The Oceanic Acid Trip: Why CO_2 impacts the oceans so drastically

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Today global warming is the topic on everyone's tongue, and "green living" has been on the rise for nearly a decade. Greenhouse gases are the enemy, and carbon dioxide (CO_2) is an extremely potent greenhouse gas that is often the target of a great deal of discourse, policy and research. Anthropogenic CO_2, that is to say CO_2 generated by burning of fossil fuels, cement manufacturing and other human activities, has been on the rise since human industrialization and has lead to notable climate change, and frightening implications for the future of our planet. In the rush to live green, it is easy to forget, or even be unaware of, how the planet's oceans are affected by CO_2 emissions, and the immense role they play in climate change. The oceans are undergoing acidification, as explained below, which is thought to be a result of human activities. Acidification may have vast impacts on the oceans and ocean processes including nutrient cycling, fitness of some organisms, overall productivity, availability of nutrients, to name a few. Acidification also feeds back on the atmosphere and impacts global climate change as well. This paper will explain the basics of acidification and will then discuss some (certainly not all) of the impacts of acidification and the latest research on the topic.

The oceans have a huge capacity for carbon sequestration. In fact, they have absorbed over one third of the anthropogenic carbon dioxide produced since 1800 (Sabine et al. 2004) and have the potential to absorb up to 80% of the anthropogenic carbon, albeit over the course of millennia (Sabine & Tanhua 2010). Increasing atmospheric CO_2 increases the atmospheric partial pressure of CO_2 (partial pressure is the contribution of carbon dioxide's pressure to the total pressure of the system) such that today the partial pressure of atmospheric CO_2 is about 7ppm greater than that of oceanic CO_2 (Sabine et al. 2007). As a result, CO_2 dissolves into the ocean according to Le Chatelier's Principle. Le Chatelier's Principle is important for understanding the nature of physical and chemical equilibria and is important in understanding carbon's impact on the ocean. Simply put for our purposes, Le Chatelier's Principle says that an increase in concentration of one reactant of an equilibrated reaction will shift the reaction in favor of the products (the reverse for a decrease in concentration) (Wikipedia contributors 2010). Therefore increasing the partial pressure of atmospheric CO_2 (which is effectively an increase in concentration) shifts more CO_2 into the dissolved aqueous state, increasing the concentration of CO_2 in the water (which is abbreviated pCO_2).

When the ocean absorbs large amounts of CO_2, an interesting reaction takes place that ultimately has a significant impact on marine ecology as well as global climate change as a whole. When atmospheric CO_2 is dissolved in water, it forms carbonic acid (H_2CO_3), which dissociates to form H^+ ions. The basic reaction describing all this is:

$CO_2 + H_2O \xrightarrow{\longleftarrow} H_2CO_3 \xrightarrow{\longleftarrow} H^+ + HCO_3^- \xleftarrow{\longrightarrow} 2H^+ + CO_3^{2-}$ (Doney et al. 2009).

This reaction shows us that CO_2 dissolved in water yields H^+ ions. By Le Chatelier's Principle we can see that, when large amounts of CO_2 are dissolved in the ocean, the reaction shifts to the right and the end result is an increase in the concentration of H^+ ions. This yields a lower pH and greater acidity of the water: acidification. Of course it would have been safe to assume that carbonic *acid* increases acidity, however the reaction is useful to see. Carbonic acid is indeed the key acid in this case (rather than HCO_3^-) because 90% of dissolved carbon exists as bicarbonate (HCO_3^-) due to more complex chemical and physical details (Feely et al. 2009). This means that the excess H^+ ions produced from carbonic acid will bind to any available CO_3^{2-}, to make bicarbonate, leaving a dearth of free carbonate in solution. It is precisely this scarcity of carbonate ions in solution that leads to an undersaturated state and causes the well-documented effect of impaired calcification by many marine fauna (Doney et al. 2009). In general, carbonate-saturated waters prevail at shallow depths (within the shallow layer of warmer surface water called the thermocline) due to the higher temperature of surface waters, and deeper waters tend to be more undersaturated (Sabine et al. 2004). However studies have shown that carbonate-saturated surface waters are decreasing in depth as a result of acidification, and models predict drastic undersaturation of surface waters as soon as the end of the 21^{st} century (Feely et al. 2004). This would be disastrous for pelagic (suspended in the water column) and benthic (residing on the sea bed) life since a great deal of calcifying organisms reside in these surface waters.

