The Education Program at the
New Jersey Sea Grant Consortium
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The Basics of Ocean Acidification

Overview Students perform two activities to explore how excess carbon dioxide (CO_2) in our atmosphere is changing the chemistry of the ocean and the implications this will have for marine animals. In the first activity, students test a hypothesis to determine how adding CO_2 to water affects its pH . In the second activity, students create an experiment and test their hypotheses to demonstrate how calcium carbonate, the chemical building block that marine organisms use to form shells and skeletons, dissolves in an acidifying ocean.

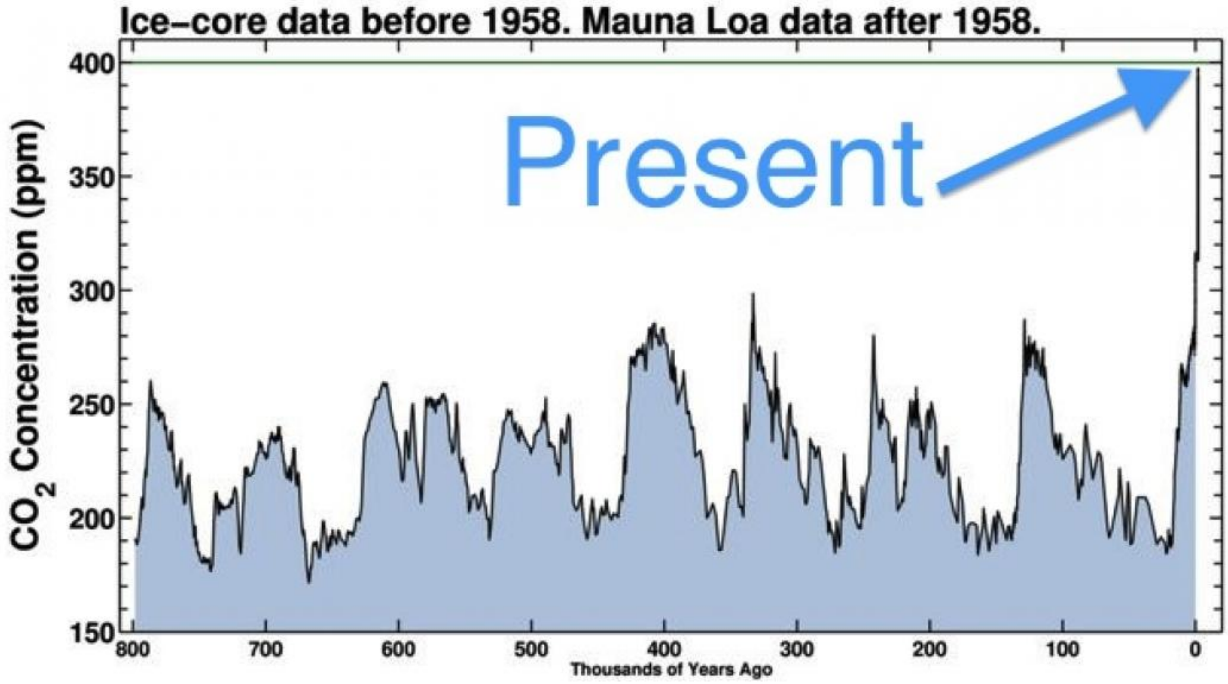
Objectives In this lesson, students will be able to:

1. Explain how CO_2 is created by combustion in our atmosphere, and then diffuses into the ocean, changing the pH and making the ocean more acidic.
2. Use the scientific method to hypothesize, test, record, and make conclusions about the effects of decreasing acidity on marine organisms that use calcium carbonate to build their skeletal structures.

Grades: 6-12

Standards: NGSS: MS-PS1-2, MS-LS2-1, MS-ESS3-5, HS-PS1-2, HS-LS2-6, HS-ESS2-2, HS-ESS3-5, HS-ESS3-6.

Background: Carbon Dioxide (CO_2) is a trace gas naturally found in the Earth's atmosphere that helps keep the climate stable. Many living things on Earth metabolize CO2, including plants during photosynthesis. However, human actions are disrupting the balance of CO_2 in our atmosphere. Excess CO_2 is released into our atmosphere, when fossil fuels, such as oil, gas or coal, are burned. Currently, CO_2 levels are at their highest ever in recorded history. Before the Industrial Revolution in the 19th century, global average CO_2 was about 280 parts per million (ppm). During the last 800,000 years, CO_2 fluctuated between about 180 ppm during ice ages and 280 ppm during interglacial warm periods. Today's rate of increase is more than 100 times faster than the increase that occurred when the last ice age ended [(1)]



Credit: Scripps Institution of Oceanography.

