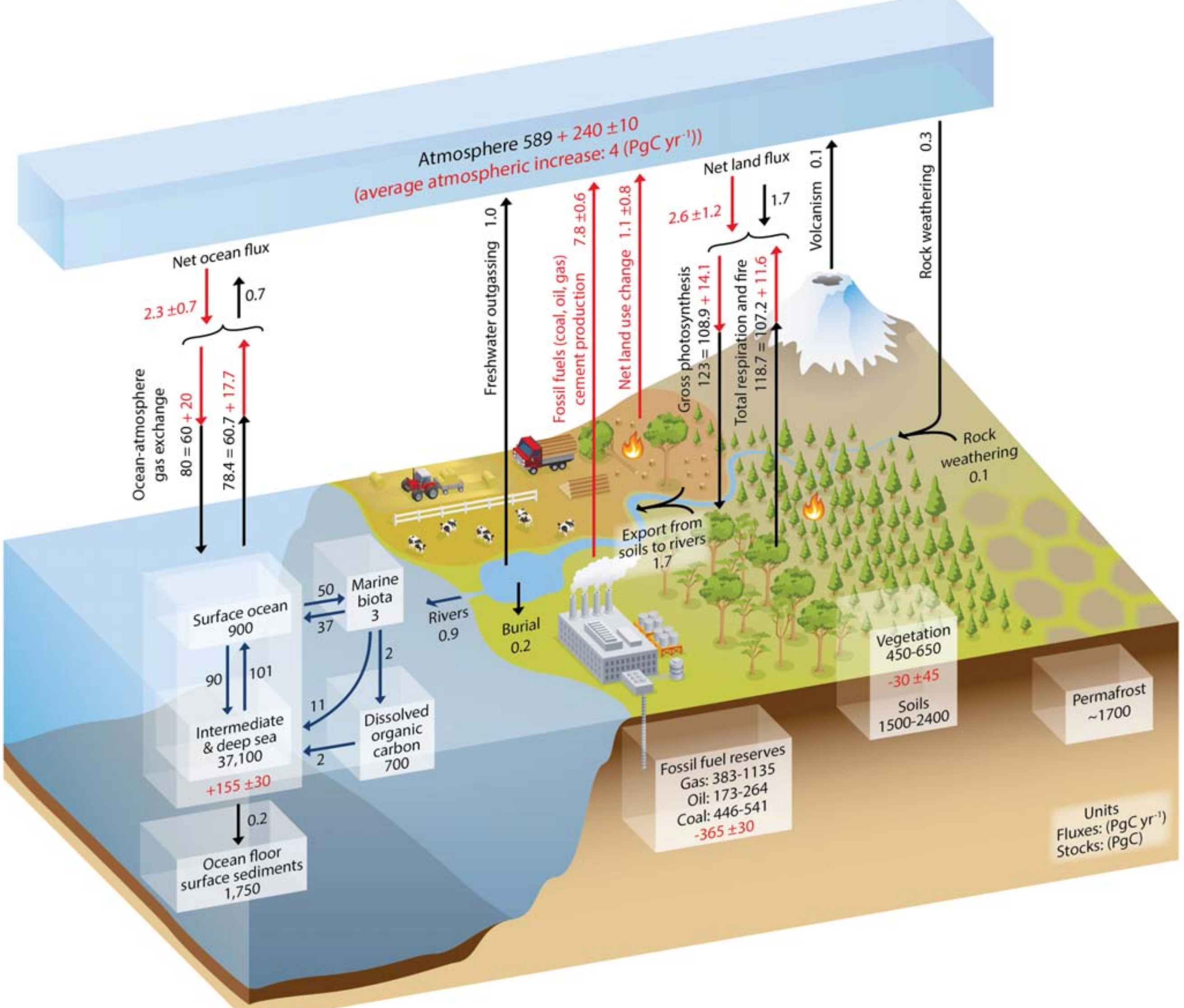

Figure 1 The Global Carbon Cycle from IPCC *CLIMATE CHANGE 2013: The Physical Science Basis - figure 6.1, p. 471*

As seen from the IPCC estimates in the black numbers in Figure 1, the mass of carbon in the atmosphere estimated for 1750 AD, before any significant alterations attributed to humans, was 589 billion metric tons of carbon. In contrast, the oceans contained 38,000 billion metric tons of dissolved carbon. (One Petagram, Pg, equals a billion metric tons.)

Due to human-caused additions of CO_2, it is now estimated by the IPCC (see red arrows under *Net ocean flux*) that each year an additional 20 billion tons of human-derived CO_2 diffuses into the oceans, but only 17.7 billion tons of it ventilates back to the atmosphere. This results in a net annual accumulation in the oceans of 2.3 billion tons of human-derived CO_2, assuming IPCC estimates are correct. At this rate it will take another 350 years before the oceans store as much additional carbon (850 billion tons) as they once did at the end of the last glacial maximum. Blaming any detrimental changes in the ocean's biosphere on additions of industrial CO_2 is purely speculative. Predictions of dangerous "acidification" ignore the fact that the oceans stored far more CO_2 just 20,000 years ago.

Furthermore, across the earth's upwelling regions, ocean surface pH is still primarily affected by the upwelling of ancient stored carbon, rather than human activities. Largely due to the burning of fossil fuels and deforestation, atmospheric CO_2 rose from 280 ppm in pre-industrial times to 410 ppm today. However, the ocean surface is seldom in equilibrium with atmospheric CO_2. For example, recent upwelling of subsurface carbon typically raises surface concentrations of CO_2 to 1000 ppm and temporarily lowers surface pH. However, upwelling of old carbon and other nutrients also stimulates photosynthesis in phytoplankton and sea grasses, which reduces pH.

