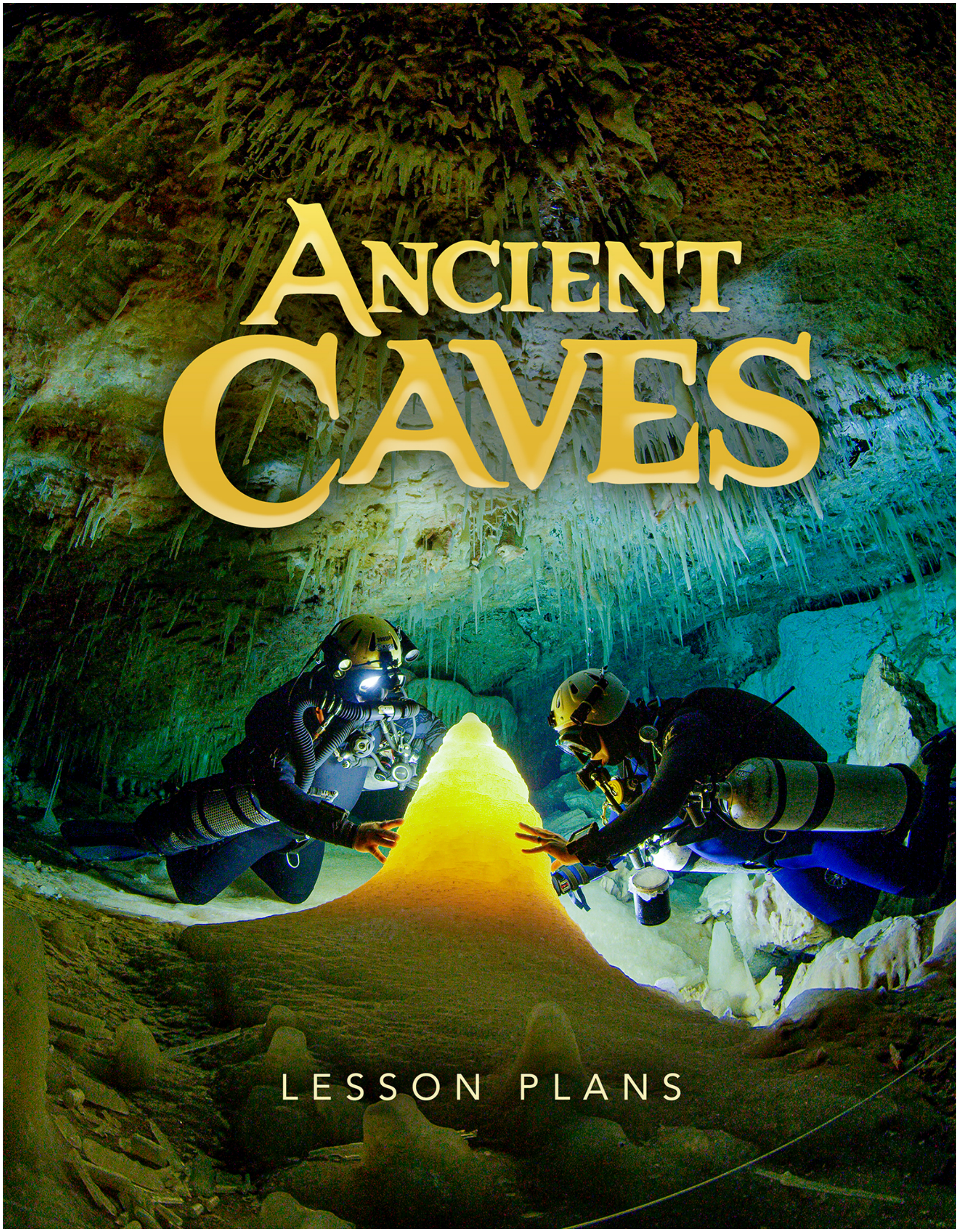
ANCIENT CAVES
LESSON PLANS

Exploring the Chemistry of Caves

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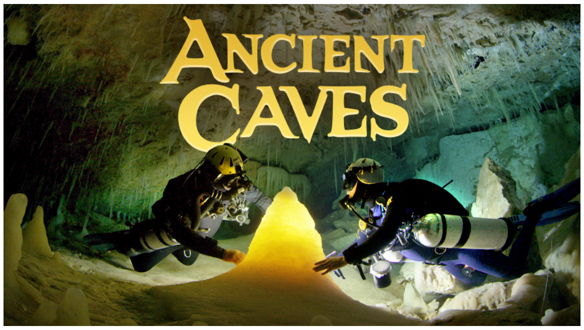

Exploring the Chemistry of Caves

Introduction and Overview for Educators

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Introduction

The film *Ancient Caves* chronicles the scientific journey of Dr. Gina Moseley as she and other scientists look to unlock the story of Earth's ancient climate record, written in the limestone layers of cave walls and in formations such as **stalactites** and **stalagmites**. In order to understand how such features can store a record of climate we need to first look at how these **speleothems** are formed and the chemistry behind their creation.

Without question, the most important material involved in cave chemistry is water, which has the unique ability to dissolve a wide variety of materials and keep them in solution. Minerals such as **calcite** (the main mineral in limestone) are dissolved and contained in the groundwater that seeps through the ceilings and walls of caves. **Stalactites** and **stalagmites** grow like icicles over thousands of years as the dripping groundwater evaporates, leaving behind layers of limestone that it dissolved and picked up along its journey. This process is presented and demonstrated in the lesson: *Speleothems and Paleoclimatology.*

Since water dissolves a variety of elements and compounds on its way to a cave, it also becomes a "fingerprint" for the environment at that period in time. In this way, the mineral composition for each layer can hold clues as to the conditions outside the cave at that time, such as temperature, vegetation, bedrock, and soil conditions.

The investigation into cave chemistry begins with observations and a question.

In the film *Ancient Caves*, we observe amazing limestone formations in caves which become flooded as sea levels rise during warmer interglacial periods. Cave divers literally risk their lives to obtain water samples and limestone features at dangerous underwater depths, in the hope of obtaining a record of Earth's climate. We know that water must dissolve the calcite that ultimately results in the layers of limestone which form stalagmites and stalactites.

So one must wonder, why doesn't the water in flooded caves re-dissolve these features? How could the deposition of limestone have happened in caves if limestone can't be dissolved in water?

So with these questions we will begin our investigation into the chemistry of caves.

Exploring the Chemistry of Caves

Audience: Upper Elementary, Middle School and High School

Much of the chemistry presented in this investigation focuses on chemical change at the molecular level, addressed in middle school and high school science curricula. However, the activities and lessons can be adapted for upper elementary students who may lack background knowledge of the particulate nature of matter.

Learning Standards: Next Generation Science Standards. Disciplinary Core Ideas

Structure and Properties of Matter
Chemical Reactions
The History of Planet Earth
Earth's Materials and Systems
Roles of Water in Earth's Surface Processes
Weather and Climate
Global Climate Change

Overview:

In "Exploring the Chemistry of Caves," students have the opportunity to learn the chemistry behind the cave formations. As stated in the introduction, this inquiry-based lesson is centered around a simple question which can arise after viewing the film *Ancient Caves.* If limestone needed to become dissolved to form stalactites and stalagmites, then why don't these limestone deposits dissolve in flooded caves? The investigation is presented in four parts, beginning with water's unparalleled property as a solvent, and examining the role of carbon dioxide and acidity in the chemical changes that happen to limestone, from its solubility to its final deposition. Each part uses hands-on activities, background text, as well as follow up slide presentations to help students understand the chemistry of caves, especially at the molecular level. The hands-on activities throughout this investigation use accessible materials, are simple to perform, and provide the evidence that supports the concepts presented in these lessons.

This investigation offers flexibility for a teacher, depending upon time and grade level. In order to answer the overarching question, parts of this investigation can be omitted or do not have to be completed in their entirety. For example, a teacher may simply wish to establish the *question and hypothesis (see part 2)* and answer the question with the activity: "*An Egg in Vinegar" in part 3.* In addition, the hands-on activities can be presented as whole class demonstrations or with lab groups.

Cross curricular connections

There are opportunities for cross-curricular connections in this investigation. For example, with the activity *"Visualizing pH with food dye." (ending of part 2)*, students can reinforce lessons from Mathematics classes focusing on decimals, exponents, and scientific notation. In the activity: *"An Egg in Vinegar" (see part 3)*, students write an "evidence based" explanation which can be used to apply lessons from Language Arts classes.

Examples of culminating activities in *Part 4: Conclusion and Summary* involve writing, but also uses art and illustration to communicate science information with a "one-pager" activity.

Going Further

Since this investigation into cave chemistry involves pH and acidity, relevant connections can be made to these chemistry concepts in our everyday life and important issues such as ocean acidification.

Time frames for implementing lessons.

Speleothems and Paleoclimatology– Three to four class periods.

This lesson provides background into the formation of speleothems and how their analysis reveals clues to Earth's past. Such information leads educators to additional lessons and classroom activities, including the activity in this lesson in which students can create their own stalactites in the classroom with everyday materials and tools.

Cave Chemistry Part 1: Water, the "Universal Solvent" Two *to four class periods.*

This lesson is estimated to take four class periods when conducted in lab groups. This would allow for an introduction, time for students to build and use their conductivity testers and have a follow up lesson. If performed as a whole class demonstration, the lesson could be completed with two class periods.

Cave Chemistry Part 2: Limestone, acidity, and pH. A question and a hypothesis. One to four class periods.

In this lesson, we first establish our overarching question as to how the deposition of limestone happens in caves if limestone can't be dissolved in water. This is followed by a classroom discussion which develops the hypothesis that it's the acidity of rainwater that gives water the ability to break down and dissolve limestone. A teacher may choose to then move on to part three of this investigation or use this as an opportunity to examine the topics of acidity and pH. The time frame for this part of the investigation can vary greatly, depending on grade level and student's background knowledge.

Hypothesis.