The ocean absorbs about a quarter of the CO_2 we release into the atmosphere every year, so as atmospheric CO_2 levels increase, so do the levels in the ocean. Initially, many scientists focused on the benefits of the ocean removing this greenhouse gas from the atmosphere. However, decades of ocean observations now show that there is also a downside: the CO_2 absorbed by the ocean is changing the chemistry of seawater through a process called *OCEAN ACIDIFICATION*. [2]

As the ocean absorbs increasing amounts of CO_2 from the atmosphere, chemical reactions take place that decrease the pH of the ocean. This lowering of pH makes ocean water more acidic. The ocean's pH has lowered by .1 pH units since the Industrial Revolution. This may not seem like much, but pH is measured on a logarithmic scale, which means a .1 difference in pH indicates the ocean has become 30% more acidic. With CO_2 continuing to sink into the ocean at extreme rates, scientists predict that the ocean could become 150% more acidic by 2100.

The Chemistry of Ocean Acidification

First, when CO_2 dissolves in seawater, most of it becomes carbonate ions and hydrogen ions ($CO_3^{2} + H^+$). This increase in hydrogen ions (H^+) decreases the pH, making the water more acidic. Secondly, the excess hydrogen ions combine with carbonate to form bicarbonate, decreasing the concentration of carbonate in the water. Carbonate ions are an important building block of structures such as sea shells and coral skeletons. Decreases in carbonate ions can make building and maintaining shells and other calcium carbonate ($CaCO_3$) structures difficult for calcifying organisms such as oysters, clams, sea urchins, shallow water corals, deep-sea corals, and calcareous plankton. Also, when too many hydrogen ions(H^+) are present in seawater without a molecule to bond with, the calcium carbonate molecules ($CaCO_3$)will break apart, the carbonates will leave behind the calcium ions to form a bond with hydrogen ions (H^+). This causes shells and structures made of calcium carbonate to dissolve. (3)

These changes in ocean chemistry can affect the behavior of non-calcifying organisms as well. The ability of some fish to detect predators is decreased in more acidic waters. When these organisms are at risk, the entire food web may also be at risk.

Ocean acidification is affecting the entire world's oceans, including coastal estuaries and waterways. Many economies are dependent on fish and shellfish, and many people worldwide rely on food from the ocean as their primary source of protein.

The Chemical Reactions of CO_2 in the Ocean

First, CO_2 reacts with water to form carbonic acid (H_2CO_{3-})

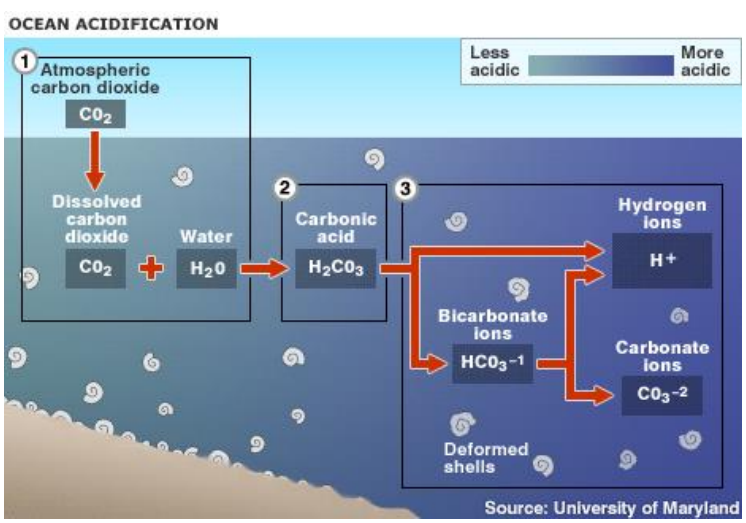
$$CO_2 + H_2O \Longleftrightarrow H_2CO_3^-$$

