## **Carbonated Oceans – Video Tutorial**

What gases are present in the oceans, and where do these gases come from?

The top three gases dissolved in the ocean are nitrogen, oxygen, and carbon dioxide. These gases come from a number of sources including the atmosphere, volcanic outgassing – primarily from underwater volcanoes, and three biologic processes: respiration, decomposition, and photosynthesis. Let's briefly review these biologic processes.

In photosynthesis, water combines with carbon dioxide and with energy from light and is turned into sugar, releasing oxygen gas as a byproduct. This process is performed by autotrophic organisms throughout the ocean (bacteria, algae, and seaweeds) as a means of storing light energy in the form of sugar. The result: major source of waste oxygen and sink for carbon dioxide.

The reverse of this process happens during respiration. Sugar stored in the body of an organism is burned in the presence of oxygen and converted into heat energy, which is used for growth, reproduction, and other metabolic processes, processes that ALL organisms undergo. Water and carbon dioxide are waste products. Result? Respiration uses up oxygen and releases carbon dioxide.

How does decomposition fit in? It is a process that is similar to respiration and has the same results, but it happens when the sugars in dead carcasses, feces, exoskeleton molts, and other organic debris are broken down in the presence of oxygen, mostly by bacteria. Same results – removes oxygen and produces carbon dioxide.

Now let's ask which of our three major gases in found in the highest abundance in the ocean. Solubility is the term we use to describe a gas's ease in being dissolved in a liquid. Every gas has a different solubility, and that solubility can change as the liquid's characteristics change, like temperature and salinity.

Of the three gases listed here, which do you think is found in the greatest amount in the total volume of the ocean? In this case, the primary reason for the high abundance is because of its incredibly high gas solubility. This particular gas is one that really likes to be dissolved in liquids. The gas with the highest solubility and abundance in the ocean is carbon dioxide. Not very surprising when you remember that it's also the gas of choice for dissolution in sodas – hence the name carbonation. It's a striking difference from the atmosphere, where Nitrogen is our major component, and Oxygen comprises most of the rest. Carbon dioxide is a very minor component in the atmosphere – only 0.04 % -- or 0.4 parts per thousand – or 400 parts per million. However, because of the greenhouse effect, even small amounts of carbon dioxide play a major role in regulating the temperature of our planet. And, it is the most important gas dissolved in the oceans.

Is carbonation in the oceans equal everywhere? Since gas solubility changes in all types of water, the abundance of gases will as well. What are some things that can increase gas solubility and hence increase ocean carbonation? Let's use soda as an example. Sodas are bottled at bottling plants, where high pressures are used to increase the carbonation. When the sodas are opened, that pressure is released, the solubility decreases, and the carbon dioxide exsolves or bubbles out. When sodas are warmed (especially after they've been left out and open for awhile), the solubility decreases, and there is less carbonation. We call these sodas flat. And what's the difference between carbonation in seltzer water, with no dissolved salt or sugar, and colas, with plenty of dissolved sugar? Carbon dioxide is more soluble in the pure water, and hence seltzer water has more carbonation than sugar sodas or salty water. Let's watch some demonstrations of gas solubility.

Here you see the result of reducing pressure on a carbonated beverage and the resulting decrease in gas solubility and thus release of carbon dioxide gas.

Here you see what happens to carbonation in a soda when you add salt. The water will dissolve the salt and the increased ions will reduce the solubility of carbon dioxide, and hence the carbon dioxide will bubble out.

And here you see what happens when you increase the temperature, make it warmer. Again that will decrease gas solubility, and we should see the carbon dioxide gas bubble up.

## Pause now.

What does changing solubilty mean for the ocean's carbonation? Where is carbonation highest and lowest in the oceans and why? This graph shows carbon dioxide content increasing to the right on the X axis and depth in the oceans increasing

as we move down the Y axis. The surface of the oceans is at the top. What do we see? Carbon dioxide is lowest at the surface but increases quickly as we descend into the oceans. Why? A number of reason we've already discussed. Photosynthesis is the dominant biological process at the surface, and it removes carbon dioxide and produces oxygen. However here, respiration dominates -- just under the ocean's surface layer, where a large group of organisms collectively known as the deep scattering layer congregate during the day to avoid their predators. That respiration produces carbon dioxide. Decomposition dominates in the deep ocean, because that's where decaying organic material falls and collects. Decomposition is also a source of carbon dioxide. Also, if you look at this simplified bathtub cross-section of the world's oceans – equator in the middle – poles on the ends, you can see that the deep water of the world's oceans is coming from the poles, where its cold temperature gives it a high density. It sinks there, and spreads out under the warmer surface waters of the equator and tropics. Note: pycnocline. a term you can see in this image, is the boundary between two different density water masses – less dense on top – denser below. So when we descend across this pycnocline into the deep oceans at the equator, tropics, or mid latitudes, we're moving from surface waters, warmed by the sun, to deeper waters fed by the poles. The temperature should get colder. And of course the pressure will also increase. As we know, colder temperatures and higher pressures increase gas solubility, yet another reason for greater carbonation at depth.

