CHAPTER 5: LIMESTONE

Since limestone gets its own chapter, it must be pretty important. In fact, it is one of the handiest rocks on the planet. It can be used in almost every industry, from construction and manufacturing to agriculture and food science. To understand its many uses, we need to study its chemistry, so we'll be doing a lot of chemistry in this chapter. But first, let's look at the many different kinds of limestone and where they are located.

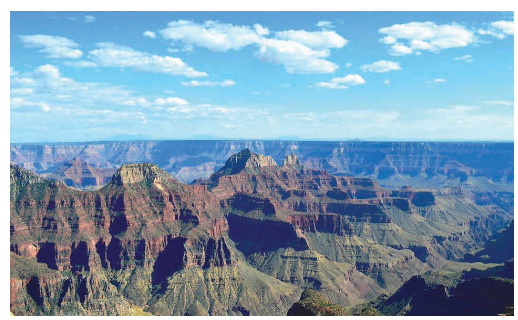
Calcite and aragonite are both made of $CaCO_3$.

The word "limestone" is a very general word meaning any rock that contains over 50% calcium carbonate, $CaCO_3$. We've already met $CaCO_3$ as the mineral **calcite**. Actually, we've also met $CaCO_3$ as the mineral **aragonite**. How can these minerals look so different and yet be made of the same stuff? (And neither of these look anything like limestone.) Think about graphite and diamond. Both are made of nothing but carbon atoms, yet one is black and soft and the other is clear and hard. The arrangement of the atoms is what makes the difference. The atoms in graphite are arranged into flat sheets of hexagons. The atoms in diamond are locked into a strong framework. In calcite and aragonite, the $CaCO_3$ crystals have been squeezed into different crystal shapes. We looked at some basic crystal shapes back on page 10. Calcite and aragonite have different crystals shapes while still being made of the same stuff. They formed under different circumstances in different environments. Calcite can take other shapes, too, especially if there are some stray metal atoms in the area. Blue, orange and brown calcite don't look like clear calcite or aragonite.

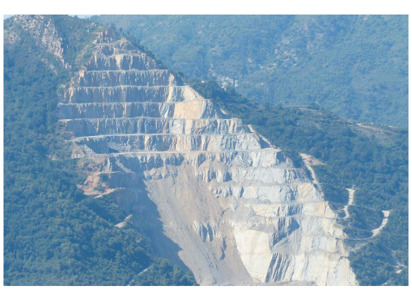
Calcite and aragonite are very pure examples of calcium carbonate. There might be small amounts of other atoms mixed in, but the amount is so small that we can basically ignore it. In limestone, however, large amounts of other stuff can be present. A rock can be called limestone as long as it is more than half calcium carbonate. This means that there are many types of limestone and they can look quite different. Here are some notable examples of limestone formations around the world.

"James Bond Island" in Thailand is made of limestone. (It became famous after being featured in a James Bond movie.)

Limestone landscapes like this are at various places around the world, including central China.



The Grand Canyon has layers of limestone. One of the layers is called the Redwall Limestone.

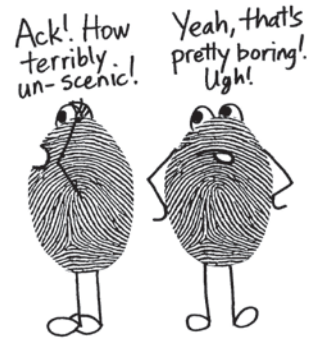


This is a limestone quarry, where blocks of limestone are being cut for use as building stones.

The famous white cliffs of Dover, on the coast of England, are made of chalk, a type of limestone.

Caves are made of limestone. This is Bears Cave in Transylvania, Romania.

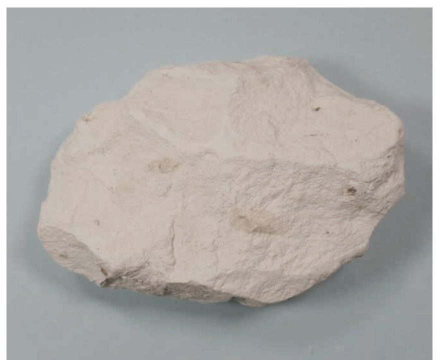
Here is another limestone landscape. (This is just down the road from where the author lives.) It's a much more typical limestone formation—not spectacular at all. Most of the eastern USA has limestone like this. It might look boring on the surface, but limestone landscapes are often full of interesting caves and caverns underneath. Limestone areas with caves are called **karst** landscapes.



Limestone can be white, gray, brown, tan, pink or even kind of bluish or yellowish. Some limestones are soft, like chalk. Other limestones are very hard and make excellent building stones. Some limestones have fossils, others do not. O**ö**litic limestone has tiny dots or spheres, similar to what we saw in o**ö**litic chert.

Here are some samples that show the wide variety in limestones.

This is that boring gray limestone in the picture above. Not much to look at, but very useful to many industries.



This is **chalk**, the stuff that those white cliffs of Dover are made of. Some chalks are harder than others.

This limestone is called **coquina**, using the Latin word for seashell. This is basically a cemented lump of tiny seashells.

