

Ocean Acidification

From A Geological and Chemical Perspective

Timeframe

1 Fifty minute class period

Target Audience

High school chemistry or earth science students (grades 9-12)

Materials

- PowerPoint presentation

For each group:

- 1 Student Data Sheet (at back of lesson)
- 4 Erlenmeyer Flasks or other clear containers (500mL capacity)
- 4 types of water (see "Activity" section for further instruction on making waters):

1. Fresh water (tap is ok, store-bought distilled (DI) water is best)
2. Cretaceous seawater (fresh water with 5g baking soda added per 10L or seawater with 2.5g baking soda added per 10L)
3. Modern seawater (fresh water with ~2.5g baking soda added per 10L, seawater, or artificial seawater)
4. Estuary water (approximated by filling the flask with half fresh water and half modern seawater)

- Bromothymol blue pH indicator dye
- Straws or tubes for blowing into water
- Bromothymol blue pH color reference scale (on student data sheet)
- Stopwatch

Description

This lesson plan emphasizes balance between natural geologic processes and human activities affecting ocean seawater acidity, as measured by pH, and discusses how human activities are altering these processes to cause a **rapid** decline in ocean pH (termed **ocean acidification**).

Objectives

- Students will develop a basic understanding of the logarithmic pH scale and how an increase in CO₂ in the ocean will lead to a decrease in pH (increase in acidity).
- Students will be able to identify how differences in ocean alkalinity affect the rate at which ocean acidification occurs.
- Students will gain experience developing a testable hypothesis and testing that hypothesis with an experiment.

Teacher Background

Carbon is an element that is the chemical backbone of all known life.

What does that mean? *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 of the fossil fuels we use today were beginning to be formed. When we burn fossil fuels much of this long-stored

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Teacher Background (Continued)

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.

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 (CO₂) reacts with seawater (H₂O) to form carbonic acid (H₂CO₃). The carbon from the carbon dioxide has been **colored orange** to illustrate the storage effect.



Carbonic acid is a weak acid and separates (or more exactly, dissociates) to form one bicarbonate ion (HCO₃⁻), 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

Key Vocabulary

pH

CO₂

Ocean acidification

Alkalinity

Corrosivity

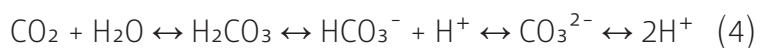
Buffering capacity

Teacher Background (Continued)

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 CO₂ increases the seawater will become more acidic (more CO₂ being absorbed by the oceans ultimately leads to more hydrogen ions – see pH equation to the right). 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 CO₂ gas initially absorbed into seawater is now in bicarbonate form. After this happens, more room will have been created for even more CO₂ gas from the atmosphere to be absorbed by the oceans. We are steadily increasing the concentration of CO₂ in the atmosphereⁱ by burning fossil fuels primarily, but also because of loss of vegetation (land use changes). The increase in atmospheric CO₂ 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 (CO₃²⁻), 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 CO₂ 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

How Do We Measure Acidity?

The pH scale is used to measure the acidity of a solution, like seawater, and is based on the negative **logarithmic** concentration of hydrogen ions. It is important to note that the pH is effectively an indicator of the acid-base balance of any solution. In seawater pH reflects the relative abundance of carbonic acid and associated (inorganic) carbon molecules.

$$\text{pH} = -\log_{10}[\text{H}^+] \quad (3)$$

As the concentration of hydrogen ions goes up, pH goes down, and acidity increases. A 10-fold **increase** in the concentration of hydrogen ions means a **decrease** of 1 unit in the pH scale. The mean global pH of seawater is 8.1. However, in the last 150 years, the pH of the ocean has decreased by 0.1 units. That does not sound like much of a change, but because pH is measured on a **logarithmic scale**, this equals an approximate 30% increase in acidity!

Teacher Background (Continued)

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.

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-enrichment (more and more CO₂ being absorbed by the oceans), 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**. A term called “**corrosivity**” is determined by how many carbonate ions are in seawater. Similar to a glass of water that salt is added to, initially the water is corrosive to the salt and dissolves it. After adding more and more salt, at some point the glass of salty water will not dissolve any more salt. At this time the solution is **saturated**

Can We Just Add Bicarbonate?