One classroom period may be needed to develop the question and hypothesis, including an activity demonstrating the differences in pH between rainwater, tap water, and seawater. However, more time may be needed if the activity is done as a lab activity in lab groups.

Background information in acidity and pH.

Presenting background information on acidity and pH may take two class periods. Students may already have background knowledge of acidity and pH; thus, a teacher may not want to address those topics to the extent presented here. Conducting the lab activity, “Visualizing pH and acidity with food dye” is intended to be completed in one class period.

Please note: *Acidity in this lesson refers to the concentration of hydrogen ions in an aqueous solution. To keep things a bit simpler, acidity and the formation of hydronium ions H_3O^+ has been left out of the lesson, but this is a concept that a teacher may want to integrate, especially at the high school level.*

In addition, students in upper elementary or middle school may not have background knowledge around the particulate nature of matter, such as ions, molecules, and atoms. The chemistry of acids and pH can be simplified by referring to acidity as “dissolved hydrogen” in water. pH can be expressed as “the amount of dissolved hydrogen in water.“

<u>Cave Chemistry Part 3: Experimentation: Testing our hypothesis</u>*. Two to Five class periods*

In part 3 of this investigation, students test the hypothesis that acidity gives rainwater the power to breakdown and dissolve limestone, with three activities. The first is “An Egg in Vinegar” in which students track what happens to the limestone shell of a chicken egg in acetic acid (vinegar) versus tap water. The activity, results, and follow up, involve three class periods and offers an opportunity for students to write an evidence-based explanation for their results. At this point it is clear that an acidic solution can breakdown and dissolve calcium carbonate, and students can infer that being acidic, gives rainwater the ability to breakdown calcium carbonate and answers our question.

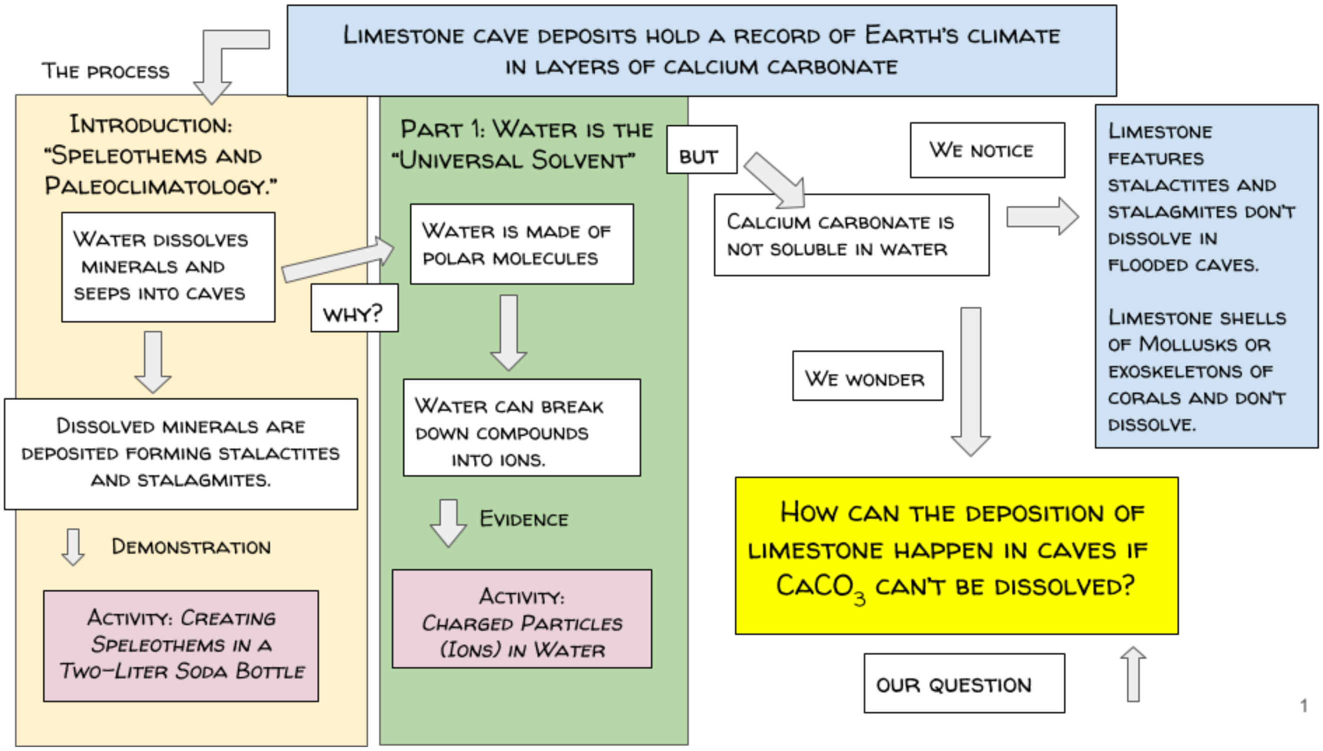
If wishing to go further, students can demonstrate why rainwater is acidic in Activity 2: “How does rainwater become acidic” and then confirming that this acidic water is able to breakdown calcium carbonate in Activity 3: “Dissolving limestone (calcium carbonate) in acidic water.” Each activity can be completed in one class period.

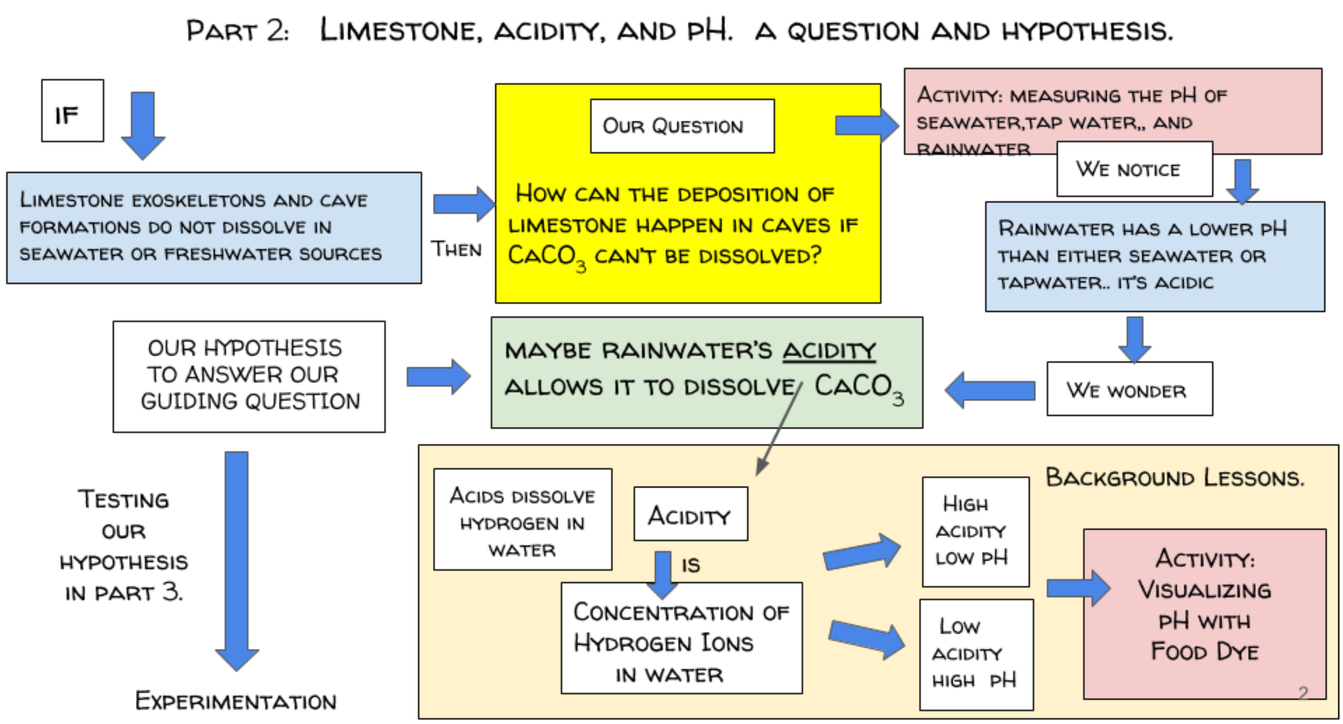
<u>Cave Chemistry Part 4: Conclusion and Summary. The deposition of limestone.</u>