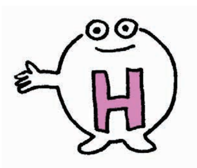
This is **oölitic limestone**. Up close, it looks like it has tiny spherical egg shapes embedded in it.

This is **fossiliferous** (fossil-containing) limestone. Not all specimens are as loaded with fossils as this one.

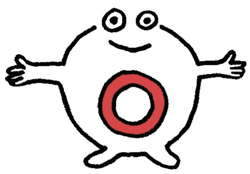
Travertine is considered to be a type of limestone. In chapter 4, we learned that it forms around hot springs.

If a limestone is gray or brown, that means that it has a lot of impurities in it, such as clay, iron, magnesium, and sulfur. If a limestone has a significant amount of magnesium, the name of the stone changes from limestone to **dolomite**. In dolomite, the magnesium atoms actually go in and replace some of the calcium atoms. Some of the molecules switch from being $CaCO_3$ to $MgCO_3$. This substitution is possible because calcium and magnesium atoms both have the same electron arrangement in their outer shells.

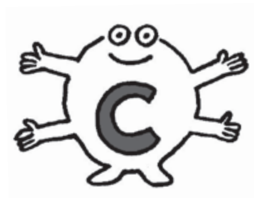
To study limestone further, we need to learn a little more chemistry. But that doesn't mean we have to be boring. Let's make it fun! We'll represent the atoms as little cartoon characters with a certain number of hands. The hands will represent the number of bonds that the atoms would like to make. For example, we learned that both carbon and silicon have 4 electrons in their outer shell but would like to have 8. That means that they would like to make 4 bonds, to fill those empty places. Oxygen has 6 electrons in its outer shell and would like to have 8, so it would like to make 2 bonds. Calcium and magnesium both have 2 electrons in their outer shell and would like to have 8, but they know it is probably unrealistic to hope for 6 other atoms to bond with. It is better for them to just share the 2 electrons they have. That means that Ca and Mg are looking to make 2 bonds, just like oxygen is. Hydrogen is a tiny atom and can only ever make 1 bond. So here is our cast of characters:



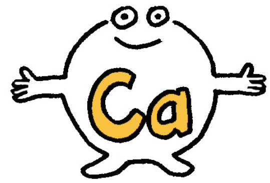
HYDROGEN



OXYGEN



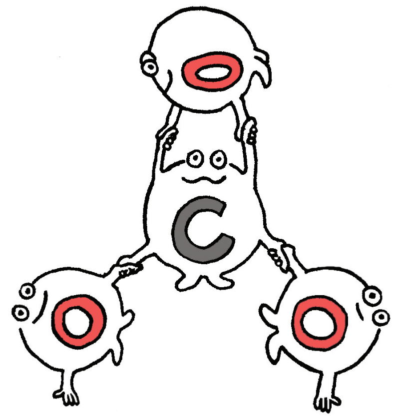
CARBON

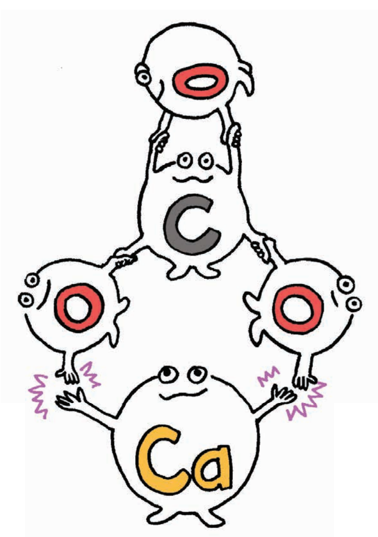


CALCIUM

MAGNESIUM

These guys can hold hands in various ways to make different molecules. First, let's meet **carbonate, CO_3**. This group of atoms is extremely common in chemistry. (Most high school chemistry classes require you to memorize it.) It is made of 1 carbon atom attached to 3 oxygens. Carbon is very flexible about bonding, and it reaches out two hands to one of the oxygens, making that oxygen very happy. This is called double bonding. The double-bonded oxygen has both hands occupied, so it is content. The other oxygens are attached with only one hand so they still have one hand free and can bond with something else. If a hydrogen atom and a sodium atom happen to come by, they will each pair up with an oxygen, making $NaHCO_3$, which you know as baking soda, the white powder that you put into muffins and cookies to make them puff up in the oven. If a calcium atom happens to float past a carbonate molecule, it will want to hold hands with both oxygen atoms, making $CaCO_3$, calcite.