As observed along the Oregon coast, when stimulated by the nutrients brought to the surface, photosynthesis quickly draws down 1000 ppm surface concentrations of CO_2 to just 200 ppm, and greatly raises surface pH long after upwelling events subside.[7] Coastal oceans are also affected by nutrient run-off from landscape changes, and freshwater inputs from rivers and streams. Coastal phytoplankton blooms can increase pH to 8.6–9.0. But large drops in pH always follow, as phytoplankton blooms decay and respire CO_2.

Researchers caution that "our awareness of the variability and complexity of pH regulation in the coastal ocean is currently disconnected from OA [ocean acidification] projections, which are based on general circulation models (GCMs) focused on anthropogenic CO_2 as the main driver, with little capacity to resolve the coastal ocean."[8]

In contrast, in the open ocean there is only a little upwelling, so surface pH varies much less. There, climate models assume the ocean's surface pH should be largely determined by diffusion of atmospheric CO_2 into the ocean's surface. However, the effects of upwelling are still in play. Recent research reveals that significant amounts of organic matter and nutrients are pumped offshore, away from coastal upwelling regions.[9] Organic matter that reaches the open ocean is subsequently consumed by bacteria, which releases CO_2 and lowers pH. Thus, biological interactions confound the analyses of change in open ocean pH.

To determine to what degree increased CO_2 from burning fossil fuels is affecting surface pH today, we must not just consider CO_2's chemical reactions with water. We also must account for the great variety

of biological interactions. To evaluate how rising atmospheric CO_2 is affecting the ocean's surface pH, we must fully understand the ocean's carbon cycle. How much CO_2 is transformed into organic matter? How much organic matter gets pumped to sequestration depths and how long is it sequestered? How quickly is organic matter respired via digestion or decay? When and where is CO_2 upwelled back to the surface and ventilated to the atmosphere?

II. Transforming CO_2

CO_2 supports ocean life through photosynthesis by phytoplankton

CO_2 Reactions in the Ocean: The Inorganic Pathway

CO_2 reacts with seawater, releasing hydrogen ions and temporarily lowering pH

CO_2 can enter the ocean's surface waters from the atmosphere, by the upwelling of carbon-rich water from below, or via respiration and decomposition of organic matter. No matter the pathway to the surface, CO_2 can then embark on two very different transformative pathways.

In the *inorganic pathway*, CO_2 interacts with water molecules and in the process releases Hydrogen ions (H+) that lower pH. Or it can enter the *organic pathway*, during which CO_2 is incorporated into organic matter via photosynthesis. That organic matter then moves through the food web. In the process of photosynthesis, H+ ions are consumed, and pH rises. Ocean dynamics and complex interactions between those two pathways largely determine how pH varies throughout the oceans.

In the *inorganic pathway*, CO_2 interacts with water molecules to form carbonic acid, which quickly breaks down into bicarbonate and carbonate ions by releasing H+ ions. At pH 8.1, only one percent of the CO_2 entering the water remains as CO_2. Over 90 percent is promptly converted to bicarbonate and H+ ions. Another nine percent sheds an additional H+ ion to form carbonate ions. The 38,000 billion tons of carbon stored in the ocean exists in some combination of those three inorganic forms: CO_2, bicarbonate ions, and carbonate ions. Collectively they are referred to as Dissolved Inorganic Carbon (DIC). Changes in pH can readily convert DIC constituents from one form to another. For example, as H+ concentration increases, H+ is more likely to rejoin a bicarbonate ion and convert back to CO_2. Such conversions critically affect the ocean's carbon cycle.

Only DIC in the form of CO_2 gas is capable of ventilating from the ocean. More importantly, only DIC in the form of CO_2 can be used in photosynthesis. Nonetheless, as 99 percent of the CO_2 is converted to bicarbonate and carbonate ions, H+ ions are released. The greater the H+ concentration, the lower the ocean's pH.

Although Dr. Ken Caldeira purposefully promoted the term "ocean acidification" to generate public concern about possible effects from increasing CO_2, the term "ocean acidification" has evoked undue fears and misunderstandings. As *New Yorker* journalist Elizabeth Kolbert reported, "Caldeira told me that he had chosen the term 'ocean acidification' quite deliberately, for its shock value. Seawater is naturally alkaline, with a pH ranging from 7.8 to 8.5—a pH of 7 is neutral—which means that, for now, at least, the oceans are still a long way from actually turning acidic."[10]

Buffering molecules can remove H+ ions and thus raise pH. Because oceans contain high concentrations of buffering molecules, surface ocean pH is alkaline, averaging above pH 8.[11] With fewer buffering molecules, rain water registers a truly acidic pH of approximately 5.6. Children gleefully dancing in rain puddles and catching "acidic" raindrops on their tongues, certainly do not suffer from the rain's acidification.

Although climate models suggest the ocean's surface pH has dropped from pH 8.2 to 8.1 since 1750,[12, 13] that change was never measured. The pH drop is merely a modeled conjecture that is, unfortunately, constantly repeated as fact. The concept of pH was first introduced by Danish beer brewers in 1909 and the pH concept was not modernized until the 1920s. Citrus growers later developed field instruments to measure pH in the 1930s. Despite our sophisticated global fleet of 4,000 Argo floats that measure ocean temperature and salinity, only 10 percent also measure ocean carbon chemistry, and just 40 floats measure ocean pH.

Measured trends in ocean pH only began in the 1990s, which is far too short a time period to allow a robust analysis separating the myriad of factors affecting pH. Moreover, the use of shells as proxy evidence for the ocean's pH is problematic, as we now know shells are formed under very different internal pH conditions. Nonetheless, when isolated from the effects of the organic pathways, the results of the inorganic pathway are rather clear-cut. As seen in Figure 2,[14] if scientists equilibrated sterilized seawater with pre-industrial CO_2 concentrations of 280 ppm, sea water would average an alkaline pH of 8.2. If sterilized seawater equilibrated with today's atmospheric CO_2 concentrations of 410 ppm, sea water drops to about pH 8.1. If sterilized sea water is equilibrated with a CO_2 concentration of 1000 ppm, pH will fall to about 7.8.