In the ocean, pH is effectively a result of the ratio of two main components of the dissolved inorganic carbon system: the combined CO₂ and H₂CO₃ in proportion to CO₃²⁻. It is important to note that while alkalinity or buffering capacity helps prevent changes in pH, simply adding bicarbonate to normal seawater will actually initially lower pH, because a solution of bicarbonate only has equal parts of CO₂ and CO₃²⁻ and will have a pH of about 7.7. Typically that solution will have excess CO₂, and if that outgasses (more CO₂ in the solution than in the atmosphere), the pH will rise to a value closer to modern ocean pH (depending on how much bicarbonate is initially added).

Teacher Background (Continued)

with respect to salt. Fortunately for marine organisms that build shells, the oceans are saturated in most places with respect to calcium carbonate, 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 may make waters corrosive to existing calcium carbonate structures with enough CO₂.

We know that ocean pH was lower in the Earth's past (paleo-oceanographers can determine the acidity of the ocean back as far as 400 million years ago), although it hasn't been as acidic in the last 1 million years. More importantly, **ocean acidity has never changed as fast as it is changing today**, even though during some periods in Earth's history, such as the Cretaceous, the levels of CO₂ were up to four times greater than today. Still, during that time a lot of shell building organisms evolved and thrived! **What do you think was happening?** *The alkalinity of the ocean was twice what it is today!*

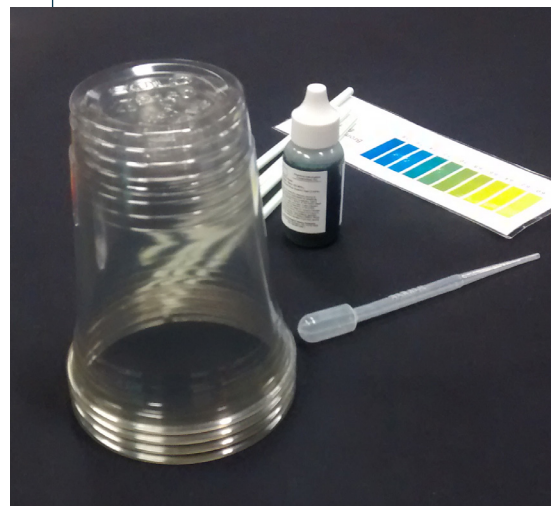
Preparation

Because tap water can be rich in minerals (and thus have a high alkalinity) it is better to start with distilled water. Purchase two 2.5gal jugs of distilled water from the store. The first jug will serve as the source of fresh water. The second jug will be made into the Cretaceous water. To this jug, add 5g (1 teaspoon) of baking soda (the recipe for this water is 5g baking soda per 10L fresh water, and 10L = 2.5gal). Label each jug! This can all be done before the activity is to start.

Activity Introduction

One of **the most critical jobs the oceans have is to store carbon**. Today we will do an experiment to understand how an increase in carbon dioxide leads seawater to become more acidic, a process called **ocean acidification**. We will also learn that ocean acidification is partially managed by the **alkalinity** of the ocean.

- When carbon dioxide (from sources such as the burning of fossil fuels) is added to the ocean, it becomes more acidic. This hurts the ocean's ecosystem and ocean-related industries.
- Differences in **Alkalinity**, or the carbonate chemistry of the ocean, controls the ocean's ability to buffer the increase in CO₂ and slow down acidification.



Each group will need: 4 cups or flasks, bromothymol blue (with dropper), bromothymol blue pH color reference, and 4 straws.

Guiding Questions:

Activity Introduction

- Gauge students' understanding of pH. Review pH as a logarithmic scale:

$$\text{pH} = -\log_{10}[\text{H}^+]$$

- If we have a pH of 7, is our material basic, acidic, or neutral?
- If the acidity of a substance increases to 10 times as much, what happens on the pH scale? *It decreases by 1 unit.*
- In the last 150 years, the pH of the ocean has decreased from 8.2 to 8.1. What percentage of increase in acidity does this equal? *30%!*

- Unfortunately, changes in alkalinity occur across **geologic timescales** (caused by the erosion of rocks on land and deposition of erosive materials in the ocean), and cannot keep up with changes in CO₂ levels which are increasing on a **seemingly daily basis**! For example, in the Cretaceous, CO₂ levels were up to **4 times** greater than today, but the alkalinity of the ocean was **twice** what it is today, so shells and other marine life flourished.
- The air we breathe out is 100 times more concentrated in CO₂ than our modern atmosphere. An exhaled human breath is about 3.7% CO₂ⁱⁱ while the modern atmosphere is ~0.04% CO₂ⁱⁱⁱ. We can use the fact that our breath is high in CO₂ to investigate what happens when CO₂ is added to waters with different **alkalinities** or **buffering capacities**. Using baking soda (sodium bicarbonate) we can create different types of water masses.

