

Ocean Acidification: Mini-Lab, Graphing, & Analysis**Background Information**

Carbon is an element that is the chemical backbone of all known life. All known life forms rely on carbon. Our Earth has a carbon cycle. That means carbon is always on the move. Plants use carbon dioxide (CO₂) and sunlight to generate energy and grow. The carbon then becomes part of the plant. When we eat plants (or eat things that eat plants), some of the carbon becomes part of us; some is exhaled in our breath. When plants die they sometimes are buried and turn into fossil fuels like coal and oil over millions of years. In fact, during the Carboniferous Period in the distant past, roughly 360 to 300 million years ago, nearly all the fossil fuels we use today were beginning to be formed.

When we burn fossil fuels much of this long-stored carbon quickly (re)enters the atmosphere as carbon dioxide. This is in contrast to the carbon dioxide we exhale, which was only obtained by plants in the food we eat within the past couple of years. One of the most critical jobs the oceans have is to store carbon. The oceans contain the largest reactive pool of carbon on the planet, and without the benefit of carbon storage in the oceans, the current atmospheric carbon dioxide levels would be at least 25% higher than they are today.

Carbon in the form of carbon dioxide can be removed from the atmosphere when absorbed by the ocean through a physical process called diffusion. Diffusion occurs when there is more of something in one area relative to another, and that material moves to the area with less. Prior to the combustion of fossil fuels the oceans were actually a small source of CO₂ to the atmosphere, but they have become a large “sink” for CO₂. In fact, in the last 150 years, 25-35% of all CO₂ from the burning of fossil fuels has ended up in the ocean, and it will stay there for a long time.

Understanding pH Chemistry

Whether a substance is an acid or a base depends on the concentration of hydrogen (H⁺) ions compared to the concentration of hydroxide (OH⁻) ions in solution. A pH scale is used to measure the concentration of hydrogen (H⁺) ions.

- 1) Look at the pH scale diagram on the color handout, take a few minutes to examine the relationship between the pH value (1-14) and the concentration of hydrogen (H⁺) ions compared to the concentration of hydroxide (OH⁻) ions. Also pay attention to the logarithmic scale on the left which illustrates how much the concentration of H⁺ ions change relative to the neutral pH of 7.

Key points to know about the pH scale and acidity:

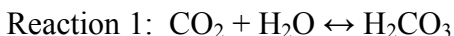
- a. The lower the pH value, the more acidic the solution.
 - b. The higher the pH value, the more basic (alkaline) the solution.
- 2) The pH scale is based on a logarithmic scale (powers of ten). For example, pH 7 is ten times more acidic than pH 8. pH 6 is 100 times (10 X 10) more acidic than pH 8. This means that even a small change in pH can significantly change the concentration of H⁺ ions in seawater.
 - 3) The term "acidity" does not mean the same thing as a solution being an "acid." For example, if a pH value of a substance changes from pH 10 to pH 9, the concentration of H⁺ ions increases making the substance more "acidic" but not making the solution an acid. To be an acid, the pH value must be less than 7. This concept will become important in understanding ocean acidification.

Adapted from:

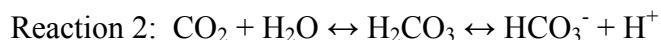
- 1) <https://serc.carleton.edu/eslabs/carbon/7a.html>
- 2) http://blogs.oregonstate.edu/smile/files/2016/02/OceanAcidification_revised.pdf
- 3) http://www.soest.hawaii.edu/mguidry/Unnamed_Site_2/Chapter%205/Figures/Box3SeawaterSaturationState.pdf
- 4) <https://www.nature.com/articles/nclimate2479>

The oceans are naturally equipped to absorb large amounts of carbon dioxide from the atmosphere with little change to seawater chemistry. This is possible due to the natural buffering system of the oceans. The same way antacids buffer a sour stomach, the ocean's buffering capacity slows changes in the ocean chemistry. To explain the ability of the oceans to store carbon and the buffering capacity of seawater we need to understand what happens when carbon dioxide enters the ocean.

Several chemical reactions occur when the oceans absorb carbon dioxide. The first is that carbon dioxide (CO_2) reacts with seawater (H_2O) to form carbonic acid (H_2CO_3).