Such laboratory measurements are the basis for assuming that ocean surface pH must have dropped due to the burning of fossil fuels. However, equilibration between atmospheric and surface ocean CO_2 requires one to two years. During that time surface pH naturally fluctuates driven by the seasons, storms and ocean oscillations that upwell low pH waters. Because CO_2 is constantly incorporated into and released from organic matter, the ocean's surface pH changes hourly, daily, and with the seasons. The surface waters are rarely in equilibrium with the atmosphere.

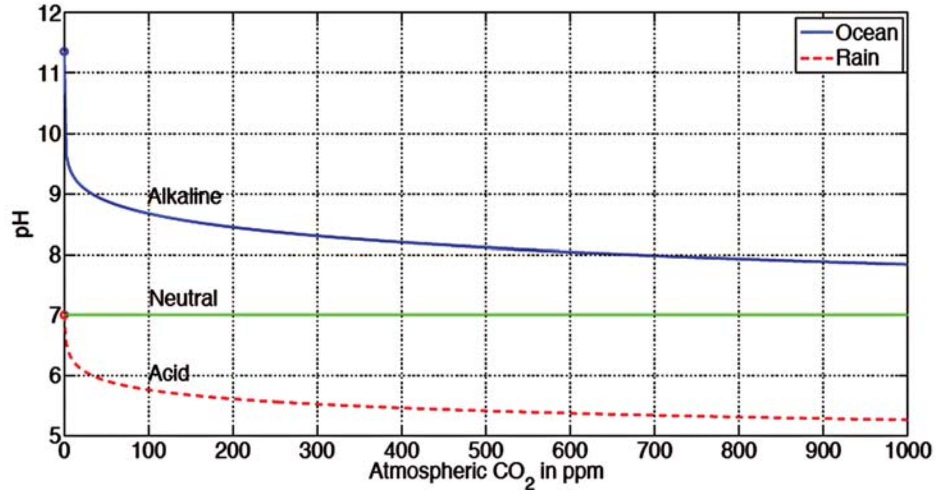

Figure 2. Effects of increasing CO_2 on ocean pH and rainwater pH.
Courtesy of Cohen and Happer

Life Alters Earth's Chemistry

Through photosynthesis, ocean organisms created oxygen and dramatically reduced atmospheric CO_2 in the early years of the Earth

Our neighboring planets, Venus and Mars, each have atmospheres comprised of over 94 percent CO_2, less than four percent nitrogen, and only trace amounts of oxygen. Evidence suggests earth's primordial atmosphere was very similar. However, due to the evolution of oxygen-producing photosynthesis, living organisms completely changed the earth's chemistry. Due to organic pathways that sequester CO_2 into organic matter, the earth's atmosphere now contains just 0.04 percent CO_2, 78 percent Nitrogen and 21 percent Oxygen. If our current CO_2 emissions increased 10-fold with no increase in photosynthesis, the atmosphere would still only contain 0.4 percent CO_2. However, evidence indicates photosynthesis has increased over the past 200 years.

Photosynthesis converts CO_2 into organic matter that becomes incorporated into sugars, carbohydrates, oils, and proteins. Organic matter that reaches the ocean floor can be sequestered for millions of years. Photosynthesizing algae converted CO_2 into oils faster than bacterial decay could cycle those oils back into CO_2. Thus, the world's vast petroleum reserves were created. Land plants also converted CO_2 into starch and wood products. That organic matter was also produced faster than bacterial and fungal decay could convert it back to CO_2. Thus, massive peat and coal deposits were generated. Overall estimates of stored fossil fuel reserves range from 2,000 to 10,000 billion tons. Plants were rapidly colonizing the land between 360 and 300 million years ago. During that geologic period so much carbon was sequestered, it was named the Carboniferous. Photosynthesis so greatly outpaced respiration that atmospheric oxygen levels rose to 35 percent, nearly double today's concentration.

The persistent sequestration of CO_2, both on land and in the ocean, dramatically reduced atmospheric CO_2. Although precise numbers are debated, ancient atmospheric CO_2 concentrations fell from over 6000 ppm down to just 280 ppm by 250 million years ago.[15] CO_2 concentrations then rose after the great extinctions of the Permian. Rising concentrations of CO_2 plateaued during the Age of Dinosaurs. During this Cretaceous period before the meteor-caused extinctions, CO_2 concentrations averaged 1500 ppm. Since then CO_2 sequestration continued, with CO_2 concentrations falling to 180 ppm during glacial maximums.

Having evolved in a high CO_2 environment, photosynthesizing plants and algae became increasingly starved for CO_2, just as modern plants and algae are today. Because plants evolved in high CO_2 environments, modern commercial greenhouses inject an extra 1,000 ppm of CO_2 into their greenhouses, which stimulates plant growth. The stressful consequences of lower CO_2 concentrations drove the evolution of carbon concentrating mechanisms in plankton and C4 photosynthesis in land plants.[16] Accordingly, due to rising CO_2 concentrations, scientists are now observing a greening of the planet.[17]

If ocean photosynthesis and marine productivity improves, and all the added CO_2 entering the ocean is sequestered into organic matter, there would be no change in ocean pH. And indeed, marine

productivity has increased.[18] Although a few researchers have reported short term decreases in ocean productivity,[19] often associated with El Niño events, a growing consensus reports an overall increase in marine productivity as the earth warmed. Productivity increased after the last glacial maximum ended,[20] and increasing organic sediments on the sea floor suggest increased carbon sequestration.