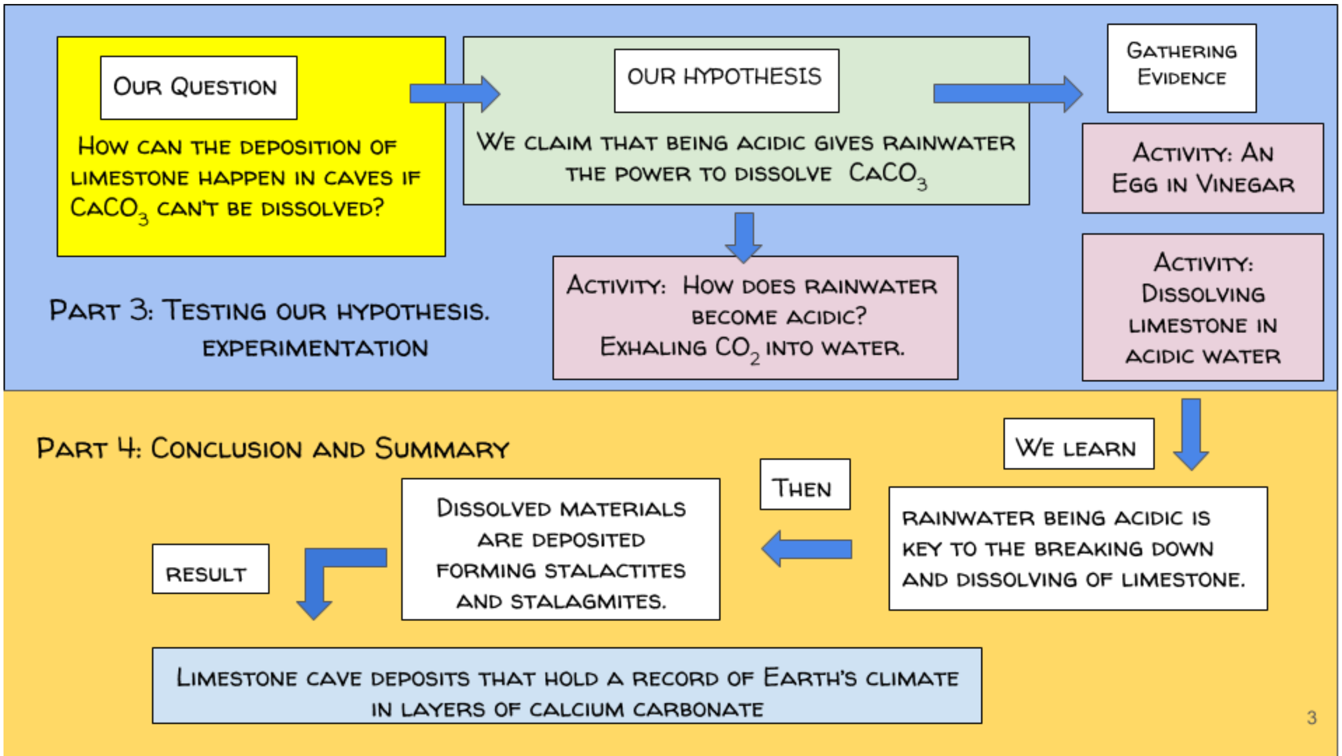
One class period with independent follow up activities beyond the classroom.

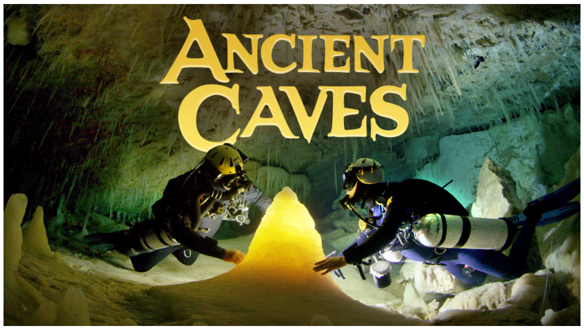
In the final part of this investigation, the chemistry behind the formation of limestone features in caves is summarized. The entire process from the formation of acidic rain and breakdown of limestone to its deposition in caves is presented step by step using graphics in a slide presentation. The culminating activities in part 4, allow students to communicate their knowledge with writing or through the use of illustration with a “one-pager” activity.

Lesson Overview. Graphic Organizer



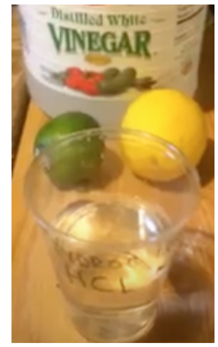



Our Question
How can the deposition of limestone happen in caves if $CaCO_3$ can't be dissolved?
Our Hypothesis
We claim that being acidic gives rainwater the power to dissolve $CaCO_3$
Gathering Evidence
Activity: An Egg in Vinegar
Activity: Dissolving limestone in acidic water
Activity: How does rainwater become acidic? Exhaling CO_2 into water.
Part 3: Testing our hypothesis. Experimentation
Part 4: Conclusion and Summary
We learn
Rainwater being acidic is key to the breaking down and dissolving of limestone.
Then
Dissolved materials are deposited forming stalactites and stalagmites.
Result
Limestone cave deposits that hold a record of Earth's climate in layers of calcium carbonate
3



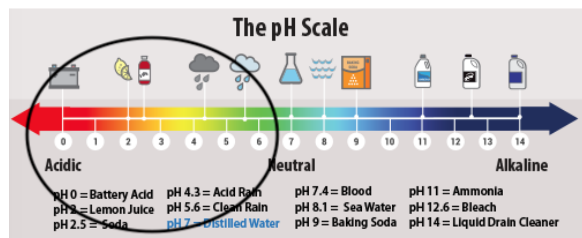
Exploring the Chemistry of Caves

Student Resource: Background Vocabulary



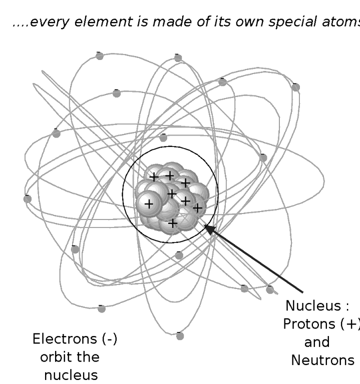
Acids: Compounds that when dissolved in water release positively charged hydrogen ions (H^+). They are corrosive and have a sour taste.

Acidity: The strength of an acid or the concentration of hydrogen ions in an aqueous solution;. The greater the acidity, the lower the pH.

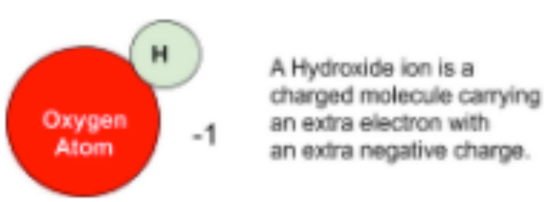


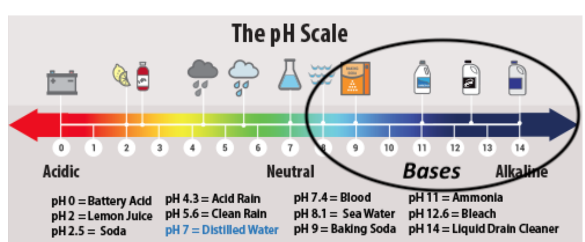
Aqueous solution: A solution in which water is the solvent

Atoms: The tiniest particle of an element that is still identified as that element



Bases: Compounds with a high pH that when dissolved in water release negatively charged hydroxide ions (OH^-).





Calcite: The natural form of the compound calcium carbonate ($CaCO_3$). Calcite is a rock forming mineral and is the main component of limestone and marble. The exoskeletons of many marine creatures such as Molluscs and corals are also composed of calcite/ calcium carbonate.

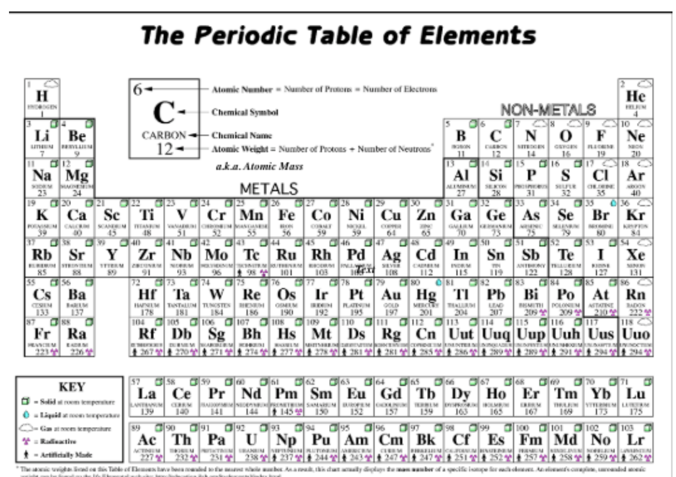
Chemistry: The science that deals with the composition of matter and how it changes to form new substances.

Columns: Cave deposits formed from the fusion of *stalactites* and *stalagmites.*

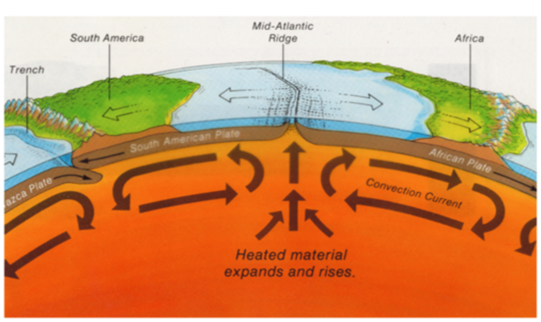
Compounds: Single, unique materials made from two or more elements chemically combined.
Compounds are nothing like the elements from which they are made

Dissolve: When a solvent physically breaks a substance down into its individual molecules, ions, or atoms spread throughout the solvent. Since, one cannot see separate molecules or atoms, a solution is clear when materials are dissolved. If you can see it, then it is NOT dissolved.

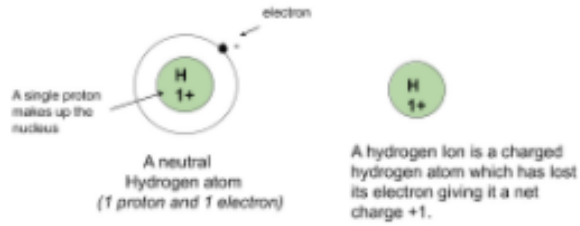
Elements: Basic materials made from just one kind of atom.
All matter is made from one or more elements.



Geology: The study of the Earth. From "*geo-*" meaning Earth, and *"-ology"* meaning the study of a subject. Geology is the science that looks at the structure and composition of the Earth and how it changes.

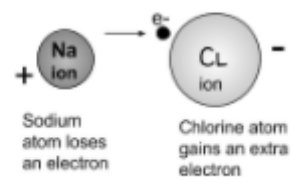


Hydrogen ions: Hydrogen atoms which have lost their electron giving them a positive charge: H^+. Essentially, hydrogen ions are a single proton.



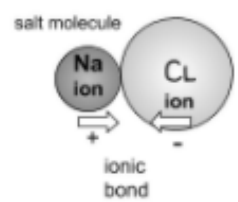
Interglacial Periods: Periods of warmer climate between ice ages lasting roughly 10,000 years.