Carbonic Acid is a weak acid that rapidly breaks down into bicarbonate (HCO_{3-}) plus hydrogen ion which then can lower pH

$$H_2CO_{3-} \Longleftrightarrow H^+ + HCO_3-$$

Bicarbonate dissolves into carbonate ions (CO_3^{2-}) and adds more hydrogen ions further drop of pH

$$HCO_3- \Longleftrightarrow H^+ + CO_3^{2-}$$



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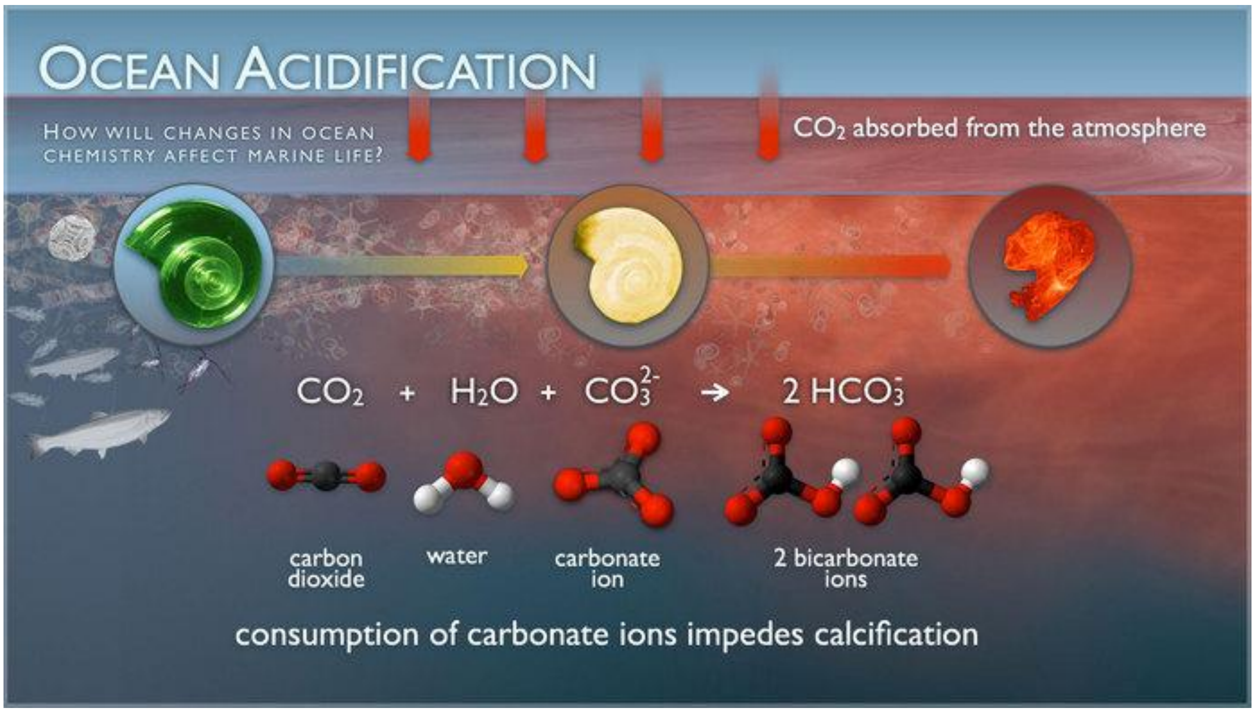
At first glance it may seem that ocean acidification is producing more carbonate ions; however, the chemical reactions can go in either direction. In fact, the chemical reactions does reverse, and with more CO_2 creating more H^+ ions and making the water more acidic, carbonate ions are very attracted to H^+ and bond with the extra H^+ ions to produce bicarbonate. This reduces the carbonate available to combine with calcium to create calcium carbonate structures used by marine organisms to make skeletal structures for life.