Similarly, studies have shown that marine photosynthesis dramatically increased in upwelling zones after the end of the Little Ice Age, which arguably lasted between 1400 and 1800 AD. That increased productivity was also accompanied by increased burial of organic matter.[21] Between 1998 and 2012, the loss of sea ice increased Arctic productivity by 30 percent.[22] Unfortunately, despite increased productivity, the IPCC admits, "changes due to variability in ocean productivity are not considered" when modeling ocean pH.[23]

Organic Pathways Counteract the Inorganic Pathway

Plankton convert H+ and bicarbonate ions back to CO_2 for photosynthesis, restoring pH

CO_2 that enters the ocean is quickly converted to bicarbonate ions via the inorganic pathway. This is problematic for every marine photosynthesizing organism. They cannot use bicarbonate ions directly, yet all organisms require CO_2 to photosynthesize. So successful photosynthesizing plankton evolved an enzyme (carbonic anhydrase) to counteract the inorganic pathway. To regenerate CO_2 for photosynthesis, carbonic anhydrase rapidly combines the abundant bicarbonate ions with available H+ ions.[24] In the process, carbonic anhydrase raises the pH of surrounding waters.

The more abundant H+ ions are, the more readily they can join with bicarbonate ions and re-form CO_2. High H+ concentrations enhance carbonic anhydrase's conversions. For this reason, corals concentrate H+ ions in their vesicles where photosynthesis occurs, causing their internal pH to fall to an acidic 4.5.[25] The removal of H+ from the surrounding waters to regenerate CO2 for photosynthesis causes the pH in the corals' surrounding waters to rise to 8.5 or more during the day.[26]

To make matters more challenging for marine photosynthesis, CO_2 diffuses 10,000 times more slowly through water than through the atmosphere. Thus, during an algal bloom the available CO_2 and bicarbonate ions are rapidly consumed and depleted locally. Because competition for carbon is great, most photosynthesizing plankton also evolved CO_2 concentrating mechanisms. As carbonic anhydrase converts bicarbonate ions into CO_2, photosynthesizing bacteria concentrate that CO_2 in specialized compartments called carboxysomes. Similarly, several groups of algae concentrate CO_2 in pyrenoids.[27]

Carbonic anhydrase enzyme is such a critical biological component for converting bicarbonate ions and controlling pH that it became ubiquitous among living organisms. Various forms of the enzyme evolved to control internal pH in most organisms. For example, an essential human enzyme contributes to maintaining our blood pH in a narrow alkaline state, between 7.35 to 7.45, despite our constant release of CO_2 from cellular respiration.

Confusion in the Calculation of Carbon Budgets

Surface productivity varies widely and it and average pH are difficult to measure

To track the carbon cycle accurately, scientists construct carbon budgets. But the numbers haven't been adding up. First we must estimate how much of any added CO_2 gets transformed into organic matter, and then how much organic matter is exported to deeper waters. But calculating surface ocean productivity has been quite problematic.

This problem was addressed in the 2010 peer-reviewed paper titled *Assessing the apparent imbalance between geochemical and biochemical indicators of meso- and bathypelagic biological activity: What the @$]! is wrong with present calculations of carbon budgets?*[28] Depending on the assumptions made by various researchers, surface productivity could be exporting as much as 100 to 1,000 times more organic carbon to the deep ocean food webs than had been previously reported.

The growing awareness of abundant marine life thriving between 200 and 1000-meter depths, known as the mesopelagic or twilight zone, is now altering our understanding of ocean carbon budgets. When organisms extract the energy from organic matter, oxygen is consumed, and CO_2 is respired. By analyzing how much oxygen is being consumed, at least two to three times more organic matter than previously assumed must be exported from the sunlit surface waters.[29] With growing evidence of higher rates of organic matter formation and higher rates of organic matter export to sequestration depths, it is more than reasonable to hypothesize that enough CO_2 is being sequestered to prevent any significant change in the ocean's surface pH.

III. Sequestering CO_2

CO_2 is stored for millennia in deep oceans, awaiting upwelling

Separating Photosynthesis from Respiration

pH is raised by day and reduced by night, and varies with many natural factors

The pH in any given region of the ocean is largely determined by a balance between photosynthesis and respiration. If photosynthesis sequesters all the human-added CO_2 in the sunlit surface waters into organic matter but that matter is completely digested and recycled in those same sunlit waters, the organic pathways would have no effect on surface pH. The pH of those surface waters would indeed be determined by how much CO_2 is being added. However, photosynthesis and respiration are separated over time and space. Where photosynthesis dominates, pH is higher. Where respiration dominates, pH is lower.

Photosynthesis only happens during the day in the upper sunlit layers, typically the upper 100 meters but as low as 200 meters in clear water. In contrast, respiration happens throughout the day and night and at all depths. During the day when photosynthesis dominates and CO_2 is being consumed, surface

pH rises. But with no photosynthesis, night-time respiration dominates, releasing CO_2 and lowering pH. Thus, the daily and seasonal pH around coral reefs fluctuates between 8.6 during a summer's day, and 7.7 during winter nights.[30]

Because organic matter sinks, photosynthesis and respiration are also separated by depth. Depending on the rates of sinking, CO_2 sequestered in organic matter, if respired, will be increasingly released at greater depths. As a result, while surface pH hovers around 8 and higher, the pH in subsurface layers rapidly falls to 7.6 by depths of just 250 meters. The depth at which CO_2 is respired back into the water critically affects the carbon cycle. The greater the depth at which organic matter decomposes, the longer the time span before any respired CO_2 returns to sunlit surface waters. The sequestering of CO_2 at depth largely explains why the oceans hold 50 times more CO_2 than the atmosphere.

Most organic matter is quickly consumed and respired, so its carbon and nutrients are simply recycled in the surface waters. As much as 90 percent of the carbon is recycled in the upper 200 meters as slowly sinking organic matter is rapidly decomposed. However, those calculations are being reconsidered as the needs of the food webs at lower depths are better understood. At depths of 200 meters or less, respired nutrients and CO_2 can get mixed back into the surface waters during winter storms. In contrast, if organic matter sinks below 1000 meters, the nutrients and CO_2 released at those depths will typically not return to the surface for hundreds to thousands of years. In some regions, organic matter only needs to sink to depths below 400 meters to sequester its CO_2 for a century or more.[31] If organic matter gets buried in the sediments of the ocean floor at any depth, CO_2 can be sequestered for millions of years.