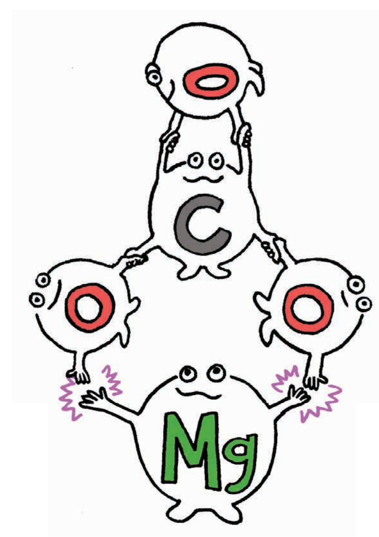




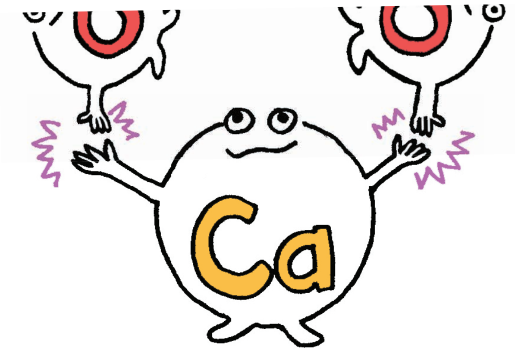
LIMESTONE $CaCO_3$

The mineral calcite is made of trillions upon trillions of these $CaCO_3$ molecules. The way they stack together makes a rhombohedral pattern, which gives calcite its rhombohedral crystal shape. If other atoms are present, it messes up this crystal pattern. If limestone was made of pure $CaCO_3$, it would look like a piece of calcite (shown on page 47). Since limestone does not have a distinct crystal shape, we know it must have other things mixed in. Geologists all know that limestone is not pure, so they go ahead and use the formula $CaCO_3$, and just assume that everyone knows that limestone is not pure.

As mentioned on the previous page, one thing that can get mixed into limestone is the element magnesium, Mg. If an Mg atom floats past a $CaCO_3$ molecule, it is able to kick the Ca out of the way and take its place. (Pure $MgCO_3$ is called magnesium carbonate and is a white powder, like baking soda.) When limestone has a lot of Mg in it, we change its name to **dolomite**. Its formula has both Ca and Mg inside parentheses, telling us it could be either one.

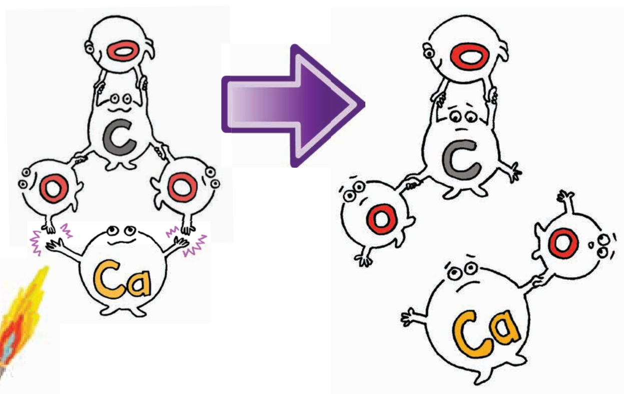


DOLOMITE $(Ca,Mg)CaCO_3$



You may have noticed that in both the $CaCO_3$ and $MgCO_3$ molecules there are purple zigzag lines right where Ca and Mg are holding hands with the oxygens. This is an important feature. The hand-holding that is going on between the calcium and the oxygens is not the same type as between the carbon and the oxygens. The bond between the carbon and the oxygens is called **covalent** bonding. We saw this type of bonding inside the silicon tetrahedron, SiO_4. We are showing covalent bonds as hands joined together. The calcium and magnesium atoms are not forming **ionic** bonds, not covalent bonds. We are showing ionic bonds as hands *almost* touching, with zigzaggy purple lines around them.

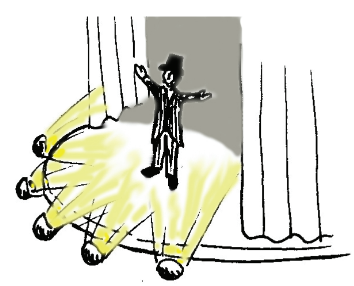
Even though covalent and ionic bonds are strong enough to hold rocks together, they are not impossible to break. In fact, let's break some right now! We'll need to apply heat. We'll use a propane gas torch that can reach about 2000° C (3000° F). Considering that water boils at 100° C (212° F) that's some serious heat! Let's torch a piece of limestone, $CaCO_3$. (Yes, we know it is not pure $CaCO_3$.)



It looks like the heat managed to break two bonds, giving us two smaller molecules, CaO and CO_2. But wait—isn't CO_2 just carbon dioxide? Yep, this little molecule floats away and is gone! CaO is a solid, though, so it can't float away. The scientific name for CaO is **calcium oxide**, but it is often called by its informal name, **quicklime**. In this case, the word "quick" doesn't mean "fast," but "alive." This name was given several hundred years ago by people who witnessed water being poured over CaO. The CaO sputtered and spit and fizzled as it melted, acting very lively, so they called it quicklime, meaning "living lime."

If you go to the YouTube playlist, there is a video in the lime section, made by some professional chemists at the Royal Institution in England. They heated large blocks of limestone in a kiln in order to drive out all the carbon dioxide. The blocks didn't look like they had changed very much, but when they took them outside and sprayed them with a hose... well, you can watch it for yourself. This "quick" reaction produces a lot of heat, too. In fact, calcium oxide can be used as an instant source of heat. Just add water!