Ions: Atoms or molecules with a net electric charge due to the loss or gain of one or more electrons



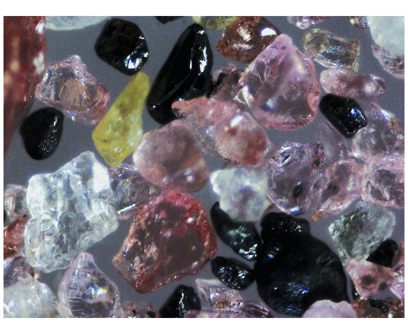
Ionic Bonds: Chemical bonds formed between positive and negative ions which happen when electrons are exchanged between atoms to complete their outer shells of electrons. Negative ions attract positive ions which hold atoms together to form molecules.

Molecules formed from ionic bonds happen when the atoms of metals chemically bond with atoms of nonmetals.

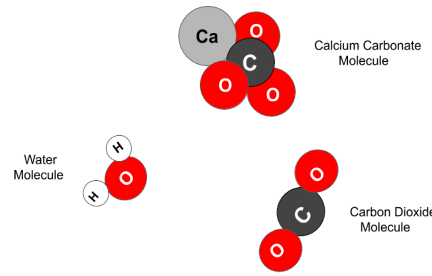


Limestone: A sedimentary rock made primarily from the calcium carbonate ($CaCO_3$) exoskeletons of marine creatures, including corals and Mollusks.

Mineral: Minerals are solid, naturally forming, inorganic elements and compounds that form rock

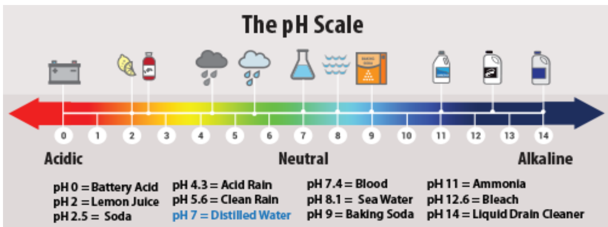


Molecules: Particles formed when two or more atoms are chemically combined in a very specific combination. The tiniest particles of a compound that still can be that compound are its molecules

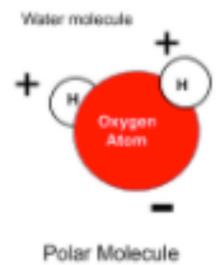


Paleoclimatology: The study of ancient climate.

pH: A measure of a solution's acidity. It measures the concentration of H+ ions in a solution.



Polar Molecule: A molecule with a negatively charged end and an opposing positively charged end , such as seen in a water molecule



Precipitate: A solid material deposited from a solution from a chemical reaction or evaporation.

Radioactivity: The property of certain elements such as uranium, or isotopes such as carbon 14, in which the unstable nuclei in their atoms spontaneously decay by releasing neutrons and protons until reaching a stable nucleus.

Soluble: Able to be dissolved

Solvent: A liquid that dissolves materials…. like water

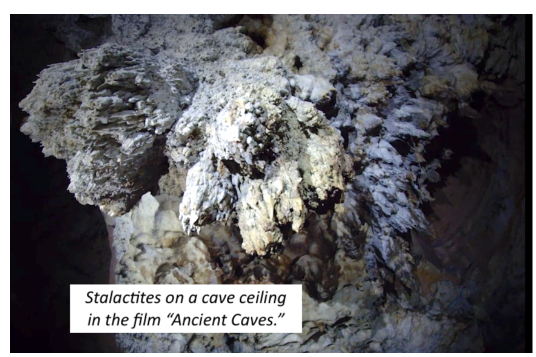
Solution : A mixture of materials dissolved in a solvent… like seawater.

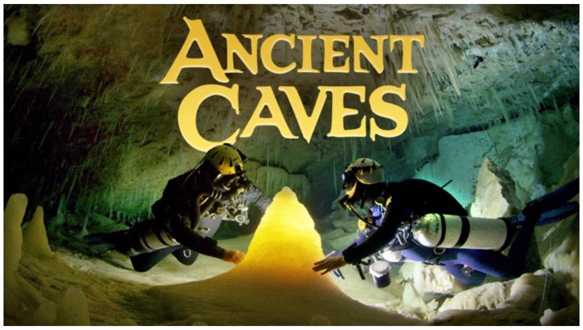
Solute: A material that is dissolved in a solvent… like salt or sugar

Speleothems: Structures in caves formed from the deposition of minerals dissolved in water such as *stalactites* or *stalagmites*.

Stalactites: "Icicle like" structures that hang from the ceiling of caves, produced as minerals precipitate from water dripping through the roof of a cave.

Stalagmites: Mounds of mineral deposits on the floor of a cave which grow upward as minerals precipitate from water dripping onto the cave floor.


Stalactites on a cave ceiling in the film "Ancient Caves."



Speleothems and Paleoclimatology:
The stories in the rocks of caves

Introduction

From the French Alps to Islands in the Bahamas, the film *Ancient Caves* follows the journey of Dr. Gina Moseley as she and other scientists look to understand Earth's climate record, written in the deposits of limestone caves. This film explores the secret world of these caves whose chambers are often decorated with amazing rock formations created through the deposition of dissolved minerals over long periods of time. The composition and structure of such cave formations, known as "speleothems," hold clues to past conditions on Earth. Thus, these formations provide profound insight into paleoclimatology, the study of ancient climate. *Ancient Caves* exemplifies the spirit of Geology, the science that uncovers the stories in rock, as scientists look to cave rocks to better understand the history of climate change and its continuous impact to our planet.

This lesson provides background into the formation of speleothems and how their analysis reveals clues to Earth's past. Such information leads educators to additional lessons and classroom activities, including the activity in this lesson in which students can create their own stalactites in the classroom with everyday materials and tools.

How are speleothems formed?

Among the many features in limestone caves, the most familiar are *stalactites* and *stalagmites.* Speleothems are rock formations built from the deposition of calcite (calcium carbonate), the main mineral in limestone.

Speleothems' formation begins as rain water absorbs carbon dioxide (CO_2) from the air and from layers of soil on its way to the cave system. As water absorbs CO_2 it forms carbonic acid (H_2CO_3), which chemically breaks down and dissolves calcite as it passes through limestone bedrock. When the water-calcite solution drips into the cave, it loses carbon dioxide to the cave air. With this loss of carbon dioxide and evaporation, the rain water cannot keep the dissolved calcite in solution. Thus, the calcite becomes "undissolved" forming a *precipitate* on the surfaces of caves. Over long periods of time, calcite deposits may form structures in caves known as speleothems.

"Icicle like" stalactites grow as calcite precipitates from drops of water hanging on cave ceilings. These drops of water deposit a tiny amount of calcite, setting a foundation for the accumulation of more calcite as this process continues. When water saturated with calcite drips on to the cave floor, the calcite deposition grows upward in layers building mounds called stalagmites. Occasionally, a stalagmite and a stalactite will meet to form a column or a pillar.

Cave Formations and Climate

Stalactites and stalagmites preserve a record of past climate because the process and rate at which they grow is dependent on climate, especially in the availability of water. Since they are formed in caves, speleothems are undisturbed and protected from the weathering and erosion that affect rock formations on the surface. Thus, they can serve as a record of climate that goes back thousands of years. As pointed out in *Ancient Caves*, stalagmites are more reliable than stalactites for obtaining climate records as they are more stable structures. Stalagmites grow upwards from the cave floors, whereas a stalactite may have reformed after breaking at some point from its own weight, rendering its record incomplete.

The layers of mineral deposition in cave deposits read like growth rings in a tree. They are indicators of how much ground water percolated into the cave. Little growth might indicate drought, whereas rapid growth could point to wetter periods of time.

Since water dissolves a variety of elements and compounds on its way to a cave, it becomes a "fingerprint" for the conditions at that period in time. In this way, the mineral composition for each layer can hold clues as to the conditions outside the cave at that time, such as temperature, vegetation, bedrock, and soil conditions.

Determining age in the layers

Scientists have long used the rate of decay in radioactive elements or isotopes to determine the age of different materials including rock. Uranium, a radioactive element decays into thorium at a predictable and reliable rate. By measuring how much uranium has decayed into thorium, scientists can determine the age of layers in speleothems.

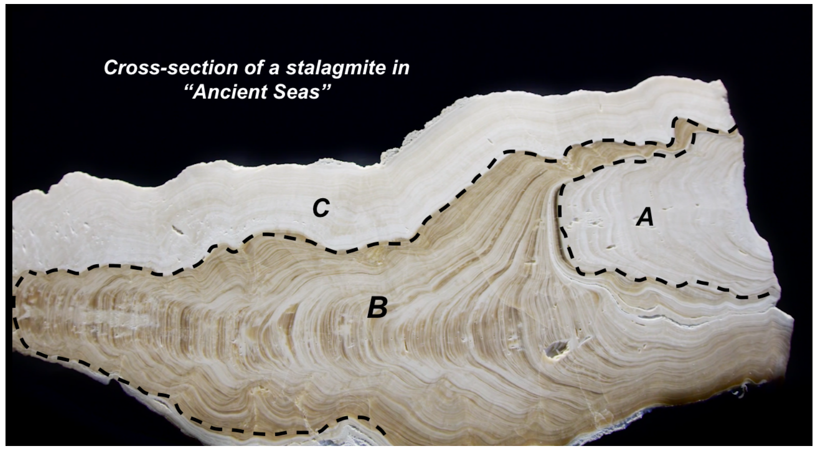
Trace amounts of uranium from the bedrock above a cave system can dissolve into ground water, becoming part of the minerals deposited in each layer of a speleothem. Thorium is not soluble in water; thus, the most recent layers of a growing speleothem contain only trace amounts of uranium and no thorium. As time passes, the uranium in these layers decay to thorium. Scientists determine the age of the layers by measuring the ratio of thorium to uranium. The higher this ratio, the older the layers in the speleothem.