$CO_2 + H_2O + CO_3^{2-} \Longleftrightarrow 2\ HCO_3^{2-}$



Credit: PMEL NOAA

Excess CO_2 in our Ocean

Pure water is neither acidic nor alkaline (basic); it has a pH of 7.0. But because seawater contains many dissolved substances, it is actually slightly alkaline (basic), with a pH near 8.2. The chemical reaction with excess CO_2 creates more H^+ ions, making seawater more acidic. However, scientists do not think the seas will become truly acidic (with a pH less than 7.0), but rather less alkaline (basic) because of a decrease of carbonate ions. Marine organisms need carbonate ions to build their shells; however, while the total amount of carbon in solution increases as more CO_2 dissolves in seawater, the concentration of carbonate ions actually decreases. In tropical waters (temperatures at or above 77°F or 25°C), when the amount of CO_2 with a measurement known as the partial pressure of CO_2 (pCO_2) reaches roughly 1,800 ppm, the decreasing supply of carbonate ions crosses a threshold, where aragonite, the form of calcium carbonate commonly used to build seashells, begins to spontaneously dissolve. Aragonite is more soluble in colder waters, and cold water absorbs more CO_2 from the atmosphere than warm water. As a result, the threshold at which aragonite dissolves in cold water will occur well before the pCO_2 in the oceans reaches 1,800 ppm. Scientists expect that the cold, fertile Southern Ocean and North Pacific Ocean will reach this threshold by—or before—2070. The only way to stop this from happening is to drastically reduce the amount of CO_2 in our atmosphere. Because carbon tends to stay in the oceans for a long period of time, however, we'll have to wait for the ocean to catch up.[(4)]

A review of pH might be necessary to complete the activities. For lessons on pH see:

<http://njseagrant.org/wp-content/uploads/2014/03/ph.pdf>

<http://njseagrant.org/wp-content/uploads/2014/03/ph_booklet.pdf>

<http://www.abc.net.au/science/surfingscientist/pdf/lesson_plan16.pdf>

Citations

1. NOAA. Earth System Research Laboratory. NOAA Global Monitoring Division. May 10, 2013. < http://www.esrl.noaa.gov/gmd/news/7074.htm> Web. 4, May 2016

2. NOAA. PMEL Carbon Program. NOAA. <http://www.pmel.noaa.gov/co2/story/Ocean+Acidification> Web.4, May 2016

3. Ocean Portal, and Jennifer Bennett. "Ocean Acidification." Ocean Portal. Smithsonian Institute. Web. 4 May 2016. <http://ocean.si.edu/ocean-acidification>.

4. Madin, Kate. "A Risky Shell Game." Oceanus Magazine. WHOI, 4 Dec. 2009. Web. 4 May 2016. <http://www.whoi.edu/oceanus/feature/ocean-acidification--a-risky-shell-game>.

Activity 1: Combustion and Ocean Acidification

Adapted from <http://www.oacurriculumcollection.org/product/combustion-lab-institute-for-systems-biology/>

Introduction:

Students will perform a simple lab to observe how humans create CO_2 by combustion and how easily CO_2 is absorbed by water. This lab relates to how the burning of fossil fuels, such as natural gas, oil and coal, create an excess of CO_2 in our atmosphere, which causes ocean acidification. In this activity, the burning (or combustion) of the candle represents the burning of fossil fuels, the air in the combustion test tube represents the Earth's atmosphere, and the water represents the ocean. The pouring of water into the combustion test tube represents how wind, waves, and ocean currents physically move seawater , which allows CO_2 to dissolve into it. The Bromothymol blue (BTB) helps students to better visualize the change. Please remind students this lab is just a visualization to help them better understand ocean acidification; this lab creates super- fast reactions in relation to time and on a much, much, much smaller scale than in Earth's actual atmosphere and ocean.

Combustion is the process of burning organic material in the presence of oxygen to produce heat energy, CO_2, and water. Examples of some organic materials include wood, paper, and fossil fuels (natural gas, oil, or coal). These organic materials, and other organic materials that combust, all consist of carbon and hydrogen. They may also include oxygen and some other elements. When the organic material is burned in a complete reaction, the carbon releases in the form of CO_2. See the chemical equation below as an example of combustion:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \text{ + Energy (heat)}$$

$$Glucose + Oxygen \rightarrow Carbon\ Dioxide + Water \text{ + Energy (heat)}$$

$$CH_4 + O_2 \rightarrow CO_2 + H_2O \text{ + Energy (heat)}$$

$$Methane\ (natural\ gas) + Oxygen \rightarrow Carbon\ Dioxide + Water \text{ + Energy (heat)}$$

About 25-40% of the CO_2 from the burning of fuels is dissolved in water and will affect the pH of the water, which is creating havoc in our oceans.

Materials

- Dilute Bromothymol blue (BTB)
- Two test tubes with stoppers
- Candle
- Match or other device to light the candle

Procedure

Briefly introduce your students to the topic of combustion and how this creates CO_2. Then have students research ocean acidification and how an excess of CO_2 in our atmosphere from combustion or the burning of fossil fuels (coal, gas, oil), is being dissolved into the ocean and changing the ocean's pH.