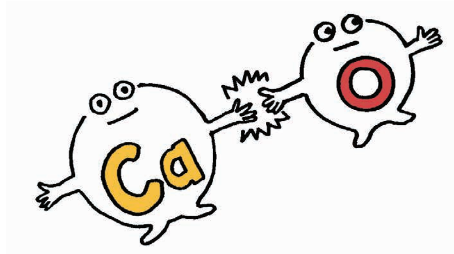
Calcium oxide, CaO, turns out to be very useful stuff. As we just mentioned, when you add water to CaO it produces heat. (A chemical reaction that produces heat is called **exothermic**. "Exo" means "out" and "thermo" means "heat.") CaO has been used as a warming device at the bottom of self-heating soup cans. (It sits in a separate cannister, apart from the food.) Besides heat, it also generates light. Before the days of electricity, cylinders of calcium oxide were heated with natural gas burners to produce a very bright, white light in theaters. We still use the term "in the limelight," meaning something that is getting a lot of attention.

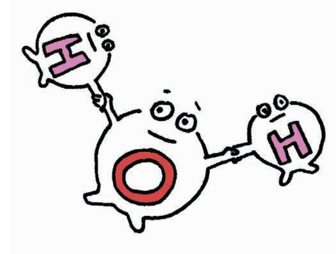


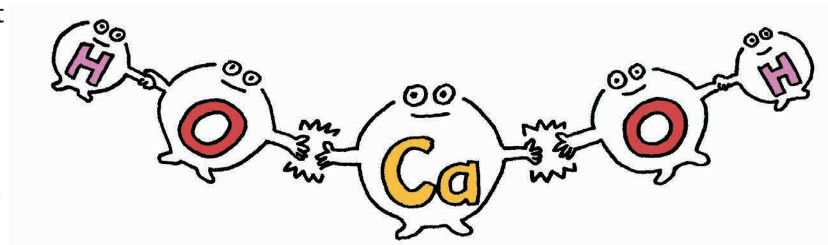
a actor standing in the limelights

Calcium oxide is important in other ways, too. It is vitally important in the manufacturing of steel, glass, paper, porcelain and cement. It can be used to neutralize acids and improve drainage of clay soils. CaO can also be turned into a safer form, $Ca(OH)_2$, that can be used to put stripes on football or baseball fields. A long time ago, powdered lime was even used as a weapon. Soldiers would launch bags of lime powder onto their enemies. The lime would create a huge, white dust cloud and the enemy soldiers would get lime in their eyes. Eyes are watery, so the lime gets activated and burns your eyeballs. Sports fields are a much nicer use of lime.

Let's look at what happens when we add water to CaO. Both the Ca and the O atoms have a hand free and would like to find someone to hold hands with. Along comes a water molecule, H_2O. The O looks over and thinks that he could try to steal one of the hydrogen atoms off the water molecule. Hydrogen atoms are relatively easy to steal, so this is what happens. That leaves water as just an OH. The calcium is glad to bond to the O in that OH. The final result is that the calcium looks like it is holding on to 2 OH's. The cartoon makes it easy to understand but is hard to draw. If we use just letters to represent this arrangement, we write it like this: $Ca(OH)_2$







$Ca(OH)_2$ is properly called **calcium hydroxide**, but is informally called **slaked lime**. (It is also called pickling lime, builders' lime, or caustic lime.) In its pure form, $Ca(OH)_2$ is a white powder, but usually plenty of water has been added to make it, so often it looks like a thick, white pudding. If a lot of water is added, it is called limewater.

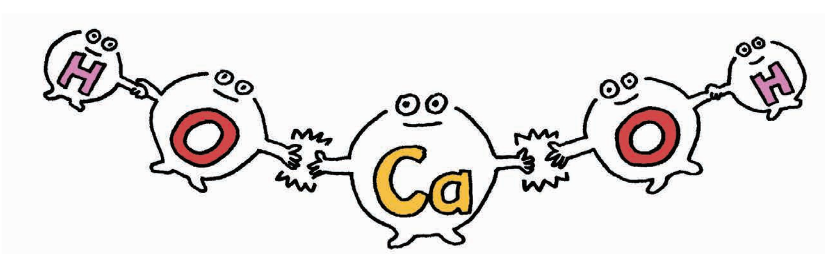
Calcium hydroxide is very useful in the food industry. Since it is sometimes called pickling lime, obvious it can be used to make pickles. It is also used to process sugar beets or sugar cane, and it is added to fruit juices to fortify them with calcium. It is very helpful when making corn tortillas because it helps the corn flour to stick together. At the other end of the food spectrum, (meaning when food has turned to waste), calcium hydroxide can be used by sewage treatment plants to help take particles out of the waste water.

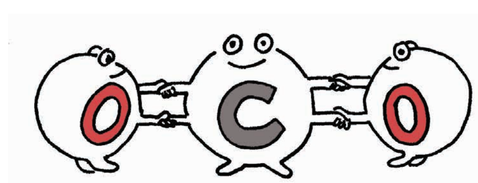
How would all this chemistry look if we used just letters and numbers, not cartoon characters?