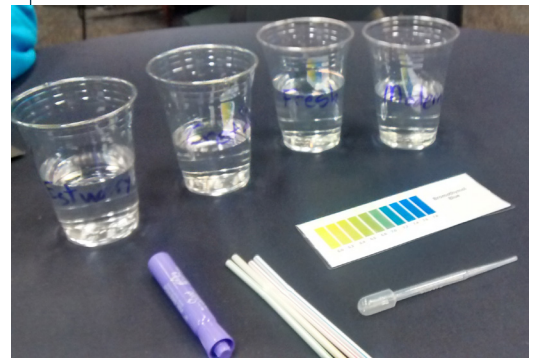
Activity:

Instructions written for 4 students groups. These can be expanded for more groups by starting with more water in the Preparation.

- Ask students to label their flasks (or clear cups) and fill them with the water to create one of each of four types of water. This will be an exercise in how to create dilutions:
 - Fresh water**
 - Cretaceous seawater**
 - Modern seawater** – The students will have to dilute the Cretaceous water to make this type. This could be done by adding ½ Cretaceous water and ½ fresh water to their container. If students are measuring out amounts of water (this is ideal), have them add 250mL Cretaceous water and 250mL fresh water to their container (500mL total).
 - Estuary water** – The students will have to dilute the Cretaceous water to make this type. This could be done by adding ¼ Cretaceous water and ¾ fresh water to their container. If students are measuring out amounts of water (this is ideal), have them add 125mL Cretaceous water and 375mL fresh water to their container (500mL total).
- Have students add a straw or length of tubing to each flask for blowing. Ask students about the characteristics of the different types of water using the **Guiding Questions** to the right.



Testing the CO₂ levels of human breath



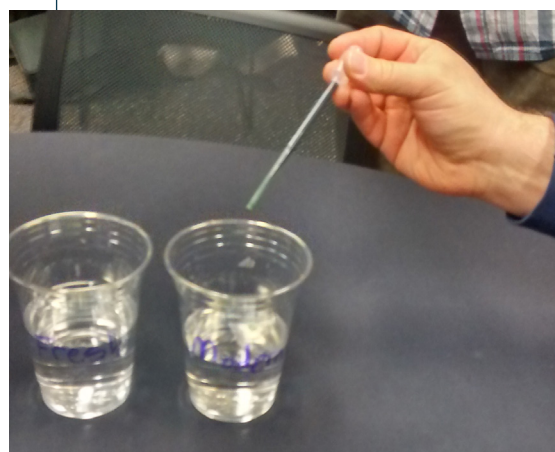
Activity Set-up: 4 cups labeled with different water types, bromothymol blue color reference, straws, dropper

Guiding Questions: Pre-Experiment!

- Ask students about the characteristics of the four kinds of water. What do they think are the differences between the four types of water with regard to pH, CO₂ content, and alkalinity? Which has the highest alkalinity? The lowest?
- What is the difference between Cretaceous Seawater and Modern seawater? Why?
- What is an estuary? Why did we mix the Cretaceous seawater with fresh water to make Estuary water?
- What properties of the water affect its alkalinity?

Activity Continued

3. Have students write hypotheses about what will happen to the different kinds of water when CO₂ is introduced via blowing.
4. Ask students to add bromothymol blue to each water sample (start with **2** drops but keep adding until they see a noticeable color change) to measure the initial pH. Record onto data sheet at Time 0.
5. **Conduct the experiment!** Begin blowing and every 30 seconds, use the bromothymol blue indicator chart on the data sheet to record the change in pH in relation to the addition of CO₂ for each water sample.