Calcium carbonate is constantly dissolving into the water and being replenished by organisms in a state of equilibrium. However when the water is especially undersaturated with $CaCO_3$, some organisms simply cannot generate $CaCO_3$ fast enough to outpace its dissolution. As a result, their calcium carbonate skeletons dissolve and the organisms perish (Doney et al. 2009). Nutrients circulate in the ocean by means of the biological carbon pump (discussed below) and pelagic calcifiers are essential contributors to this process (Hofmann & Schellnhuber 2009). Thus there is cause for concern since acidification diminishes the phytoplankton (pelagic, photosynthetic organisms) populations that are crucial for carbon sequestration and circulation. A recent paper also emphasizes the role of benthic organisms, specifically echinoderms (starfish, urchins, sand dollars and the likes), in carbon sequestration and $CaCO_3$ secretion. Lebrato et al. (2009) traveled the globe sampling echinoderm populations and determining their carbon content. They determined that echinoderm carbon storage, while less than pelagic storage, is quite significant and should be considered in carbon models. Lebrato et al. also note that most echinoderms reside at shallow depths, and therefore would be greatly impacted by the expansion of undersaturated waters mentioned above. We can see that acidification is a serious threat to the livelihood of many species by means of $CaCO_3$ dissolution.

A great deal of research has shown the detrimental effect of increased oceanic CO_2 concentration on calcifiers: mostly corals but some planktonic organisms as well (Fabry 2008). Recent studies in the arctic have also shown clear evidence in benthic macroorganisms of $CaCO_3$ dissolution due to carbonate undersaturation (McClintock et al. 2009). Coccolithophores are a type of phytoplankton that are very widespread and have a significant impact on ocean ecology and nutrient cycling, which is why a number of coccolithophore species have been studied extensively. A seminal study by Riebesell et al. (2000) established the idea that coccolithophores (specifically *E. huxleyi*, a prevalent and important species of coccolithophore) decrease calcification with increased pCO_2. However, recent studies have shown that some coccolithophore species, or even some individuals within a single species, are not negatively affected by increased pCO_2 as would be expected. Langer et al. (2006) found that two important species of coccolithophore do not react to increased pCO_2 as predicted. Instead, one species appeared to have no response to changing pCO_2, while the other exhibited non-linear behavior with pCO_2 change, and had an optimum pCO_2 level at the elevated contemporary levels. Iglesias-Rodriguez et al. (2008) studied the impact of acidification on *E. huxleyi*. To the surprise of many researchers, they found that calcification and overall production in *E. huxleyi* actually *increased* with acidification, in direct contrast to previous findings. The researchers explained these unusual results by emphasizing the novelty of their methodology. Whereas most previous experiments increased acidity by the addition of acid, Iglesias-Rodriguez et al. bubbled CO_2

through the seawater, which, they claimed, better simulates environmental conditions. Langer et al. (2009) explored these discrepancies and concluded that different strains of *E. huxleyi* exhibit different behavior in response to elevated pCO_2. The mechanism by which a species or strain may resist or even flourish in elevated carbon levels is unclear, however there are probably some intracellular regulatory mechanisms at work. There are clearly a variety of different responses to acidification in the ocean, making modeling and predictions of climate change and oceanic changes quite difficult and unreliable. Calcification plays a crucial role in the biological carbon pump and other effects in the ocean with far-reaching implications. Further research is needed to better understand changing calcification rates in different organisms so that we may better predict the effects of emissions.