The first step, where we heated the limestone, would look like this: $CaCO_3 \rightarrow CaO + CO_2$ *(This used heat.)*
The second step, where we added water, would look like this: $CaO + H_2O \rightarrow Ca(OH)_2$ *(This made heat.)*

We can add a third and final step to this series. $Ca(OH)_2 + CO_2 \rightarrow$ ________ + ______

What molecules will be on those blank lines? Here are the cartoon molecules on the left side of the arrow. Before turning the page, you might want to study this situation and take a guess as to how these atoms could rearrange themselves to make two different molecules. (Hint: This series of equations is called the limestone cycle. In a cycle, you get back around to where you started.)

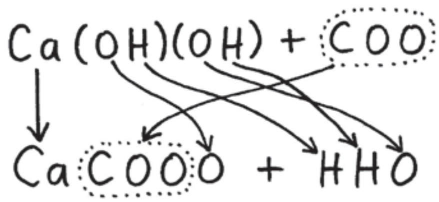


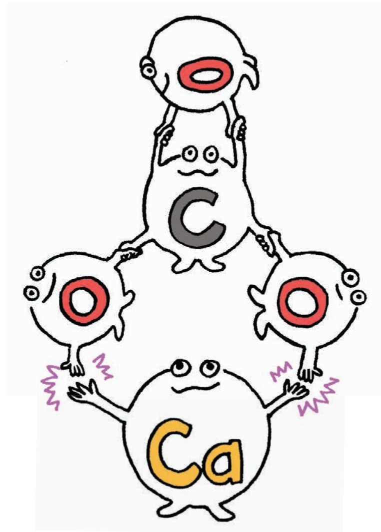


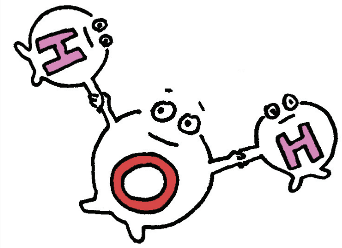
This is how these molecules rearrange. We have limestone again! Adding carbon dioxide to limewater produces one calcium carbonate molecule and one water molecule. The water will evaporate, leaving just the limestone. Here is how we write it.
(The "aq" stands for "aqueous" which means "in water.")

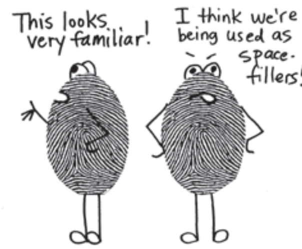
$Ca(OH)_2\ (aq) + CO_2 \rightarrow CaCO_3 + H_2O$

This is how the atoms reshuffled:



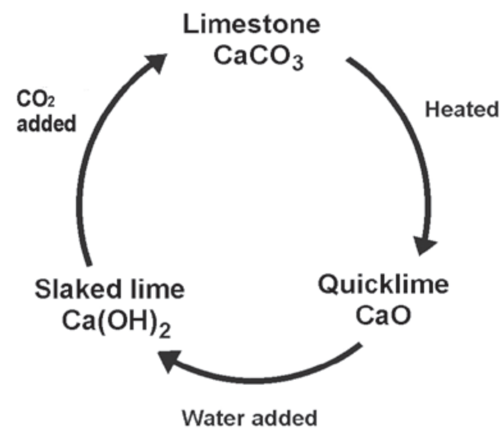






So now we are back at the beginning of what is called the **limestone cycle**. Not all chemical reactions are as easy to study as this one. Many reactions are "one way" and you can't ever get back to where you started. Also, in this cycle the math works out very nicely. In a lot of reactions you need 2 of one thing and 3 of another in order to get the molecules rearranged correctly.

The last part of this cycle is something you can observe for yourself. You can dissolve a few spoonfuls of pickling lime (or agricultural lime) into a glass of water. Let the water sit overnight. In the morning the water will be clear but there will be some white powder at the bottom of the glass. Pour just the clear water into another glass. (This clear water is "limewater" and still has lime in it.) Then use a straw to blow bubbles into the water. The carbon dioxide in your breath will be enough to allow some tiny particles of $CaCO_3$ to form.



Now, for the grand finale! Just one more chemical equation for this chapter. This equation is also key to understanding limestone. This reaction isn't a cycle, but is just as interesting because it works both forwards and backwards. (Don't worry about the tiny 2+ and 2- signs. Just look at the letters.)

$$\mathbf{H_2O + CO_2 + CaCO_3 \leftrightarrow Ca^{2+} + 2H^{+} + 2CO_3^{2-}}$$

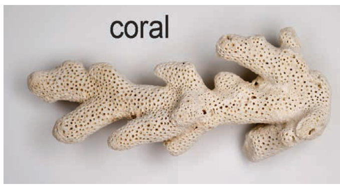
Carbon dioxide is a gas, but it can be dissolved into water. The fizzy bubbles in carbonated beverages are made of carbon dioxide. The bubbles appear as the CO_2 comes out of the solution and goes back into the air. On the left side of this equation we see CO_2 dissolved in H_2O. There is also limestone on this side of the equation. (Imagine selzter water being poured over a piece of limestone.)

On the right side we see what happens. The calcium atom comes off the limestone and floats around by itself. The H_2O and CO_2 combine with the remaining CO_3 to form 2 hydrogen atoms (ions) and 2 molecules of carbonate. Everything on the right side is dissolved in water.