How does carbonation affect the rest of the oceans? Actually carbonation plays a primary role in regulating and determing the pH of the oceans. To understand why, we have to review some basic chemistry. H-2-O, or water, is an incredibly stable molecule. It can dissociate into a positive hydrogen ion and a negative hydroxide ion, but it does so only in very small amounts. Even in small amounts, it plays an important role. As long as the amount of H+ and OH- are equal to each other, a solution is considered neutral. But when H+ increases (or OH- decreases), and there's more H+ in the system than OH-, we call the system acidic. The larger the difference, the more acidic. And the reverse, more OH- than H+, will cause the system to become increasing basic.

pH is a measurement of the activity or concentration of the H+ ion. This equation explains the relationship. Remember that the concentration of H+ in liquid is usually very very small, so we show it as a fraction – one over 10 to an exponent. That exponent is our pH number. As the pH or exponent gets larger, the denominator of the fraction gets larger, which means the entire fraction is now a smaller and smaller number, and the concentration of the H+ ion is low. High pH number = low H+ concentration = basic solution. When the exponent decreases, the denominator gets smaller, which makes the fraction bigger. Low pH = high H+ = more acidic.

Here is a list of common substances and their associated pH and H+ and OH- concentrations. Notice that pure water and blood have a pH of 7, with equal H+ and OH-, and thus are considered neutral. But again notice what that concentration really is – H+ has a concentration of 1 over 10 to the 7th or 1 over 10 million!

Pause now.

To demonstrate how carbonation affects pH of the oceans, we need to study the following chemical reaction. We'll start by reading it from the left.

Carbon Dioxide + water combine to create carbonic acid, which then dissociates by losing one H+ ion and becoming bicarbonate, a negative ion. Bicarbonate further dissociates by losing one more H+ ion (now we have two) and becomes a carbonate ion.

These molecular images show you what the molecules and ions in this equation actually look like. Oxygen is shown as a red ball. Carbon, black; hydrogen, white. Note: These are symbolic images that correctly capture the components of the molecule and its shape. They do not all, however, show the correct relative sizes of these atoms. Hydrogen should be the smallest.

The double-sided arrows in this equation means this equation can and does move in both directions in an attempt to reach an equilibrium or balance point. When the system is NOT in equilibrium or balanced, one side gets weighed down like in this image. The result? The equation will move in the direction necessary to undo that imbalance. And therein lies the important of this equation to the oceans. Notice that carbon dioxide is on the left and the hydrogenplus ion that leads to increased acidity on the right. Whenever one of these is increased or decreased, the equation will move in the direction necessary to undo that change. Let's see how that works.

Let's start with a balanced equation -- equilibrium for all components. Now let's try to change the pH by adding H-plus ion to the oceans. That weighs down the right side of the equation and makes it no longer balanced. The system senses it's out of equilibrium, and the chemicals in this equation react with each other to undo the inbalance. How? The H-plus ions

combine with surrounding carbonate to create bicarbonate, which then combines with more H-plus to create carbonic acid, which then breaks down into carbon dioxide and water. Equilibrium restored. H-plus concentration restored. pH restored.

What happens if we try to do the opposite? Remove H-plus? That also puts the system out of equilibrium and the other components of this chemical reaction become very active trying to undo the change. Carbon dioxide + water combine to form carbonic acid, which then dissociates into H-plus and bicarbonate, which further dissociates into carbonate and more H-plus. Net result: the H-plus that was removed is restored. pH is restored.

We call this particular reaction a BUFFERING reaction, because its equilibrium regulates the ocean concentrations of H-plus and hence ocean pH. It is VERY difficult, therefore, to change the pH of the oceans.

Let's look at some ball-and-stick models to see better how this chemical reaction happens. Here you see a carbon dioxide molecule, and we will bring in a water molecule. C-O-2 for the carbon dioxide. H-2-O for the water molecule. These two molecules can combine to create carbonic acid, which I will demonstrate. (MUSIC)

Here you see carbonic acid releasing a hydrogen ion. It can release one or 2 in order to buffer the pH of the surroundings and ensure that it maintains the same pH.