Very small bits of organic matter will dissolve in water and not sink. That dissolved organic matter can only be sequestered in deep waters by ocean currents and eddies. For example, in the north Atlantic where ocean water is exceptionally salty and dense, when Atlantic water approaches the Arctic, its dense water cools and sinks to the ocean floor, sequestering dissolved organic and inorganic carbon for a thousand or more years until upwelled near Antarctica.

In addition, there are other dynamics. Not all dissolved organic carbon needs to sink deeply in order to sequester CO_2 for thousands of years. Some organic carbon molecules are so complex that they are not easily digested or decayed. Some organic carbon exists in oxygen-depleted waters where decay is inhibited. So, in addition to the 38,000 billion metric tons of dissolved inorganic carbon, there are 700 billion tons of dissolved organic carbon floating in the oceans.

The separation of coastal photosynthesis from open ocean respiration causes open ocean pH to be lower than regions where surface photosynthesis and respiration are balanced. More importantly, measured trends of slightly increasing open ocean DIC and decreasing pH at the Hawaiian oceanographic station (HOT) and the Bermuda station (BATS) may not be indicators of growing human-caused "acidification" as some have hypothesized.[32] Increases in coastal marine productivity and higher rates of laterally-transported organic matter from the coastto the ocean interior, where it has been respired, can also cause decreasing pH trends in the open ocean.

The Biological Pump

Sinking organic matter takes CO_2 to varying depths, removing it from the surface on time scales from seasons to millennia

When organic matter passively sinks to sequestration depths (400 to 1000 meters) before being decomposed, its respired CO_2 can be trapped in deeper water for centuries and millennia with no effect on surface pH. The faster organic matter sinks, the more carbon will be sequestered. Rapid sinking can export organic carbon below the 1000-meter sequestration depth within days, well before decomposition can release CO_2. Some climate modelers suggest that without the pumping of carbon to depth, atmospheric concentrations of CO_2 would be *two times higher* than today.[33] The biological pump maintains a high pH in surface waters, and then pH declines with depth as organic matter decays.

In contrast, other modelers have chosen only to emphasize dynamics of the inorganic pathway. They suggest that once CO_2 enters the oceans' surface waters, it slowly diffuses downward as DIC. Thus, their models conclude that atmospheric CO_2 causes the greatest "acidification" at the surface. These models simulate a very slow diffusion into the ocean's interior. To estimate rates of diffusion, many models rely on tracers, such as CFCs. CFCs are unnatural compounds that do not decompose. They were produced for use in modern refrigeration in the 1930s. This initial introduction of CFCs allows researchers to estimate how fast CFCs spread through the ocean since then. Although CFCs reveal how quickly inert molecules will diffuse to ocean depths, CFCs do not participate in organic pathways or the biological pump. So, CFC-driven models will always underestimate the export of carbon.

The reality that pH is highest in surface waters and then decreases rapidly with depth cannot be generated by models with slow diffusion from the atmosphere downwards. It is now estimated that 90 percent of the difference in pH between surface waters and deeper waters is maintained not by diffusion, but by the biological pump. When transformed into organic matter, CO_2 can be rapidly exported downwards thousands of times faster than CFC diffusion, where it is concentrated at depth.

It is best to differentiate the biological pump into at least three different dynamics: 1) a passive gravity-driven pump causing organic matter to sink, 2) an active pump driven by vertical migrations of living organisms that actively carry carbon from the surface to depth, and 3) a calcium carbonate pump in which inorganic calcium carbonate shells sink, carrying DIC in the form of carbonate ions to depth.

The passive gravity pump is the major driver determining the pH gradient. Heavy bodies and large particles sink rapidly. For example, anchovy and sardine fecal pellets sink 780 meters in a day.[34] Diatoms account for half of the ocean's photosynthesis. Despite their smaller size, single-celled diatoms with heavy silica shells are dense. Living diatoms are observed on dark ocean floors, suggesting a sinking rate between 120 and 720 meters per day.[35]

It was once believed that less-dense microscopic bacteria must sink extremely slowly, so that any respired bacterial CO_2 would remain in the ocean's surface layers. That belief biased most estimates of how much carbon gets recycled in the oceans' sunlit layers. However, new observations have determined that bacteria clump together and form heavy aggregations, speedily carrying carbon downward from the surface layers at rates of 440 to 640 meters a day.[36]