We can reverse this process, and go from the right side back to the left side. If we have water that contains calcium atoms (ions) and molecules of carbonate, and hydrogen ions, these can react together to form one molecule of water, one molecule of carbon dioxide, and one molecule of solid limestone. That means that our watery solution (on the right) will produce one molecule of a gas, CO_2, and one molecule of a solid, $CaCO_3$. A gas and a solid will come right out of the water!

When a solid comes out of a liquid, we call this **precipitation**. This is what happens when you blow CO_2 bubbles into limewater— tiny white particles appear seemingly out of nowhere. The atoms were there all along, but were dissolved in the water so they were not solids. The addtion of carbon dioxide made them form a solid.

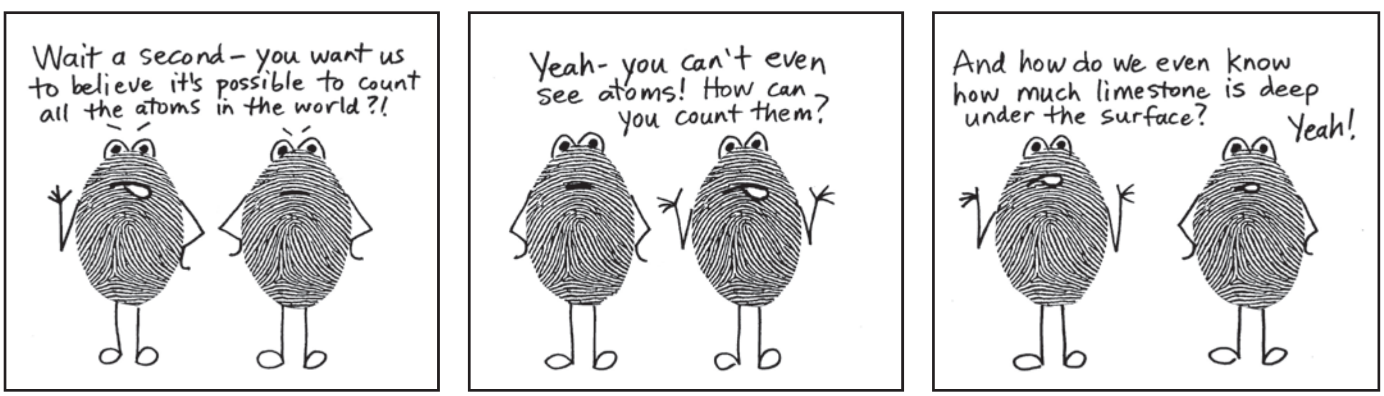
Now here's where we get to take a side track off into biology. Many sea creatures can take these molecules out of the sea water. It's not called precipitation when they do it, however. It's just called making a shell. Scientists still don't comletely understand how these animals do this. They do know that the part of their body responsible for this task is the **mantle**. The mantle is just one section of their soft, squishy bodies. The mantle is somehow able to extract the calcium and carbonate out of the water and use it to fill a very thin protein framework that they've built. (Your body does something similar when it builds bone, but it uses calcium, phosphorus and magnesium.) A mineralogist would classify a seashell as **organic** $CaCO_3$.



Geologists have wondered how much of earth's limestone was formed by sea creatures. There are places in the world where we can observe limestones being formed from shells and corals. When the creatures die, their shells fall to the bottom and begin to collect. The shells can dissolve over time, and, if conditions are right, the tiny bits of shell can be cemented together to form a hard rock. But was all limestone in the world made this way?

If we look at limestone under a microscope, we see tiny clasts. These clasts might be made of shells, rocks, crystals, or even microscopic poop particles. If these microscopic clasts get coated with thin layers of calcite, they will turn into oölitic limestone (shown on page 48). If the clasts happen to be very large shells, you get coquina. The clasts are cemented together with either calcite or aragonite crystals, both of which are made of $CaCO_3$. There are also places in the world where we can observe $CaCO_3$ precipitating directly out of the water without the help of shell-making sea creatures. Apparently, limestone can come from either organic or inorganic processes. Could the vast amount of limestone covering large areas of the world have been made by organic process alone? Let's use that equation again, along with some data about how much carbon dioxide limestones have absorbed.

First, we need to count all the carbon atoms in the world and find out how many of them are in limestone.



Remember, 3/4 of the earth's surface is covered with water. Is most of the carbon in the oceans, then?

Good questions! Of course, we can't really count atoms. Our numbers will be rough estimates, not exact counts, and we'll have to count **grams**, not individual atoms. (One gram is about the weight of a paper clip. There are trillions upon trillions of atoms in one gram.) Fortunately, several people have already done these calculations for us. (They are listed in the bibliography in the limestone section.) They've estimated figures like the volume of the oceans, the number of plants and animals on the earth, the amount of limestone that we know about, and the approximate amount of carbon in a gram of each substance.

The number of grams of carbon in the atmosphere is about 720,000,000,000,000,000. Wow, that's too many zeros! We can make this number easier to look at by putting all of those zeros into scientific notation: 10^{16}. The tiny number, in this case, 16, tells you how many zeros we have removed. So we can write 72 x 10^{16}, and that means 72 with 16 zeros after it. Ready for the rest of the results?