Bromothymol blue (BTB) indicates changes in pH and the presence of CO_2. This activity uses BTB to indicate if we have captured CO_2 gas from our combustion experiment and how the CO_2 gas changed the pH of the water.

<table>
<tr><td colspan="2">
1. Label your two test tubes "air" and "combustion."

2. Pour approximately 5mL of dilute BTB into the test tube labeled "air." Cap the test tube and shake for approximately 10 seconds. Observe the BTB solution. Do you notice any color change?

3. Set the first test tube aside and record observations in your lab notebook.
</td></tr>
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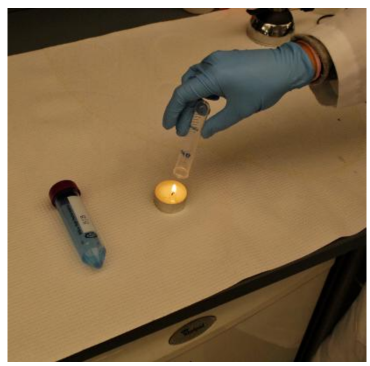
4. Now, light the candle.

5. Uncap the test tube labeled "combustion" and hold it upside down above the flame for 10 seconds. Be sure to use a glass test tube or a plastic test tube that will not melt when held close to a flame.

6. While the test tube is still upside down, cap the test tube.
</td><td></td></tr>
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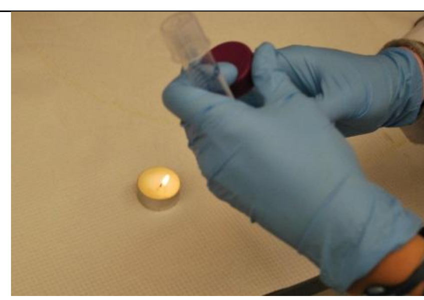
7. Once capped, the "combustion" test tube may be inverted. Uncap the BTB solution.
</td><td></td></tr>
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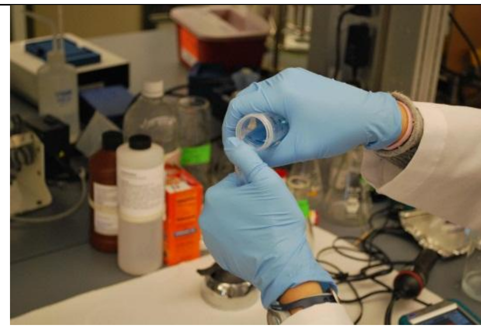
8. Carefully uncap the "*combustion"* test tube and replace the cap with your thumb. Roll your thumb to create a very small opening and quickly pour approximately 5mL of dilute BTB solution into the test tube.

9. Recap the "*combustion"* test tube and shake for approximately 10 seconds.



10. Compare the BTB in the test tube labeled "air" to the BTB in the test tube labeled "combustion." Record your observations in your lab notebook.

Please answer these questions in your lab book:

11. Which gas was captured in the "combustion" test tube?

12. Why did combustion change the water's pH?

13. What does a change from blue to yellow in the bromothymol blue and water solution indicate in relation to the pH?

14. List four (4) activities that humans do which combust fossil fuels.

15. How can you relate this experiment to CO_2 in our atmosphere and ocean acidification? What does the test tube represent? What does the air and water symbolize? What does the burning of the candle represent? How does pouring the water into the combustion test tube relate to ocean currents and waves?

16. How might humans reduce the amount of CO_2 that enters our ocean?

For more background information on how CO_2 and the ocean interact, go to:

<http://www.ehow.com/video_12257480_carbon-dioxide-enter-sea-water.html?cp=1&pid=1&wa_vrid=bd06c879-a1c0-4a16-8a12-9c3961f8aac1&wa_vlsrc=continuous>

<http://www.soest.hawaii.edu/oceanography/faculty/zeebe_files/Publications/ZeebeWolfEnclp07.pdf>

<http://www.pmel.noaa.gov/co2/story/Ocean+Carbon+Uptake>

<http://www.usc.edu/org/cosee-west/Oct06-2012/Background/Oceana_CO2.pdf>

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Activity 2: Where Did My Shell Go? or How Carbon Dioxide Affects Marine Life

Introduction:

Students will observe how water that is super-saturated with CO_2 has the ability to dissolve calcium carbonate, a building block used by mollusks, crustaceans, and coral to build shells and skeletal strucures. This activity is for illustrative purposes only, as seltzer water is much more carbonated and acidic than ocean water. While seltzer water allows students to observe how CO_2 and acidic water affect calcium carbonate, it should be noted that in this activity, seltzer affects the calcium carbonate much more quickly than seawater. With a limited amount of time in class, we have to speed up the process in our model so we can see the affects of ocean acidification in a short amount of time.