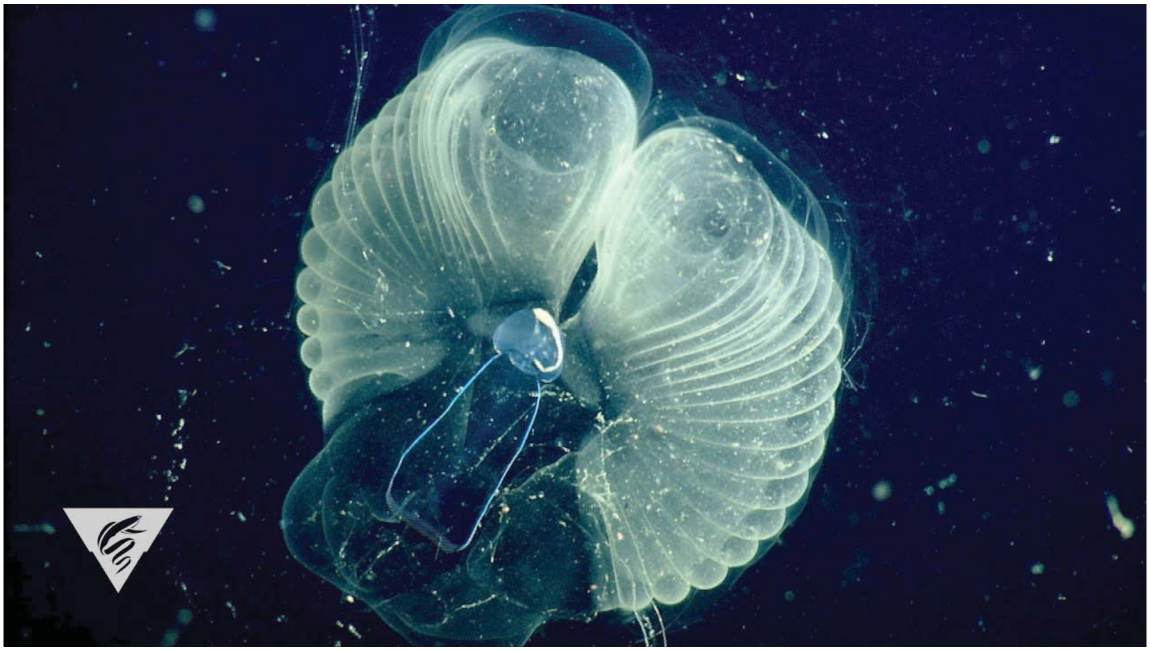

Figure 3. A larvacean with its filter feeding mucus net. *Photo courtesy of NOAA.*

Furthermore, the ocean is filled with abundant organisms that filter bacteria and small organic matter from the water using mucus nets that rapidly export carbon. Clogged by organic debris, larvaceans (Figure 3) discard their mucus nets up to 20 times a day, and those nets export carbon downward at rates of 800 meters a day.[37] Likewise, filter-feeding salps sink 1700 meters in a day.[38] Jellyfish sink between 850 and 1500 meters in a day.[39] Faster yet, filter-feeding snails, called sea butterflies with heavier calcium carbonate shells, sink 1700 to 2200 meters in a day.[40] Rapidly sinking bodies remove carbon from surface waters to sequestration depths.

Active Carbon Pumping via Vertical Migration

Many organisms feed on plankton in surface waters at night and transport carbon back to the depths

The transport of carbon to sequestration depths does not only depend on passive sinking. As noted, the *mesopelagic zone* exists between depths of 200 and 1000 meters. There, pH ranges from 7.8 to 7.3. During World War II, newly developed sonar technology unintentionally alerted scientists to robust populations of mesopelagic organisms. Sonar scientists were initially fooled into thinking strong sonar echoes were caused by a “false” ocean floor. But the echoes were caused by billions of organisms.

We now understand that about half of those organisms rise to the surface layers and feed on surface plankton each night when marine predators cannot see them, and then return to mesopelagic depths in the morning. During this process they transport carbon downwards from the surface, enabling carbon

to reach sequestration depths more quickly than would be possible via passive sinking. This is the largest migration on the planet.

The mesopelagic was once considered an ocean desert. But it is clear now it supports a highly diverse fauna. Abundant mesopelagic zooplankton attracted numerous jellyfish species that hunt only in the mesopelagic. In turn, leatherback turtles evolved to specialize on those jellyfish as they rise and fall back into the mesopelagic. It is now believed that mesopelagic fish, like lantern fish, are the most abundant fish in the world, exceeding a mass of over a billion tons.[41]

The Colossus Squid and related smaller squid species evolved to feed on this great abundance and in turn, the abundance of squid attracted toothed Sperm Whales that evolved to hunt mesopelagic squid. (Moby Dick was a Sperm Whale.) The increasing awareness of mesopelagic abundance gradually called into question early estimates of surface productivity and organic matter export. Sustaining the enormous mesopelagic abundance requires far greater surface productivity than had been previously estimated.[42]

In addition to daily vertical migrations, some of the world's most abundant zooplankton evolved an annual vertical migration. Feeding on summer phytoplankton blooms, trillions of copepods store carbon as fats in order to survive their winter hibernation. They then swim down to below the pycnocline where they hibernate through the winter, respiring CO_2 from their stored fats.[43] The pycnocline is a layer in the oceans where there is a rapid increase in the water's density. Dense waters below the pycnocline resist rising into the less dense surface waters. Thus, the copepods' respired CO_2 gets sequestered below the pycnocline.

Ocean productivity has been underestimated for many reasons. Traditional methods of estimating the amount of exported organic carbon relied on sediment traps that sampled sinking organic matter at various depths. However, those sediment traps fail to measure carbon transported by "swimmers" whose vertical migrations pump tremendous amounts of carbon to sequestration depths. In addition, not all surface productivity is transported downwards. The same physical dynamics that promote coastal upwelling of old nutrients and carbon to the surface also pump nutrients and organic carbon laterally into the open oceans. Researchers suggest that together with unused upwelled nutrients, about 36 percent of the organic matter produced along the coast. is exported toward the open ocean.[44, 45]

Upwelling Completes the Ocean's Carbon Cycle

Ancient sequestered carbon and nutrients are reintroduced along coast lines and Antarctica, temporarily lowering pH but promoting bursts of life

The persistent sequestering of carbon in the deep ocean would eventually starve phytoplankton in the surface waters if not for ocean dynamics that constantly recycle DIC and other critical nutrients back into sunlit surface waters. Oceanographers now agree most of the bottom waters that had sequestered carbon and nutrients for thousands of years are eventually upwelled around Antarctica.

New research finds those upwelled waters are then transported northward below the surface and upwelled to the surface again 30 to 50 years later along coastal upwelling regions such as Peru or

Africa's Benguela region. Furthermore, recent studies using carbon-14 as a tracer have shown carbon-rich and nutrient-rich waters that are upwelled along the coast are transported across entire ocean basins, sustaining marine food webs.[46, 47] Because upwelling of nutrients and DIC is absolutely critical for ocean productivity, much of the productivity is modulated by a carbon cycle that can encompass thousands of years.