ATMOSPHERE: **72** x 10^{16}
PLANTS and ANIMALS: **200** x 10^{16}
COAL, OIL and GAS: **413** x 10^{16}
OCEANS: **3740** x 10^{16}
LIMESTONE: **6,000,000** x 10^{16}

Plants take in CO_2 and use it for photosynthesis. Animals eat the carbon-containing plant sugars.

The amount of carbon locked up in limestone is thousands of times more than in the rest of the earth combined! The math doesn't add up. But there's more...

Let's look at this equation again: $\mathbf{H_2O + CO_2 + CaCO_3 \leftrightarrow Ca^{2+} + 2H^+ + 2CO_3^{2-}}$

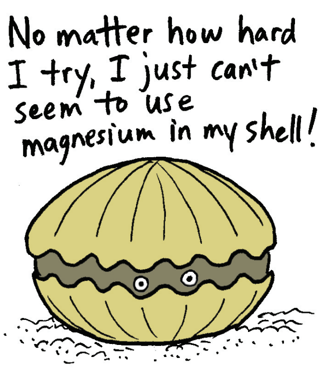
The right side would represent the ocean environment with calcium and carbonate floating around in the water. As $CaCO_3$ is created by either organic or inorganic processes, we move to the left side of the equation. On the left we see a molecule of CO_2. That CO_2 would be released either into the water or into the air. So for every molecule of limestone that is formed, a molecule of CO_2 goes into the environment. Look at how many grams of limestone we have on planet earth. Do you see a problem here? Environmentalists are already concerned that there is too much CO_2 in our atmosphere right now. They call it a "greenhouse gas" and claim that it is raising global temperatures. So if 72 x 10^{16} is too much CO_2, then what would 6,000,000 x 10^{16} have done to the planet?! But there's more...

A researcher back in the 1990s looked at some imestone he knew was old, and compared it to recently formed limestone. If limestone has always formed the same way, then all limestones should be similar. He went to the Grand Canyon and looked at one of its well-known layers of limestone. Here is a summary of his research:

Grand Canyon limestone	modern limestone ("limemud")
$CaCO_3$ looks like calcite	$CaCO_3$ looks like aragonite
clast size is 1-4 microns	clast size is about 20 microns
quartz sand grains mixed in	no quartz sand grains
fossils pointing in same general direction	fossils not in same direction
fossils of delicate, soft-bodied animals	no fossils of soft animals

The layers of limestone in the Grand Canyon have names. The most famous layers are the Kaibab Limestone, at the top, and the Redwall Limestone, a layer stained by iron oxide.

The quartz sand grains and the fossils pointing in the same direction suggests that the water was moving in one direction at the time of formation. Modern lime muds form in very calm, shallow areas. The fact that soft-bodied animals, even as soft as a jellyfish, are found as fossils in old limestone suggests that fossilization occurred very rapidly. Soft-bodied sea creatures disintegrate quickly, in a matter of weeks, if not days. But there's more...



Clams don't use magnesium.

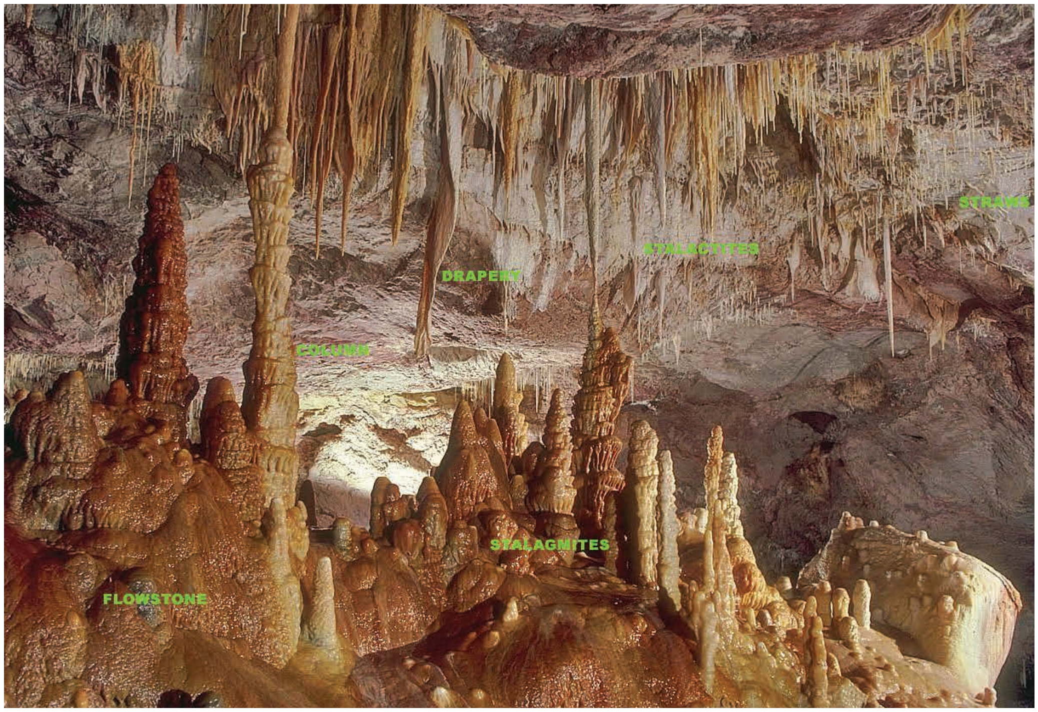
Have you ever heard of the "dolomite problem"? Of course not, because you aren't a professional geologist. Professionals of any kind don't print their problems in books for the general public to read; you have to go to their professional conferences or read their professional journals. There are quite a few problems that stump geologists; the dolomite problem is just one of them. We met dolomite on page 49. Dolomite is basically limestone in which about half of the calcium atoms have been replaced by magnesium atoms. Why is this a problem? Because most shell-making animals don't use $MgCO_3$. A few do, but not enough to account for all the magnesiusum in dolomite. Did water containing magnesium somehow got into the limestone after it was formed? There isn't any other evidence of water getting in, and the deposits are far too thick and too uniform to support this theory.