The biological carbon pump is the process of carbon transport between oceanic depths and plays a central part in the ocean's capacity to absorb carbon. Phytoplankton in the surface water takes up CO_2 from the water and fixes it using solar energy. When the phytoplankton dies, the organic carbon in its tissue sinks and is a source of organic carbon for the deep sea, where it is converted back into CO_2 (Sunda 2010). This causes a build-up of dissolved CO_2 in the ocean depths that is kept in solution by high pressure, and allows more CO_2 to enter the surface water. This is essentially the process by which the oceans sequester carbon. Calcium carbonate plays an important part in the biological pump. When a calcareous organism dies, the $CaCO_3$ serves as a ballast (a weight of sorts) and allows precious organic carbon to descend to greater depths before it is fully decomposed. Hofmann & Schellnhuber (2009) developed a model for this ballast activity to explore its effects on carbon levels in the ocean, and ultimately in the atmosphere. They knew that calcium carbonate allows the ocean to absorb more CO_2 at the surface through normal functioning of the biological pump and wondered what effect acidification had. As one can imagine, the model suggested that a situation of positive feedback (feedback on atmospheric carbon) would arise. Absorption of CO_2 at the surface leads to acidification. Acidification decreases the levels of $CaCO_3$ (as described above), which reduces the potency of the biological pump. This feeds back and lowers the amount of CO_2 that can be absorbed at the surface. As a result, climate change is accelerated since the ocean absorbs less carbon dioxide and more remains in the air. Hofmann & Schellnhuber also modeled a situation of negative feedback from acidification. This feedback arises from the fact that, when $CaCO_3$ is made, the balanced chemical equation requires that CO_2 is released. Therefore reduced calcification as a result of acidification leads to less CO_2 being released. Less CO_2 in solution means that more atmospheric CO_2 may be absorbed, and thus negative feedback that stabilizes the climate occurs. When combining the models, and assuming a continued “business-as-usual” rate of carbon emission, atmospheric pCO_2 is expected to peak in year 2200, but the negative feedback effect will lower levels again when, as the model assumes, emissions are eliminated after 2200. Levels are projected to decrease to 1400 μatm by the end of the millennium (for reference, the pCO_2 level in the year 1800 was estimated at 282 μatm). While certainly quite intensive, it seems highly unlikely that this study was able to consider every single effect of acidification on the climate. Modeling is highly variable and depends entirely on the methods, data, and assumptions used by the researchers. However it can still be useful to consider all modeling efforts in order to try to understand the big picture.

A recent study has added another piece to the puzzle of acidification’s effect on climate change that Hofmann & Schellnhuber were trying to assemble. The effect of acidification on marine levels of iron (Fe) were not clear until Shi et al. (2010) tested the uptake of Fe by phytoplankton. They found that acidification limits the ability of organisms to absorb iron because lower pH increases Fe solubility, and causes it to be held more tightly in solution. This finding has implications for the biological carbon pump and therefore on climate change. Diminished Fe availability hinders the ability of phytoplankton to fix carbon by photosynthesis (Sunda 2010). In many parts of the ocean, productivity is limited by nitrogen availability, not Fe. Sunda (2010) points out, however, that nitrogen-fixing by bacteria *is* limited by Fe, so Fe scarcity decreases the availability of nitrogen, which decreases carbon fixation all the same. Both of these pathways weaken the biological pump, so positive feedback results, similar to the positive feedback due to decalcification described above. While it may have seemed promising that negative feedback wins out in the Hofmann & Schellnhuber model, there are many factors that are not included, one of which being positive feedback due to iron stress. Furthermore, the Hofmann & Schellnhuber model assumes continued carbon emission until the year 2200, so the projected levels of carbon are still astronomical and will have catastrophic and unacceptable implications for marine life, regardless of the state of the climate. Independent of climate effects, high carbon levels lower the pH, and this has significant impacts on marine life that has already been mentioned, and will be added to below.

Hofmann & Schellnhuber (2009) do consider a significant non-climatic effect of acidification that we have not yet touched upon: hypoxia. As low calcification weakens the biological pump, organic carbon starts decomposing in increasingly shallow water. Decomposition is carried out through respiration, which requires oxygen, so new zones of hypoxia begin to develop as a result. Hofmann & Schellnhuber use their climate change models to predict patterns of hypoxia:

since global warming increases the ocean's surface temperature, oxygen solubility drastically decreases, resulting in the spread of hypoxia. Thus they show that acidification initiates the development of hypoxic zones by weakening of the biological pump, and it exacerbates hypoxia trends by impacting the global climate.

In this paper we have, beginning with the very basics of acid-base chemistry, explored the acidification phenomenon and its connection to anthropogenic carbon emissions. Acidification has a huge effect on carbonate saturation, and therefore calcification. This impact on calcification is a major way that acidification wreaks havoc on marine organisms, marine physics, and global climate change. While nearly all the studies reviewed in this paper are on the forefront of research on acidification, there remains much to be explored if we are to understand the far-reaching impacts of acidification on the oceans and the atmosphere alike. Only a handful of feedback mechanisms have been mentioned (many more exist) and future research should seek to model the real impacts of acidification, and CO_2 emissions on the whole. Of course, accurate models require accurate data and well-understood environmental interactions. Thus empirical data is of the utmost importance before useful modeling can even begin. The curiosity involving *E. huxleyi*, for example, brings up the need to understand how simple organisms act depending on their environments (it is conceivable that *E. huxleyi* behaved differently in the two studies due to their environments, their quantity, or countless other factors). A great deal of work is in store before marine acidification can be fully understood, but what is clear is that acidification is harmful. Studies of an ecological crisis like acidification are studies of the environmental reactions to continued human disregard for the environment and so we must remember to also fight acidification at its human-generated source.

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