The upwelling of deep, carbon-rich and nutrient-rich waters promotes magnificent bursts of life. Although coastal regions account for less than 10 percent of the ocean's surface, coastal regions produce almost half of all marine productivity. Accordingly, most coastal regions are associated with the world's great fisheries. However, although upwelling brings requisite nutrients to sunlit surfaces, it also brings high DIC, low pH waters. Despite the essential functions upwelling provides, the politicization of carbon dioxide has portrayed upwelling as an example of worrisome "acidification."

A few researchers claim to have estimated the amount of anthropogenic carbon that exists in the surface waters. But their methodologies are gravely flawed.[48] Their basic approach measures the amount of DIC in today's waters. They then calculate how much DIC would be present when atmospheric CO_2 was 280 ppm. By subtracting the observed DIC from the calculated pre-industrial DIC, they suggest the difference between the two represents human-added CO_2.

The fatal flaw in that approach is that it does not account for upwelled DIC that may have been generated hundreds to thousands of years ago. Studies of productivity along Peru suggest upwelling has greatly increased since the Little Ice Age ended in the 1800s.[49] Stronger upwelling brings more ancient DIC to the surface layers. This in turn will result in a gross over-estimation of any human-added DIC (CO_2). Any useful analysis must separate upper-ocean DIC derived from upwelling versus DIC-derived atmospheric CO_2.

The failure to understand upwelling was costly to Oregon's oyster hatcheries. Over-exploitation of North America's native west coast oysters almost eliminated them. In response, oyster fisheries imported the Japanese oyster. However, that species was not well adapted to the more extreme upwelling along the Oregon and Washington coasts. Larval oysters often died when exposed to cooler upwelled waters.[50] Furthermore, the more extreme tidal exchanges between the ocean and the estuaries caused free-swimming oyster larvae to be carried out to sea. Oystermen responded by developing hatcheries where larvae could safely develop, and then be released into the estuaries, where they settle and attach to surfaces.

However, the non-native Japanese oyster larvae were not only sensitive to cooler upwelled waters. They were also sensitive to the lower pH of those upwelled waters. Unknowingly, hatchery operators filled their "nursery" tanks with water drawn from the estuary at the wrong time. Water was usually drawn in the early morning, after nighttime respiration had already lowered the water's pH.

By chance the operators piped in the estuary water right after an upwelling event. Tidal flushing had brought carbon-rich, low pH waters into the estuary. The use of this unusually low-pH water meant that many hatchery larvae did not survive. Although a few patches of native oysters were unaffected, the hatchery failure was deemed a crisis caused by global warming and ocean acidification. But by simply monitoring upwelling events, hatcheries can avoid making the same mistake.

Based only on flawed calculations that failed to account for upwelling of ancient DIC, some researchers assert the upwelled water detrimental to the oysters had been acidified by human-added CO_2. In contrast, other researchers trace the origins of the water upwelled onto North America's west coast. The initial source was old deep Pacific water upwelled along the equator. Deep Pacific water is some of the oldest water in the world and unaffected by modern atmospheric CO_2.

Because any sequestered organic carbon had been decomposing for over 1,000 years, the upwelled equatorial water was rich in nutrients, with high DIC and a low pH. The equatorial waters were mixed with the California Undercurrent, which then transported the water northwards along North America's west coast, where it upwelled. Although the researchers acknowledge that other factors may be involved, the trend toward more DIC and lower pH in upwelled water can be largely explained by the increase in the volume of low pH upwelled water carried in the California Undercurrent.[51]

Portraying low-pH upwelling events as evidence of catastrophic "ocean acidification" misinforms the public. Upwelling is a vital dynamic that brings carbon and nutrients, otherwise sequestered in the ocean's depths, back to the surface. Although there may be negative consequences of low-pH and low-oxygen upwelled waters, without upwelling of low-pH waters, global marine productivity would be greatly reduced.

IV. The Shell Game

CO_2 is a friend, not a foe of shell health

Calcium Carbonate Chemistry

Carbon is essential to shell formation, and shell health has not been damaged by CO_2

Calcium carbonate minerals make up seven percent of the earth's crust in the form of chalk, limestone and marble. Calcium carbonate is also the main constituent for shells of mollusks, like snails and oysters, for coccolithophore (Figure 4) and foraminifer phytoplankton, and for coral skeletons. In seawater, *calcium carbonate* naturally forms if the concentrations of calcium ions and carbonate ions reach high levels. Tufas forming in saline lakes are an example of inorganic calcium carbonate formations. But long ago, shell-making organisms evolved the ability to concentrate calcium and carbonate ions and control shell formation.

Because concentrations of the ocean's calcium ions are abundant and stable, the ocean's inorganic calcium carbonate formation is driven by fluctuations in carbonate ions. As described earlier in the inorganic pathway, carbonate ions are one of the three forms resulting from CO_2 interactions with water. Under high pH conditions, when hydrogen (H+) ions are scant, a higher percentage of DIC exists as carbonate ions. As pH decreases, the increased number of H+ ions are more likely to rejoin carbonate ions and form bicarbonate ions. Based on those basic chemical reactions, some modelers worried that because higher CO_2 concentrations will produce more H+ ions and in turn promote the conversion of carbonate ions to bicarbonate, organisms would be denied enough carbonate ions to make their shells. However, those modelers seem unaware of shell-making biology.

In the political arena of climate change, critical factors are misleadingly ignored by those claiming that rising CO_2 leads to shell disintegration. First, shells of living organisms are protected by organic tissues that insulate the shells from changes in ocean chemistry. Mollusk shells are typically covered by a periostracum. This allows mollusks to thrive near low pH volcanic vents, or in acidic freshwater, or when buried in low pH sediments. Coral skeletons are protected by their layer of living coral polyps. When shell-forming organisms die they lose that layer of protective tissue and their shells or skeletons may indeed dissolve. However, dissolution releases carbonate ions, which buffers the surrounding waters and inhibits any further change in pH.