So how could so much limestone have formed without poisoning the planet with CO_2? Is there a good explanation for dolomite? And what about fossils? We'll investigate several ideas in chapter 7.

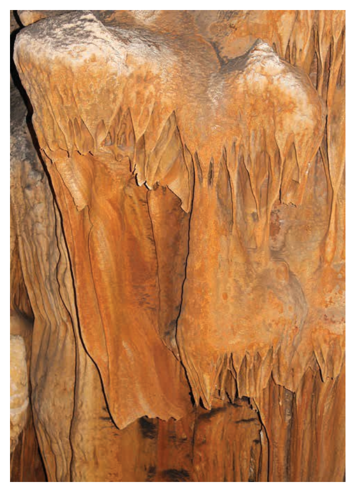
Let's go back to that equation one last time. $$\mathbf{H_2O + CO_2 + CaCO_3 \leftrightarrow Ca^{2+} + 2H^+ + 2CO_3^{2-}}$$

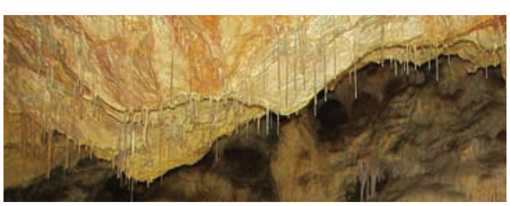
This equation can also help us to understand how caves form. The left side tells us that if water containing dissolved carbon dioxide is poured over limestone, the limestone will dissolve into the molecules on the right. Rain contains dissolved CO_2. If rainwater gets into cracks in limestone, it can gradually eat away at the rock and create holes. More rainwater begins washing into these holes and they get bigger. Gradually, the holes get larger and larger until they make empty areas we call **caves** (or caverns).

Once a cave has opened up, the water seeping in can then start making formations called **speleothems**. (Any word starting with "speleo" will have something to do with caves.) The rainwater coming into a cave has dissolved limestone in it. As the water evaporates inside the cave, the $CaCO_3$ precipitates back out again, but often in very interesting ways. The precipitated limestone can form stalactites (on the ceiling) and stalagmites (on floor), or flowstone, dripstone, and drapery. Some caves have streams or pools at the bottom.



By Dave Bunnell / Under Earth Images - Own work, CC BY-SA 2.5, https://commons.wikimedia.org/w/index.php?curid=22613190




The thin lines are "straws" that can break easily.

Cave formations are often named after what they look like. You hardly need a picture to know what these look like: shelfstone, soda straws, bubbles, pearls, bacon, popcorn, fried eggs, butterflies, twists, and corals. Sometimes other minerals are present, too, not just calcite. Gypum ($CaSO_4$) can form beautiful crystals. Some of the formations will break easily, so cavers must be careful as they explore.

Landscapes made of limestone are called **karst** landscapes. Karst is the German name for a limestone region in Slovenia. Karst is found all over the world, though, not just in Slovenia. Anywhere there is limestone, there can be a karst landscape. These pictures show two karst areas that have caves.

Karst landscapes are known not only for their caves and caverns, but also for their **sinkholes**. Sinkholes are places where the "roof" of a cave has collapsed, turning the cave into a deep hole in the ground. Sinkholes can be very small, only a few meters wide, or they can be as large as a small field.

Some sinkholes are very old, such as this deep sinkhole in Mexico. This hole has been around as long as anyone can remember. Since it has a pool of water at the bottom, the local folks have cleverly turned it into quite a tourist attraction. This sinkhole presents little danger, since it collapsed a long time ago and appears to be very stable now. Geologists probably examined the walls of the hole before allowing it to be used for recreation. They will continue to examine it from time to time to assure everyone's safety.

Photo by Luis Fernández García - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=45303372

Some sinkholes are quite new. The one in the top picture is in Spain and the hole is in gypsum, not limestone. The people walking along the road give you an idea of how large this sinkhole is.

The bottom picture is a very fresh sinkhole that opened up overnight. One day there was grass, and the next day there was a hole several meters wide.

Sinkholes in water are called blue holes. They are not whirlpools and they don't really pose any danger to boats. (It's just the idea of this deep dark hole underneath you...) This blue hole is off the coast of Belize in Central America.