Similarly, a powdered form of calcium carbonate is used in this experiment instead of a solid form because the reaction is quicker. You might relate the powder to phytoplankton or zooplankton in the ocean.

The excess CO_2 in the seltzer water creates a highly acidic solution; *acidic* means to have more hydrogen ions (H^+) in a solution. The carbonate (CO3) from the calcium carbonate (CaCO3) is more attracted to the H^+ ions, so it reacts with the H^+ ions to form bicarbonate (2 HCO_3) and leaves the calcium behind. Without carbonate, the calcium Ca^+ cannot be used to form shell or skeletal structures in marine organisms. The calcium without carbonate is left free in solution. The bicarbonate dissolves in the water and is not used by animals that form shells, and the carbonate needed is no longer available. Some shell-making organisms use excess energy to try to remove the H^+ or break down the HCO_3 around them to create calcium carbonate, using energy they might spend on feeding. This weakens the animals so that they may not have enough energy for finding food or reproduction, which could lower future population numbers.

This is the chemical process happening when oceans become acidic, causing shells and other skeletal structures of marine life to dissolve:

$CaCO_3(s) + CO_2(aq) + H_2O(l) \leftarrow \rightarrow Ca^{2+(}aq) + 2HCO_3^{-}(aq)$.

Calcium carbonate solid + dissolved CO_2 in water form calcium ions in solution and two bicarbonate ions in solution. This process may be reversed; however, because CO_2 is persistently entering our oceans due to the burning of fossil fuels, the reaction is prevented from being reversed and keeps moving to the right, creating more bicarbonates instead of the carbonates that are needed to make shells.

Materials (for each group):

1 cup of 250 ml of tap water.

1 cup of 250 ml plain seltzer (carbonated water).

2 cups with .2 grams of calcium carbonate powder.

Optional: heat plate, cups of ice, pH meter or pH indicator solution, chalk (not non-dusting), and shells found on the beach from various marine organisms.

Procedure:

1. Briefly describe ocean acidification and that it is causing the shells of marine animals--such as corals, snails, clams, and many other creatures-- to dissolve or not even form at all.

2. Provide each group of students with four containers-- one with 250 ml of tap water, one with 250 ml of seltzer water, and two with .2 grams of calcium carbonate powder each.

3. Ask students to explain what the seltzer water represents in this experiment about ocean acidification (represents ocean water with an excess of CO_2 from the burning of fossil fuels in Earth's atmosphere) and what the calcium carbonate powder represents (the chemical that makes up the shells and other skeletal structures of marine animals). The tap water represents a control in this experiment.

4. Ask students to hypothesize what they think will happen when calcium carbonate powder is mixed into tap water and into seltzer water. Ask students to write their hypothesis.

5. Have students next add the calcium carbonate ($CaCO_3$) to the containers with the tap water and seltzer water and then stir. Students should make observations for 1-3 minutes and record what they observe.

6. Be sure that students observe and record the differences in the two solutions. (In the tap water, the calcium carbonate will super saturate the water, making the water cloudy; some excess calcium will sink to the bottom. In the seltzer water, the calcium carbonate will dissolve within a few minutes. The solution should go from cloudy to clear; left over calcium will sink to the bottom.)

7. Ask students to review their hypothesis, determine if it was correct, and discuss results.

8. Ask students to research (Internet, chemistry books, or the background given in this lesson plan) how CO_2 makes the ocean more acidic and less alkaline, and what happens to calcium carbonate when in an acidic solution. Students should explain how acidification affects marine animals that create calcium carbonate to make shells and other skeletal structures. Depending on the grade level, ask students to explain the chemical reactions that take place to make oceans acidic and how acidification dissolves calcium carbonate and even prevents calcium carbonate from forming.