Ice ages revealed in speleothems

During colder periods in the Earth's history (ice ages) much of the Earth's water was tied up in ice sheets on continents causing sea levels to drop hundreds of meters. During interglacial periods (in between ice ages) sea levels rise and caves such as those in the Bahamas are flooded, as they are now. The growth of speleothems stops when caves are submerged, thus speleothems in these undersea caves can only grow during periods of lower sea level such as those experienced during ice ages.

Discussion and Follow up Questions:

The Story in a Stalagmite



In this stalagmite, it appears that there are three separate growth periods labeled A, B, and C.

1. Which growth period is the oldest? _____ Which is the most recent? _____

2. Assuming this stalagmite was removed from an undersea cave system, would each growth period represent an interglacial period or an ice age? ________________________________

Provide a reason for your choice. ____

____

3. What event would divide each growth period: an ice age or interglacial period? _________________________

Provide a reason for your choice. ____

____

4a. Which growth period would have the lowest ratio of thorium to uranium? _____

b. Which growth period would have the highest ratio of thorium to uranium? ____ Explain your answer.

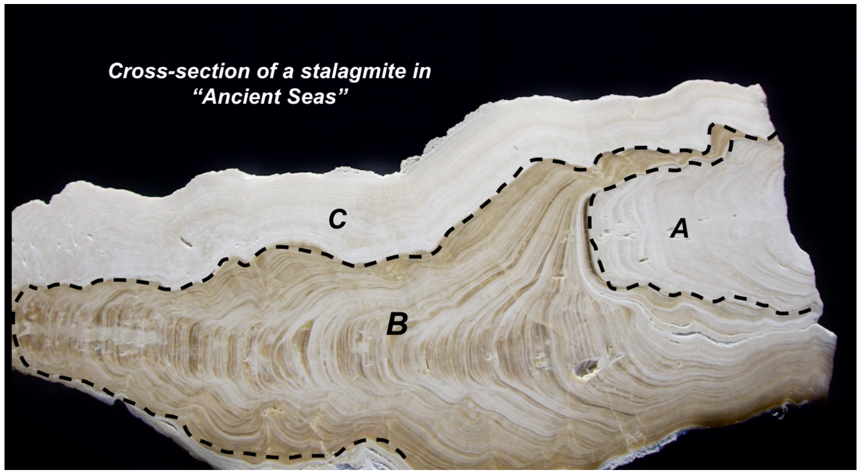
____

5. Each growth period seems to be marked by different colors to the mineral deposits.

What do you feel may account for this difference? ____

____

Answer key to *The Story in a Stalagmite.*



In this stalagmite, it appears that there are three separate growth periods labeled A, B, and C.

1. Which growth period is the oldest? ***A*** Which is the most recent? ***B***

2. Assuming this stalagmite was removed from an undersea cave system, would each growth period represent an interglacial period or an ice age? ***an ice age***

Provide a reason for your choice. ***During ice ages much of the Earth's water is tied up in ice sheets and sea levels would be much lower. Thus, the cave would be dry and stalagmites could grow .***

3. What event would divide each growth period: an ice age or interglacial period? ***an interglacial period***

Provide a reason for your choice. ***During interglacial periods the climate warms and the ice sheets melt raising sea levels. Rising sea levels would flood the cave and the process of deposition in order to form stalagmites could not happen.***

4a. Which growth period would have the lowest ratio of thorium to uranium? **C**

b. Which growth period would have the highest ratio of thorium to uranium? **A**

Explain your answer. ***Over time, uranium in the mineral layers of the stalagmite decays to become thorium. Thus as layers age, more of the uranium turns to thorium and the ratio of thorium to uranium increases.Since "A" is the oldest section of the stalgmite, it would have the highest thorium to uranium ratio.***

5. Each growth period seems to be marked by different colors to the mineral deposits.

What do you feel may account for this difference? ***The minerals that form the layers for each growth period may have a different mineral composition. This could be due to changes in the bedrock, soil, or vegetation above the cave system.***

Further Discussion

• What is the importance in analyzing the formations from caves in different parts of the world?

In order for scientists to form solid conclusions about Earth's past, evidence for periods of climate change in cave rocks from one part of the world would need to correspond to those in other parts of the world.

• What are some other types of geological evidence that can support the findings for periods of climate change found in cave rocks.

Evidence in the fossil record, evidence in ocean sediments.

• In *Ancient Seas,* divers literally risked their lives to collect a single stalagmite or a a few rock samples from dangerous depths in submerged caves. Are these enough of a sample size to make conclusions regarding the Earth's past climate?

• What other questions do students have about this topic?

Resources used for the background text and images in this lesson.

Ancient Caves. MacGillivray Freeman Films. Produced by Oceanic Research Group, Inc. 2020.

Cave Formations. National Caves Association. https://cavern.com/Learn/formations.asp

Paleoclimatology: Written in Earth. Holly Riebeek and Robert Simmon. Nasa's Earth Observatory. June, 2005. https://earthobservatory.nasa.gov/features/Paleoclimatology_Speleothems

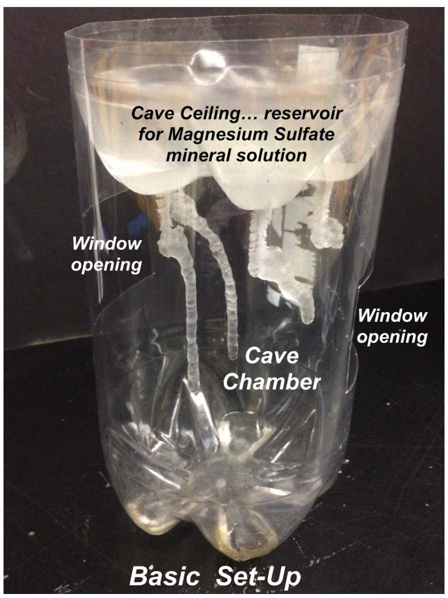
Speleothems (Cave Formations). National Parks Service. Great Basin National Park, Nevada. February, 2015. https://www.nps.gov/grba/learn/nature/speleothems-cave-formations.htm#CP_JUMP_292213

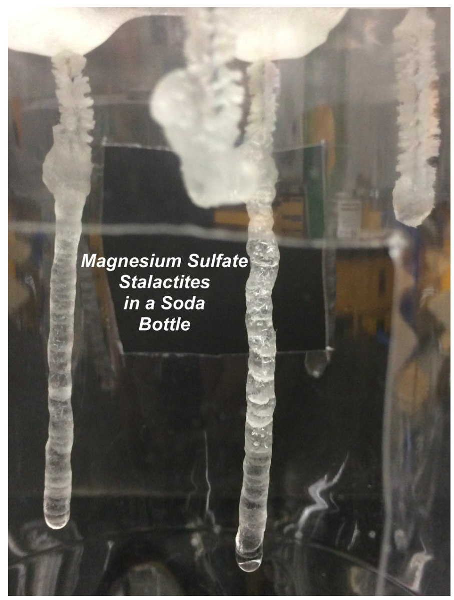
<u>Classroom Activity: Creating Speleothems in a Two-Liter Soda Bottle</u>

Can be adapted for elementary grades.

In this activity students can simulate the growth of stalactites, stalagmites, and even columns, in a two-liter soda bottle with simple tools and materials. Structures such as these form from the precipitation of minerals coming out of solution with the slow dripping of mineral-laden ground water through the ceilings of caves.

In In this lab activity, students can gain a sense of how cave deposits *(speleothems)* are formed as they see stalactites grow from a super saturated solution of water and magnesium sulfate (Epsom Salts) which
seeps through the top of a modified two-liter soda bottle representing a cave.





Time Frame: Two to three 45- to 55-minute classroom periods.

Materials: • 2 clean two-liter plastic soda bottles • white pipe cleaners
• a bag or box of Epsom Salt (Magnesium Sulfate ($MgSO_4$) • water

Tools: A large straight pin or small nail (4d) • utility knife •scissors • cm ruler

Procedure:

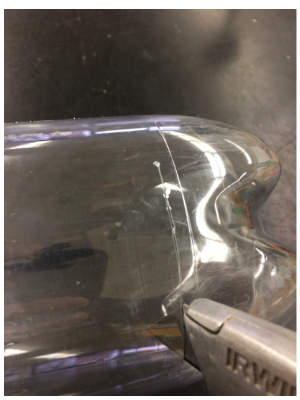
Step One: Making the "The Cave Chamber."

1) With a utility knife, carefully cut the top off of a two-liter soda bottle.

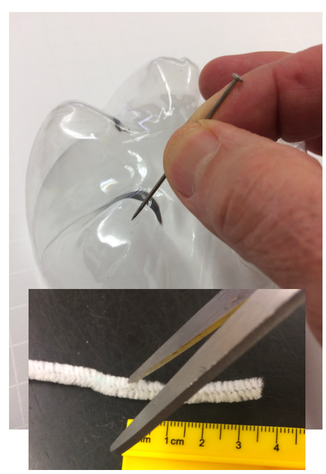
2) Then on opposite sides along the middle of the bottle, cut two 4 cm x 4 cm square windows, which will allow for air flow and a clearer view of the results.

Step Two: Making the "Cave Ceiling."

1) Cut the bottom from a second two-liter bottle just above the line on the bottle. This will rest on top of the "cave chamber" and simulate the roof of the cave.



2) With a large straight pin or tiny nail, punch a hole into the middle of each knob of this bottle bottom.



3) Cut five pieces from a pipe cleaner, each about 3- 4 cm in length. Then insert them securely into each of the five holes that you made in the bottle bottom.

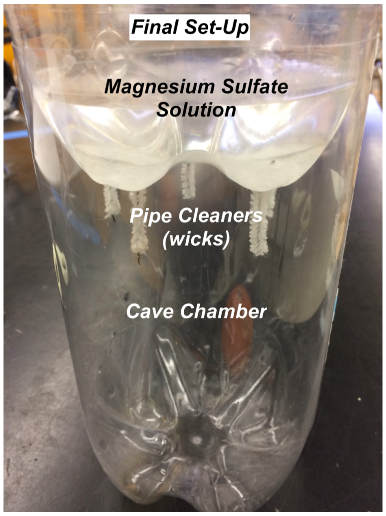
If you have trouble pushing the pipe cleaners through the holes, make the holes slightly wider, but the pipe cleaners should fit securely and not be loose.