Using a dropper to add bromothymol blue to each water type

Activity Wrap Up:

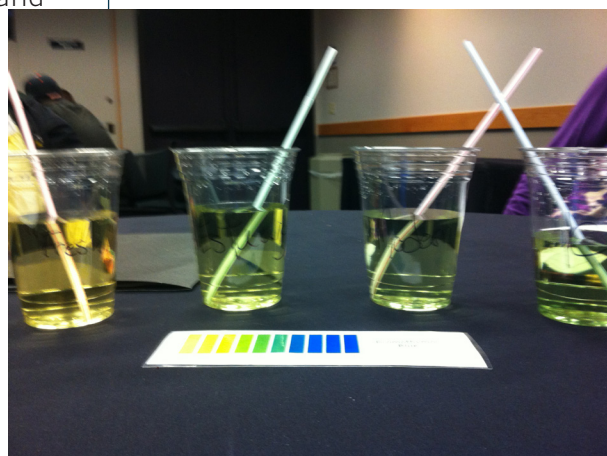
1. What did you notice about the level of pH changes between the four types of water? Are the colors the same in all types of water? Why or why not?
2. How long did it take to change each type of water? Which type took the longest to change? Which type changed most quickly?
3. Do your observations match what you hypothesized?
4. Let's review how the alkalinity differed between each type of water. How do you think the alkalinity of water plays a role in the ability for increased CO₂ to cause ocean acidification?



The water samples with bromothymol blue - which water type is the most acidic?

It should take the most time to change the Cretaceous seawater and the least time to change the fresh water. The end point will look different in each treatment too – the fresh water will turn all the way yellow almost immediately, while students will have to huff and puff for a long time to get the Cretaceous seawater to turn a muddy green.

Water with higher alkalinity is more resistant to changes in pH when an acid (in this case H₂CO₃, or carbonic acid) is added. This example demonstrates one of the more commonly used definitions of alkalinity – which can be simplified to: “its quantitative ability to titrate an acid”^{iv}.



After addition of CO₂, note color change!

Next Generation Science Standards

DISCIPLINARY CORE IDEAS:

ESS2.D: Weather and Climate

PERFORMANCE EXPECTATIONS:

HS-ESS2-4: Use a model to describe how variations in the flow of energy into and out of Earth's systems result in changes in climate.

HS-ESS2-5: Plan and conduct an investigation of the properties of water and its effects on Earth materials and surface processes.

PRACTICES:

- Developing and Using Models
- Planning and Carrying Out Investigations
- Analyzing and Interpreting Data

CROSSCUTTING CONCEPTS:

- Cause and Effect
- Stability and change
- Scale, Proportion, & Quantity

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SMILE Teachers blowing into their water samples at the Winter Teachers' Workshop 2016!

POTENTIAL EXTENSIONAL ACTIVITY:

Think about how ocean acidification affects Oregon's coastal industries: <https://www.youtube.com/watch?v=7h08ok3hFSs>

Resources:

ⁱ<http://www.ipcc.ch/>

ⁱⁱhttp://cdiac.esd.ornl.gov/pns/faq_othr.html

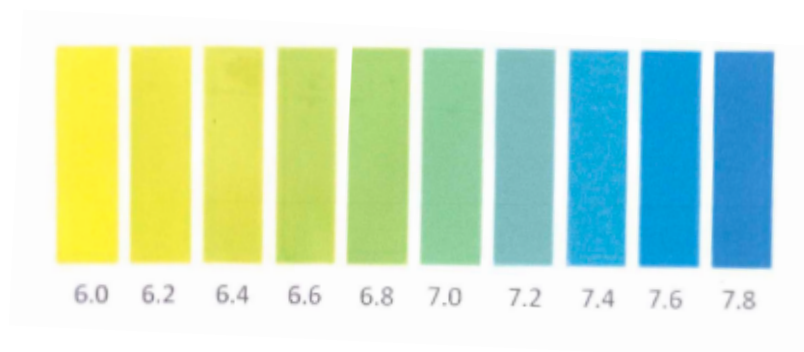
ⁱⁱⁱ Dr. Pieter Tans, NOAA/ESRL <http://www.esrl.noaa.gov/gmd/ccgg/trends>

^{iv}<http://en.wikipedia.org/wiki/Alkalinity>

For a more comprehensive treatment of alkalinity, see Zeebe and Wolf-Gladrow, "CO₂ in seawater: equilibrium, kinetics and isotopes" Elsevier Oceanography Series 65.

Student Data Sheet

Hypotheses:



Add the Bromothymol blue indicator and record your pH level! Then blow into your water samples!

Time (sec.)	pH Fresh water	pH Estuary water	pH Modern seawater	pH Cretaceous seawater	Observations