Here you see a carbonate ion picking up a hydrogen ion to become bicarbonate and a bicarbonate picking up another hydrogen ion to become carbonic acid thus removing excess hydrogen from the surroundings.

This same buffering process is at work in your stomach, maintaining a pH or acidity of your stomach. When your stomach feels too acidic (not balanced!), then you can take an antacid, like TUMS or BUFFERIN, which is just a bunch of carbonate. These carbonate ions will pick up the excess hydrogen ions that make your stomach acidic and push the buffering equation to the left, removing the hydrogen ions and producing water and carbon dioxide, which you can detect when you successfully burp it up!

## Pause now.

So this chemical equation buffers and thus maintains a steady pH in the oceans. Is there any way to change ocean pH? Look closely at the equation. With an understanding of equilibrium, what is one thing I could do to make the oceans more acidic? I could add more carbon dioxide! Let's see how that works.

What happens if we add more carbon dioxide to this equation? It sets the equation out of balance, or out of equilibrium, by weighing down the left side. Again, the surrounding chemicals become active in reactions that will undo that change. How? The CO2 will end up combining with water to produce carbonic acid, which will then dissociate into H-plus and bicarbonate ion, which will further dissociate into more H-plus and the carbonate ion.

Balance is restored, but notice that the result is to increase the H+ ion, and thus decrease the pH of the oceans. Even a small change in the concentration of H+ has a big effect on the pH of the oceans.

Increased carbon dioxide, which we know happens naturally with increasing depth in the oceans, also means increased acidity (lower pH), which causes calcium carbonate shells to dissolve. This picture shows shells from four different microscopic marine organisms typically found in the surface waters of the ocean. On the left we have coccolithophores and foraminifera, both with carbonate shells. On the right we have diatoms and radiolarian, both with shells made of silica. Let's take a look at how the carbonate shells react to acid.

Here you see hydrochloric acid that is being dropped on a calcium carbonate shell. And the reaction that results produces carbon dioxide gas, which bubbles off.

Because of increasing carbon dioxide solubility and abundance with depth in the oceans, there is a particular depth below which calcium carbonate shells will completely dissolve. This depth is called the carbonate compensation depth or CCD. What does this mean? Organisms below this depth cannot survive with calcium carbonate shells and the shells of dead organisms that rain down to the bottom of the seafloor will dissolve, if made of calcium carbonate, once they reach this depth and will not collect on the seafloor. That creates an interesting distribution of muds or oozes on the seafloor. Muds exposed to seawater at depths below the CCD will be composed almost exclusively of clays and silica shells. So even though carbonate-shelled creatures can be quite abundant in the surface waters of the ocean, their shells might be absent in the seafloor sediments below. As carbon dioxide concentrations increase in the atmosphere, they are also increasing at even greater rates in the oceans. These changes are having a big effect on the pH of the oceans. Scientists are right now studying the effects of this change, as this image shows. The shells in this image were exposed to a pH level expected to exist in the southern oceans by the year 2100. The shells dissolve after only 45 days. As the southern ocean during the summer season is one of the most productive regions of the world's oceans, any changes to the microscopic plankton that live in these oceans will have a great impact on the rest of the ocean ecosystem.

[sounds of birds on a beach with waves] What can we do? Limit carbon dioxide emissions and be prepared for the consequences if we don't!

Pause now.

[End credits]

## **Carbonated Oceans**

Geoscience Video Tutorial Produced by Katryn Wiese City College of San Francisco

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рН	[H+]	[OH-]	Example
0	10 <sup>0</sup>	10 <sup>-14</sup>	Hydrochloric acid, battery acid
1	10 <sup>1</sup>	10-13	
2	10 <sup>2</sup>	10-12	Lemon juice, vinegar
3	10 <sup>3</sup>	10-11	Soda, tomato juice
4	104	10-10	
5	10 <sup>5</sup>	10-9	Black coffee
6	10 <sup>6</sup>	10 <sup>-8</sup>	Milk, saliva, urine
7	107	10-7	Pure water, blood
8	10 <sup>8</sup>	10-6	Seawater
9	10 <sup>9</sup>	10-5	Phosphate detergents, baking soda
10	10 <sup>10</sup>	10-4	
11	1011	10-3	Milk of magnesia, ammonia
12	1012	10-2	
13	10 <sup>13</sup>	10-1	Oven cleaner, bleach
14	1014	10-0	Liquid drain cleaner