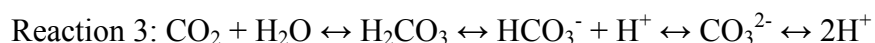
Carbonic acid is a weak acid and separates (or more exactly, dissociates) to form one bicarbonate ion (HCO_3^-), and one hydrogen ion (H^+) is released into the seawater.



Bicarbonate is the primary form of inorganic carbon in the ocean and is one of the two “products” shown in the above reaction (the other is the hydrogen ion). Consider that we have only shown one reaction from one molecule of carbon dioxide. There are actually MANY of these reactions taking place, one for each molecule of carbon dioxide, and after these many reactions occur, some hydrogen ions will remain free floating in the seawater while others will react with another carbon ion in seawater (detailed in reaction 4 below). The more hydrogen ions that float freely in seawater, the more acidic the seawater becomes. Looking back to our first equation, this means when CO_2 increases the seawater will become more acidic (more CO_2 being absorbed by the oceans ultimately leads to more hydrogen ions). This process, the uptake of carbon dioxide by the oceans and concurrent change in chemistry, has been named ocean acidification.

Note that a product of the above reaction includes bicarbonate, which is how the ocean so effectively stores carbon, because the carbon in the CO_2 gas, initially absorbed into seawater, is now in bicarbonate form. After this happens, more room will have been created for even more CO_2 gas from the atmosphere to be absorbed by the oceans. We are steadily increasing the concentration of CO_2 in the atmosphere by burning fossil fuels primarily, but also because of loss of vegetation (land use changes). The increase in atmospheric CO_2 is directly responsible for increasing mean global temperature through the amplification of a natural process, called the greenhouse effect. The increase in global temperature caused by the intensification of the greenhouse effect is called climate change (also, global warming).

Remember that free-floating hydrogen ion shown in reaction 2? Instead of being free-floating, some of these ions will combine with another important ion in seawater, carbonate (CO_3^{2-}), to form into another bicarbonate ion.



In the above reaction, you can now see all components of the dissolved inorganic carbon system in seawater. The formation of another bicarbonate ion, resulting from the initial absorption of atmospheric CO_2 by the oceans, is the primary way that the ocean naturally slows the increase in acidity on immediate time-scales. We call the ability of the ocean to take up (or “sequester”) hydrogen ions and prevent the pH from dropping its buffering capacity. We talk about the buffering capacity of seawater because it is linked to the amount of ions that can react with hydrogen ions, and that is what we call alkalinity. Alkalinity in the oceans is approximately 97% due to the total amount of bicarbonate and carbonate ions.

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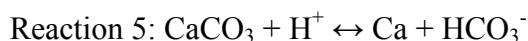
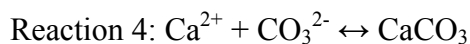
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We know that the concentration of CO₂ is changing on timescales of years, but how fast does alkalinity change? The main process adding alkalinity compounds (like bicarbonate and carbonate ions) to the oceans is the erosion and weathering of rocks on land through the hydrologic cycle. In very small amounts over long periods of time, rivers carry “alkalinity” to the oceans and leave it there, once water evaporates. Over very long time scales, 100,000’s of years, the weathering of continental rocks increases the alkalinity of seawater and increases the ability of seawater to offset pH decreases. While it may seem like a viable solution to the ocean acidification problem to simply dump “alkalinity” into the sea, a large mismatch between time-scales exists. Therefore, on the time scales important to humans (tens to hundreds of years), these processes are not fast enough to significantly buffer against ocean acidification. In other words, the buffering capacity of the planet can’t keep up with the amount of CO₂ being put into the atmosphere, and ultimately the oceans. This is essentially because the normal changes in CO₂ in the geologic past have occurred on much longer time scales, more similar to rates of weathering.

We don’t yet know how ocean acidification impacts all marine ecosystems, but we do know that some organisms that build shells (mussels, oysters, clams) or other body-parts (corals, sea urchins) made out of calcium carbonate (CaCO₃) are affected negatively. Why is that?

Remember that the more hydrogen ions free-floating in seawater from CO₂ absorption and uptake, the more carbonate ions react with hydrogen ions to form bicarbonate. This means that the amount of carbonate ions in the seawater will decrease. The more carbonate ions in seawater, the easier it is to make their calcium + carbonate shells, through a process called calcification.