9. Optional- Have students test the pH of the two different waters to observe the differences in pH levels before adding the calcium carbonate. Be sure to tell students that seltzer is a super-saturated solution of CO_2 (so much CO_2 is added to water to help create the super fizz people prefer in seltzer). This is the same CO_2 being absorbed by our oceans, making them acidic (an excess of H^+ ions) but so much that the solution is mostly carbonic acid. Students can observe the excess CO_2 gas (bubbles)that escape from the solution.

10. **Experiment Design Option 1:** Ask students to research and create an experiment to show how temperature differences either increase or decrease the dissolution of the powdered calcium carbonate. Heat plates and ice may be used, but remember to tell students not to change the volume of water when cooling and heating it. Cold water absorbs more CO_2 than hot water, so students should conclude that calcium carbonate dissolves quicker in the cool water. Students may choose to observe dissolution in temperature over time or the amount of calcium carbonate dissolved at a certain temperature. If varying the amount of calcium carbonate, start with very little (~ .05 grams) and increase by .05 grams; a little goes a long way. Ask students to relate temperature differences to the polar regions of the world compared to the equatorial regions.

11. **Experiment Design Option 2:** Students can design an experiment with solid forms of calcium carbonate to observe how the weight of the solid may change over time when placed in an acidic solution, such as seltzer water or vinegar. Students could use seashells found at the beach or store, chalk (not the non-dusting) or eggs shells. Ask students to measure and record the weight of the shell before placed in the solution, and after they remove the shell. Note that the more solid and thicker forms of shells take longer to dissolve, so the experiment may take hours or days, not minutes.

12. **Experiment Design Option 3:** Ask students to design an experiment to further explore pH values and dissolution of calcium carbonate in varying pH values. Seltzer water has a pH of about 4.5, Acetic Acid (Vinegar) 2.5, Tap Water, 7.0, a mixture of baking soda and water about 8.2, a mixture of bleach about 10. Use pH test kits or meters to measure and record pH before adding calcium carbonate. Students could use scales to measure the weight of calcium carbonate added before and after over a certain amount of time. To measure the weight of calcium carbonate at the end of the experiment, students can use coffee filters. Weigh the empty coffee filter. Pour the solution over the coffee filter to separate out the calcium, dry out the calcium left on the coffee filter, and then weigh the filter again. Make sure student realize that the changes in pH that are happening in our ocean are slower and not as dramatic.

13. **Extensions:** Ask students to research a marine organism that is affected by ocean acidification, explaining the effect on the organism, the impact on the ocean food web, as well as on humans, and some ideas for solutions. Some interesting animals to research are oysters, sea butterflies, squid, sea urchins, or cocolithophores.

    Students may also research ways to mitigate CO_2 levels in the atmosphere, ways to prevent ocean acidification, and steps that members of the class could take to slow or avert ocean acidification.

References and Acknowledgements

Smithsonian Institute Ocean Portal - < https://ocean.si.edu/ocean-acidification>

NOAA- <http://oceanacidification.noaa.gov/>

NOAA Carbon Program < http://www.pmel.noaa.gov/co2/>

Woods Hole Oceanographic Institute -http://www.whoi.edu/main/topic/ocean-acidification

Suggested For Additional Background Information and Lesson Plans:
A collaboration of Washington Sea Grant, EPA, US Fish and Wildlife and more, with the top OA lesson plans <http://www.oacurriculumcollection.org/>

Virtual Urchin- perform an amazing experiment with all the top scientific equipment and tools virtually <http://virtualurchin.stanford.edu/AcidOcean/AcidOcean.htm>

Youtube Videos with great visualizations:

Ocean Acidification by the Alliance of Climate Education <https://www.youtube.com/watch?v=Wo-bHt1bOsw>

Ocean Acidification- NC Aquarium Fort Fisher.
<https://www.youtube.com/watch?v=kxPwbhFeZSw>

NOAA Ocean Acidification - The Other Carbon Dioxide Problem
<https://www.youtube.com/watch?v=MgdlAt4CR-4>

Demystifying ocean acidification and biodiversity impacts- California Academy of Sciences
<https://www.youtube.com/watch?v=GL7qJYKzcsk>

Making Waves Podcast- Ocean Acidification- NOAA
<https://www.youtube.com/watch?v=NN_LUvfz-M4>

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