Biological Calcification

Slightly lower pH does not stop ocean organisms from converting bicarbonate ions into shell-building carbonate ions

Some climate modelers incorrectly suggest that a small drop in pH will inhibit shell-building in marine organisms.[52] This mistaken assertion is based on inorganic chemistry that correctly observes reduced carbonate ion concentrations when pH falls. However, shell-building organisms lack the ability to directly import carbonate ions. So, the ocean's concentration of carbonate ions is largely irrelevant. Shell-building organisms evolved to first import the always plentiful bicarbonate ions. Once bicarbonate ions are transported inside a shell-building compartment, H+ ions are pumped out. The resulting higher pH then causes bicarbonate ions to release their H+ and convert into the carbonate ions needed for shell-building.[,]

The fact that shell-making organisms rely on bicarbonate ions, not carbonate ions, is consistent with the earth's evolution. Fossil evidence of shell-making mollusks dates back 500 million years to the Cambrian period. During that time, atmospheric CO_2 has been estimated to have been at least 4000 ppm, 10 times today's concentrations. According to "acidification" theories, such high CO_2 concentrations would have lowered surface pH and made carbonate ions much scarcer than today. However, there would still have been abundant bicarbonate ions for shell-building.[53, 54]

The ability to make shells despite experiencing atmospheric CO_2 much higher than today was demonstrated during the Cretaceous period, when atmospheric CO_2 ranged between 2000 and 1000 ppm.[55] Nonetheless, the oceans accumulated and preserved massive deposits of calcium carbonate shells. The name Cretaceous comes from the Latin word for chalk, which is made of calcium carbonate. The massive chalk deposits resulted mostly from the organic chemistry of phytoplankton known as coccolithophores, that produce calcium carbonate "scales," or coccoliths. The famous White Cliffs of Dover are primarily the result of Cretaceous coccolithophores. So it's not surprising which despite today's rising atmospheric CO_2, oceanographers are observing increasing blooms of coccolithophores.[56, 57]

Some climate modelers have portrayed the floating ocean snails, known as sea butterflies, as indicators of "ocean acidification." But, again, observations show no unequivocal detrimental effects. A few researchers have observed snails with patches of dissolving shells that they uncritically blamed on ocean acidification.[58, 59] However other researchers pointed out that shell dissolution only occurred when shells were damaged and their protective organic tissue was breached.[60] The snails quickly repaired the shells with more calcium carbonate.

Furthermore, damaged snails shells only experienced dissolution when they were exposed to upwelling of old, low-pH carbon rich waters. So, it's not surprising that recent studies find that sea butterflies' abundance is slightly increasing.[61, 62] Finally, it is often underplayed that the process of forming of calcium carbonate both sequesters alkalinity and releases CO_2, which in turn lowers pH. Calcification contributes to the lower nighttime pH in coral reefs. Thus, the increasing abundance of calcifying sea butterflies, foraminifera and coccolithophores will result in a small declining pH trend.

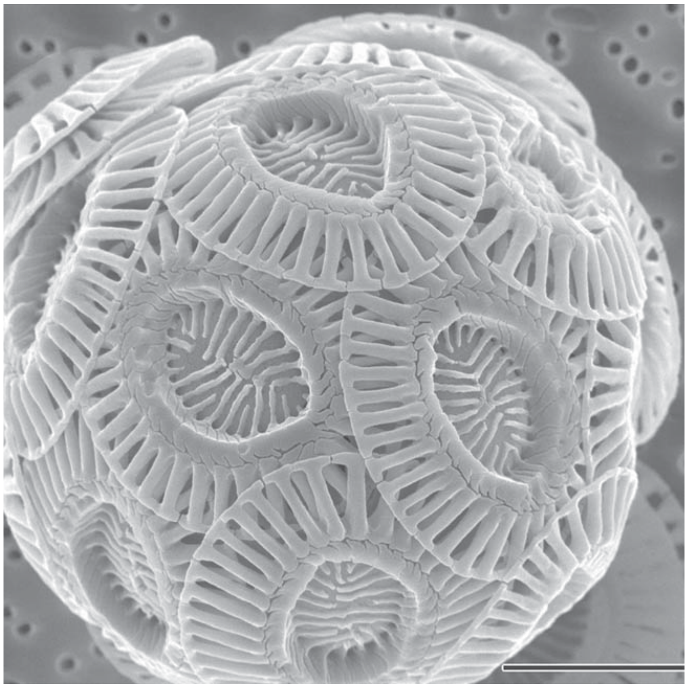

Figure 4. A coccolithophore with ornate calcium carbonate scales (coccoliths). *Courtesy of NOAA.*

V. Conclusion

The oceans will not become acidic -- CO_2 enriches the ocean food web

As of this writing, there is no unequivocal evidence to suggest that the oceans have been undergoing a drop in pH due to rising atmospheric CO_2. It cannot be assumed that CO_2 diffusing into surface waters only embarks on the inorganic pathway. More likely, CO_2 will be quickly consumed by photosynthesizing bacteria, plankton and algae. The transformation of CO_2 into organic carbon means that CO_2 will not affect ocean pH for hours to millennia, depending how that organic matter travels through the food web. Reliable measurements of ocean pH only began over the last 30 years. Science will need at least 30 more years of observations before natural ocean pH variability can be distinguished from any effects from increasing atmospheric CO_2.

Concurrent with the rise in atmospheric CO_2, there has been an increase in ocean upwelling that brings ancient carbon and nutrients to the surface. There has also been an increase in ocean productivity, transforming CO_2 into organic carbon. Greater productivity allows more organic carbon to be exported to depths where it can be sequestered for hundreds to thousands of years. It is highly likely that the recent increased productivity and increased sequestration of carbon has offset any pH effects from added atmospheric CO_2. That hypothesis needs to be thoroughly tested in order to better predict changes in ocean pH. Modeling efforts to date are woefully incomplete. IPCC models do not consider the effects of ocean productivity, and calculations of anthropogenic CO_2 in ocean surface waters fail to account for upwelling of ancient DIC.

Figure 5. A pteropod or sea butterfly. *Photo courtesy of NOAA.*

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