The pipe cleaners will serve as "wicks" to allow the Magnesium Sulfate solution to seep slowly through this "cave ceiling."

Step Three: The Final Set-up

1) Fill about one quarter to one third of our "cave ceiling" with the Magnesium Sulfate (Epsom Salt).

2) Next, place our "cave ceiling" on top of the "cave chamber" and fill the ceiling about halfway with water. As the water slowly percolates through the Magnesium Sulfate, it will become a super saturated mineral solution as it seeps through the ceiling openings and slowly migrates down the pipe cleaners.



Once the set-up is complete, place it in an area of the room where it will not be disturbed overnight and observe your results the next day. You may actually begin to see stalactites being formed within a couple of hours.

Results and Follow Up... ***The Next Day***

After letting the set up sit overnight you should see stalactites hanging from the pipe cleaners in the cave roof.

IMPORTANT: This is VERY FRAGILE. The stalactites are very fragile and can break very easily.
If you need to move the set-up do so carefully.

Observations

Look closely at the stalactites formed in the two-liter bottle. Use a magnifying glass if available.
Then answer the following:

When I look at these structures I notice: ____

____

____

I wonder: ____

____

These stalactites remind me of: ____

____

____

Discussion

If you were to carefully touch one of the stalactites you would see that it breaks very easily and appears to turn to back to a liquid or re-dissolve.   Try it.

You will see that the pieces appear to be hollow, like clear straws. This is because of the way they form.

As the water supersaturated with magnesium sulfate drips from the pipe cleaner, the minerals crystalize to form a very thin ring or shell around the water drop before it falls. As another water drop follows, the process repeats and a hollow tube of magnesium sulfate is formed.

The stalactite is made of clear successive rings or shells of magnesium sulfate. as seen in the image to the left.

The stalactites in the two-liter bottle develop in the same way that very fragile "soda straw stalactites" form in nature, as seen in the Crystal Caves of Abaco Island. (See photo from *Ancient Seas* below).

In caves, a "soda straw" can turn into a larger stalactite if the hole at the bottom is blocked, forcing the water to begin flowing on the outside surface where minerals build up on around the tube.

Going Further.

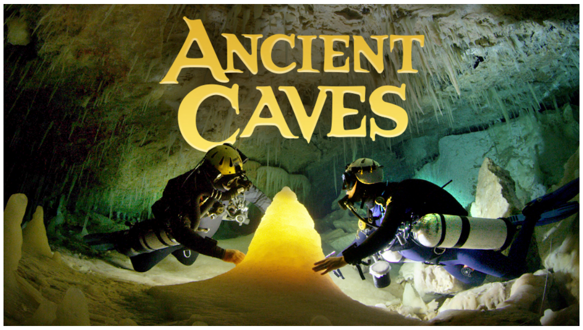
Using a magnesium sulfate and water solution for this demonstration works well as magnesium sulfate is very soluble in water, thereby forming supersaturated solutions. It might be interesting to try this with a table salt or sugar solution.

Students may want to come up with a method to build stalagmites.

The rings or shells of magnesium sulfate forming these straw stalactites mark time.   It might be interesting to put set-ups in different locations, such as near a window or in a refrigerator to compare growth rates of their stalactites and make connections to climate.

Students may try adding colored food dye to identify different points of growth for the stalactites.

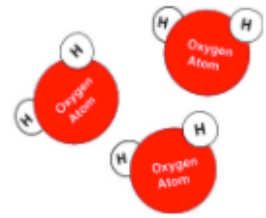
If time and equipment are available, it might be fun to make a time-lapse video of the process.



Exploring the Chemistry of Caves Part 1

Water, the "Universal Solvent"

Water and its special properties.



With just two Hydrogen atoms bonded to a single Oxygen atom, water's molecules are among the smallest and simplest molecules in the universe. Yet, without water's truly special and unique properties, life could not exist on our planet.

Water is a fluid yet dense liquid whose solid form (ice) floats on its liquid state. It is an exceptionally adhesive and cohesive liquid with a high surface tension. Water's high heat capacity allows it to absorb and store a great deal of heat before experiencing changes to its temperature or its physical state. In this way, our ocean helps maintain a temperature range suitable for life on Earth and control our climate.

No liquid dissolves more materials than water, thus earning its nickname, "the universal solvent." Not only can water dissolve a wide variety of substances, but once they're dissolved, water keeps these materials in solution and water is chemically unchanged when this happens. Water's ability to dissolve so many materials is without question one of its most impactful properties to our planet. For example, approximately 70% of the Earth's surface is covered with a saltwater ocean, representing 97% of the Earth's water. Water's ability as a solvent has ultimately led to the chemical weathering that has helped to shape our planet's surface, including the processes that have carved out limestone cave systems.

The link below is to a slide presentation which may be viewed to examine the chemistry behind water and its special and unique properties:

[The Special Properties of Water]

In *Ancient Caves*, we learn that water holds a "fingerprint of climate" in its dissolved materials as well as in the limestone of cave walls and speleothems. Thus the underlying processes involved in "writing" the story revealed in cave deposits, rests with water's amazing ability to dissolve so many materials. We will explore this property of water in the following activity.

Water, the "Universal Solvent"
How is water able to dissolve so many materials?

Classroom Activity: Charged Particles (Ions) in Water

Introduction

In the lesson: *Speleothems and Paleoclimatology* students simulated the growth of stalactites in a two-liter soda bottle, formed from a solution of water and magnesium sulfate (Epsom salt). These features formed from the precipitation of magnesium sulfate coming out of solution as the mineral laden water evaporated. This activity demonstrated the importance of water's unique ability to dissolve many materials in order to form these features in caves.

Background

*When certain materials are dissolved in water, they can often produce a solution that conducts electricity. This happens when water contains atoms and molecules with a positive(+) or negative(-) electromagnetic charge. These "charged" particles are called **"ions"** and are formed when particles exchange electrons in order to form **"ionic bonds."** In these bonds, atoms with opposite magnetic charges (+) (-), attract and bond to create the molecules that make up compounds. You may have heard of ions in sports drinks or dissolved in your bloodstream with another name, "electrolytes." These electrically charged particles such as calcium, potassium, sodium, and iron are critically important to your health as they are needed for many chemical processes in living things.*

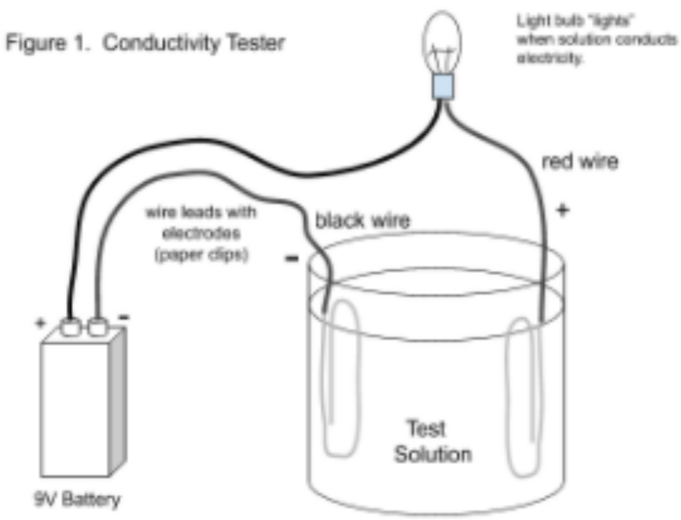
In this activity, we will test the ability of some common compounds to conduct electricity when they are dissolved in water. To do this we will use a student built "conductivity tester." Our results will help us to understand the way that water dissolves materials and will indirectly prove the existence of charged particles called ions and ionic bonds in forming the molecules of certain compounds.

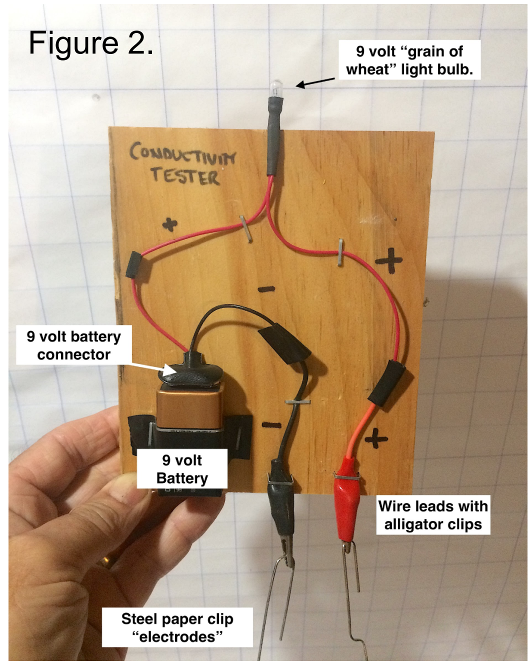
Materials for testing conductivity:
- *9V Battery*
- *9-volt battery connector*
- *grain of wheat*
- *light bulb*
- *Wire leads with alligator clips*
- *Steel paper clips*

Materials for test solutions:
- *Five beakers or clear cups* • *marking pens for labeling cups* • *spoons* • *paper towels*
- *Epsom salt (Magnesium Sulfate), Table salt (Sodium Chloride), White Vinegar, Table Sugar (Sucrose), and Distilled Water.*

Procedure: Assembling a conductivity tester. ***(See figures 1 and 2).***

Assemble your conductivity tester using the diagram below. One design is shown in fig. 2 mounted on a board, but there can be many different versions.