Fortunately for marine organisms that build shells, the oceans are saturated in most places with respect to calcium carbonate (CaCO₃), but the decrease in carbonate ions from ocean acidification lowers the saturation state and makes it harder for organisms to make shells, and in some cases, calcium carbonate shells may even start to dissolve if pH levels decrease beyond threshold levels.



Aragonite Saturation State of Seawater

In seawater calcium ions (Ca²⁺) bond with carbonate ions (CO₃²⁻) to form calcium carbonate (CaCO₃). Shells of marine organisms are chiefly composed of calcium carbonate, which is very often referred to as aragonite. Thus, calcium carbonate, CaCO₃, is aragonite. Notice that this is a reversible equation.

When the concentration of dissolved calcium ions and dissolved carbonate ions in seawater are in equilibrium, the seawater is saturated, with respect to aragonite. The Greek symbol Ω (Omega) is used to designate saturation state. So, Ω_{aragonite} means aragonite saturation state. When seawater is in equilibrium or saturation, with respect to aragonite, then Ω_{aragonite} is 1.0. When seawater is supersaturated, with respect to aragonite, then Ω_{aragonite} is >1.0. In this case conditions are favorable for aragonite (calcium carbonate) formation. When seawater is under saturated, with respect to aragonite, then Ω_{aragonite} is < 1.0, which results in the dissolving of aragonite (calcium carbonate).

When carbon dioxide dissolves into surface seawater from the atmosphere, the acidity of the surface seawater increases. If the surface acidity increases, then there are relatively fewer carbonate ions (CO₃²⁻) in seawater, and thus the value of Ω_{aragonite} decreases and so does the saturation state of seawater with respect to aragonite.

Adapted from:

- 1) <https://serc.carleton.edu/eslabs/carbon/7a.html>
- 2) http://blogs.oregonstate.edu/smiley/files/2016/02/OceanAcidification_revised.pdf
- 3) http://www.soest.hawaii.edu/mguidry/Unnamed_Site_2/Chapter%205/Figures/Box3SeawaterSaturationState.pdf
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Synopsis: Saturation-state sensitivity of marine bivalve larvae to ocean acidification

Bivalves, such as mussels and oysters, have been observed to be especially sensitive to ocean acidification. Bivalve *larvae* are particularly sensitive to ocean acidification during shell formation. The critical period of shell calcification—when the larvae hatch from their eggs to when they complete their protective shell—spans only about two days. During this time, the larvae lack the ability to feed and are dependent on maternal energy reserves retained from the egg. Failure to complete shell formation before exhausting maternal energy reserves leads to mortality. The rate at which bivalve larvae, such as mussels and oysters, can form a shell is dependent on the concentration of carbonate ions or saturation state ($\Omega_{\text{aragonite}}$) of the ocean water.

Laboratory experiments were conducted with populations of two bivalve species that inhabit the coastal waters of Oregon; the Pacific oyster and the Mediterranean mussel. The study showed that as dissolved CO_2 increased the pH of seawater decreased. Furthermore, as the pH of seawater decreased the concentration of carbonate ions or saturation state ($\Omega_{\text{aragonite}}$) also decreased; thus, having detrimental effects on shell formation. The data revealed a critical saturation state threshold where sub-lethal chronic effects, such as inhibited shell formation, progressed to acute lethal effects, such as dissolved shells and eventual mortality of bivalve larvae. This experimental work showed that successful larval development and rapid shell formation is dependent on seawater saturation state.

These findings reveal potentially serious impacts of ocean acidification on the ecologically and economically important coastal zones of the Pacific Northwest. These regions are experiencing acidification at a faster rate than the open ocean due to the California Current and the associated upwelling zones that are richer in dissolved CO_2 . As such, sustaining coastal bivalve populations, both wild and those of oyster farms, presents an increasingly formidable challenge.

Study Conducted by: College of Earth, Ocean, and Atmospheric Sciences, **Oregon State University**, Oregon Marine Experimental Station, and Department of Fisheries and Wildlife, and Department of Fisheries and Wildlife, Oregon State University (2015)

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