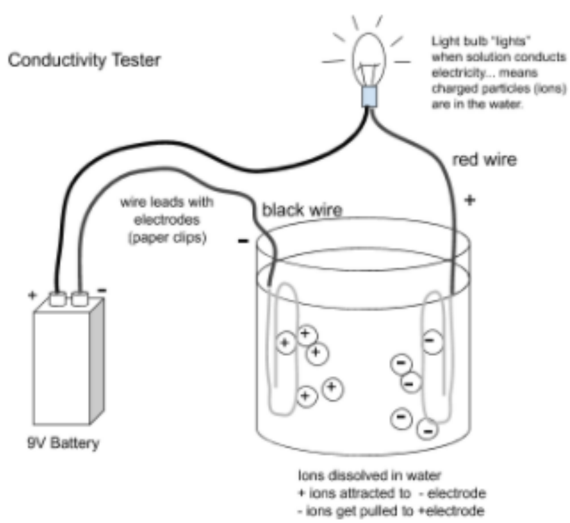


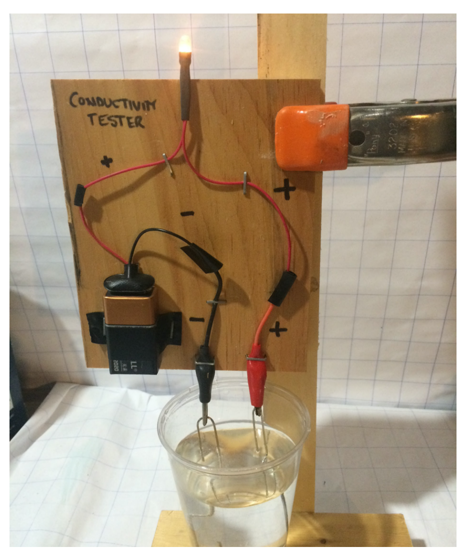


How the conductivity tester works.
An electric current is a flow of electrical charge. When a metal conducts electricity, such as with copper wires, the charge is carried by electrons moving through copper in the wires.

When a **solution** conducts electricity, the charge must be carried by **particles** moving through the solution. These particles **must have** an electrical charge. Some must have a negative charge, and some have a positive charge. These particles are **"ions."** With **ions** in the solution, the electrical charge is carried from the positive paper clip electrode in the solution to the negative paper clip electrode, thus completing the circuit and the bulb will light up.

The solution tested below contains dissolved ions (charged atoms or molecules).





Procedure continued: Preparing test solutions.

Along with distilled or pure water, we will test the conductivity of four compounds when dissolved in water:

1. Epsom Salt or Magnesium Sulfate ($MgSO_4$)
2. Table Salt or Sodium Chloride (NaCl)
3. Table Sugar or Sucrose ($C_{12}H_{22}O_{11}$)
4. Vinegar or Acetic Acid (CH_3COOH)

First: With a marking pen, label the five cups for each of the five solutions being tested.

Next: Make up your solutions of the table salt, Epsom salt, and sugar into their labeled cups.

Add about one spoonful of these materials into cups three quarters filled with distilled water and stir until the material is dissolved.

Then: Add the vinegar and distilled water into their labeled cups until they're about three quarters full.

Experiment: Testing Conductivity of Solutions

First: Check your conductivity tester by touching the paper clip electrodes to each other to test if the bulb lights. If not, you'll need to check your connections and fix any problems.

Next: Test the conductivity of each solution by placing the paper clip electrodes into the solution, being careful not to allow the paper clip electrodes to touch when in the solution.

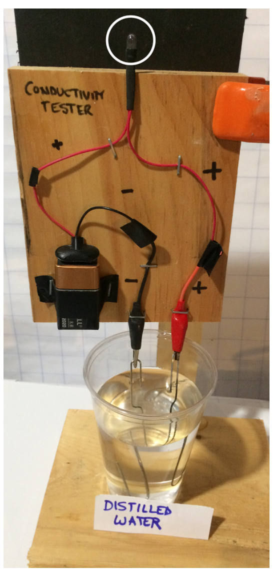
Using a paper towel, wipe off the electrodes between each test.

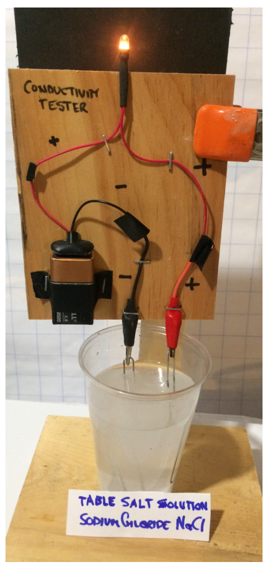
Record the results of each test in the data table below.

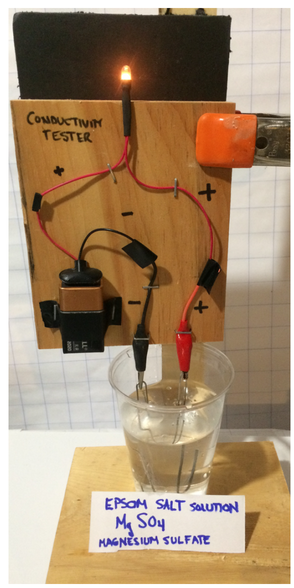
Test Solution	Conducts Electricity (bulb lights) "Yes" or "No"	Are there ions (+/- charged particles) in the solution? "Yes" or "No"
Distilled "Pure" Water (H_2O)		
Table Salt or Sodium Chloride (NaCl)		
Epsom Salt or Magnesium Sulfate ($MgSO_4$)		
Table Sugar or Sucrose ($C_{12}H_{22}O_{11}$)		
Vinegar or Acetic Acid (CH_3COOH)		

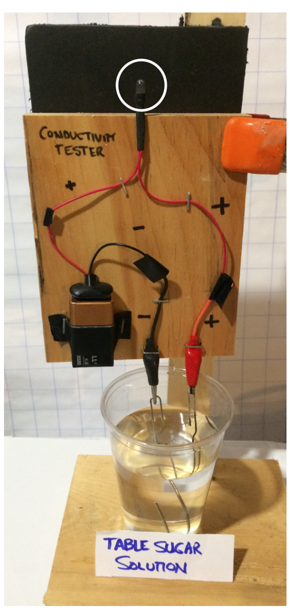
Review of our results.

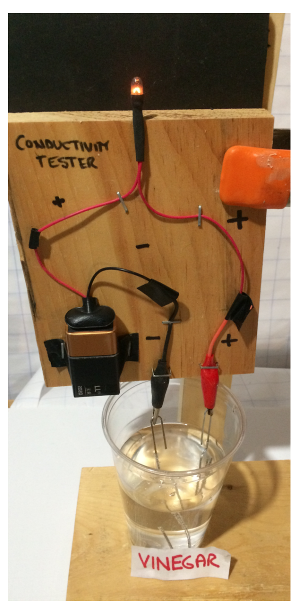
Test Solution	Conducts Electricity (bulb lights) "Yes" or "No"	Are there ions (+/- charged particles) in the solution? "Yes" or "No"
Distilled "Pure" Water (H_2O)	***No***	***No***
Table Salt or Sodium Chloride ($NaCl$)	***Yes***	***Yes***
Epsom Salt or Magnesium Sulfate ($MgSO_4$)	***Yes***	***Yes***
Table Sugar or Sucrose ($C_{12}H_{22}O_{11}$)	***No***	***No***
Vinegar or Acetic Acid (CH_3COOH)	***Yes***	***Yes***









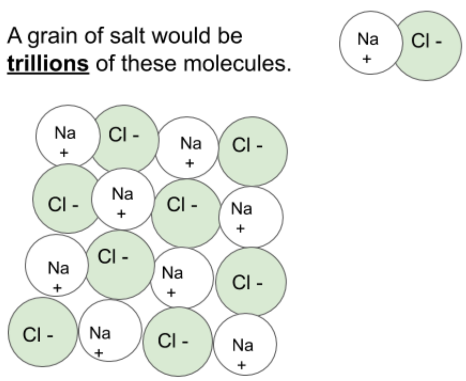


Analyzing our results.

As we examine our results from this experiment, we can see that the distilled (pure) water did not conduct electricity confirming the need for dissolved ions in order for a solution to conduct electricity.

Solutions of sodium chloride and magnesium sulfate conduct electricity and put ions into solution. Both solutions contain metals (sodium and magnesium) in their molecules. It is generally known that atoms of metals form positively charged ions as they lose their (-) electrons to the atoms of non-metals which then become negatively charged ions. With opposite electromagnetic force, the ions get pulled together and form molecules.

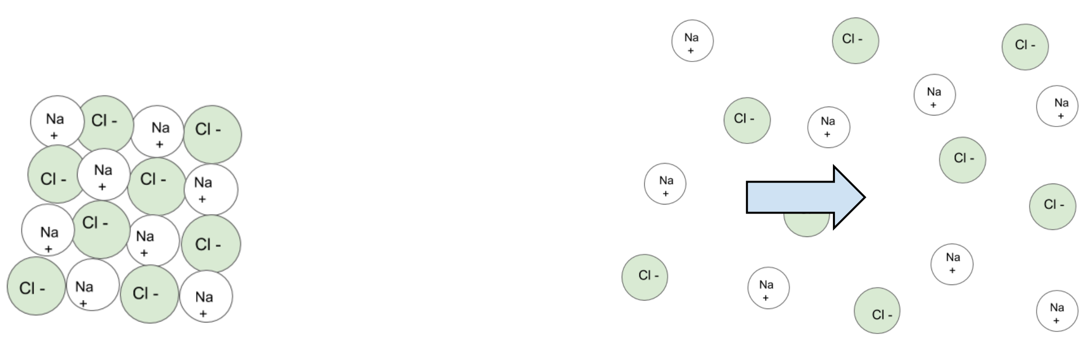
For example, in a molecule of table salt the positively charged sodium ions bond to negatively charged chlorine ions to form molecules of sodium chloride.



Molecules of Sodium Chloride NaCl.
One atom of Sodium ionically
bonded to one atom of Chlorine.

So how does salt dissolve in water?

Water must separate salt into its ions. The evidence is that a saltwater solution conducts electricity.

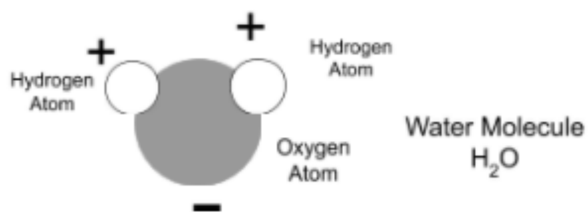


Sodium (Na+)

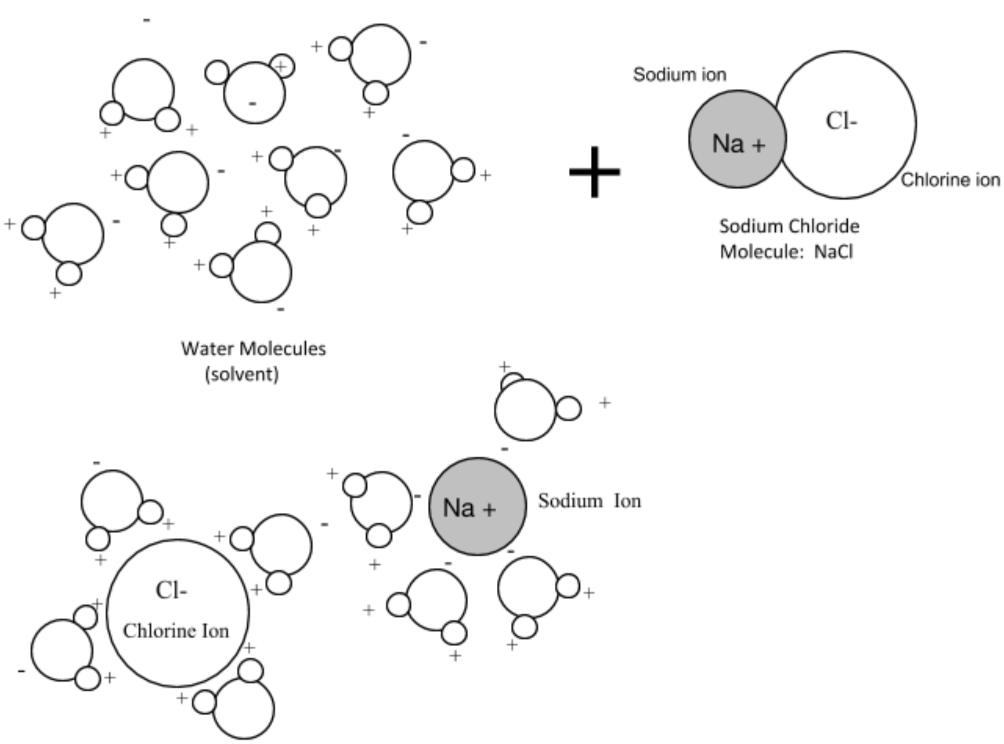
But how is water able to do this?

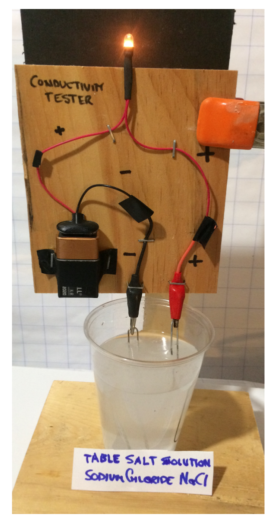
Water: "The Universal Solvent" and the Shape of Its Molecules

Water's ability to dissolve so many substances is due to the shape and structure of its molecules. Water molecules have an unequal arrangement of electrons as there are more electrons near the Oxygen atom giving that side a negative charge. At the end of the molecule, where the Hydrogen atoms are located, there is a positive charge. This results in the water molecule being a "polar" molecule with a positive end and a negative end.



Since water is a polar molecule, it is especially good at dissolving many compounds formed with **ionic bonds** such as those in table salt, Sodium Chloride. Water dissolves this compound by breaking up its ionically bonded molecules into their **ions**.

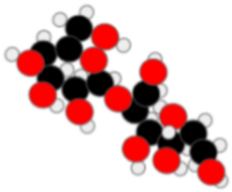




Our evidence

The positively charged (+) ends of the water molecules isolate the negatively charged (-) chlorine ion, while the (-) ends of the water molecules isolate the (+) positive sodium ion, thus water dissolves **ionically bonded** compounds by breaking them down into their ions.

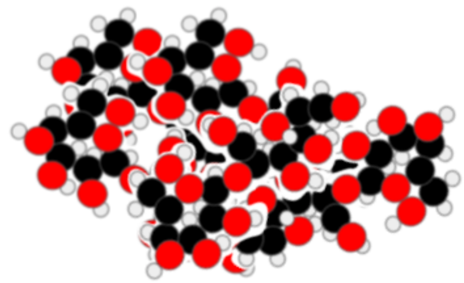
But we saw something different in the way table sugar (or “Sucrose”) dissolves in water.



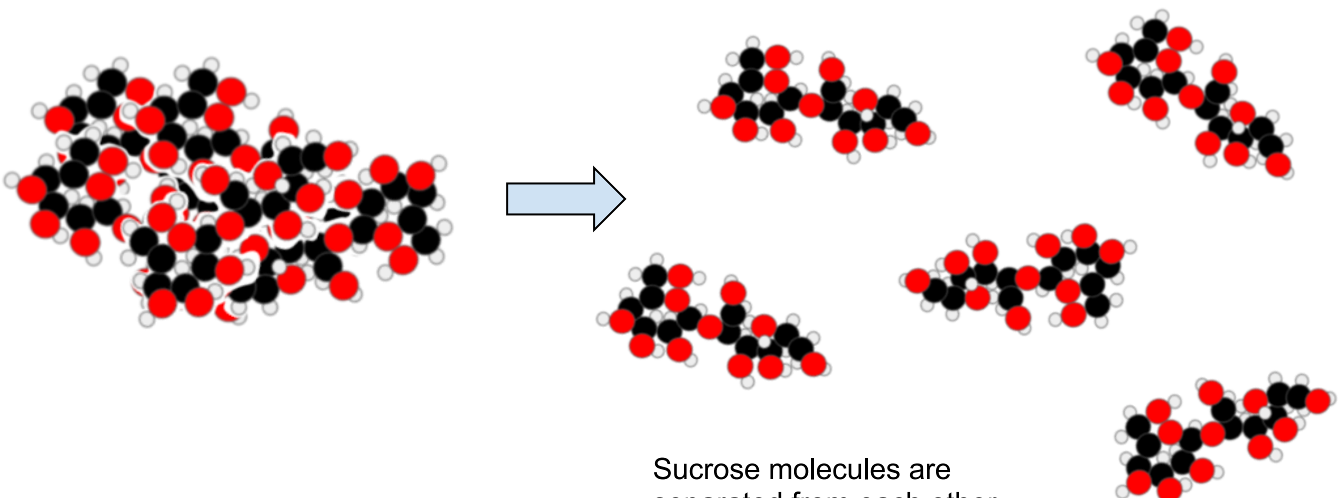
Sucrose molecule.

$C_{12}H_{22}O_{11}$.

12 Carbon atoms, 22 Hydrogen atoms, and11 Oxygen atoms held together by sharing their electrons.



In this chunk of sugar (illustrated here) there are five molecules of Sucrose.
A grain of sugar would be trillions of Sucrose molecules.



Sucrose molecules are separated from each other when dissolved in water.

Water separates individual molecules from one another which are way too tiny to see so the sugar becomes invisible when dissolved. Unlike salt, sugar is not separated into ions when it is dissolved. Our evidence is that a sugar solution does not conduct electricity.

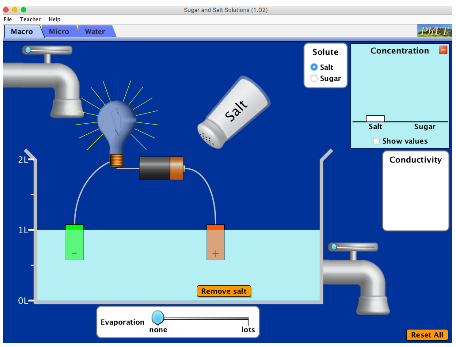
Why is this different than the way salt is dissolved in water?

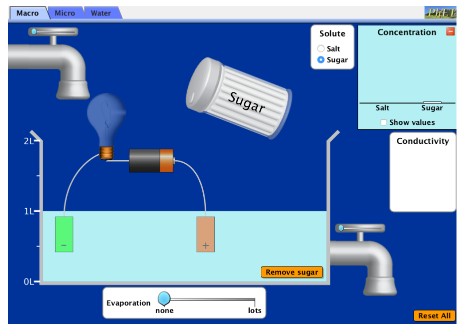
Sugar molecules are organic molecules made of the non-metals: carbon, hydrogen, and oxygen. The atoms in organic molecules like sugar are held together by covalent bonds not ionic; they share electrons in order to bond. But like salt, sugar dissolves easily in water. This is because sugar molecules (not their atoms) are held together by + and - forces from hydrogen and oxygen atoms in the sugar molecule. Thus, water dissolves sugar by separating its molecules not by separating it into ions.

To help you reinforce and improve your understanding of this lesson, I would encourage you to check out this activity: *Sugar and Salt Solutions*, from PHET Interactive Simulations produced by the University of Colorado at Boulder. *(images from this simulation are shown below).*

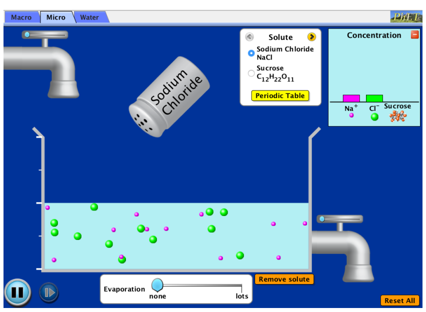
https://phet.colorado.edu/en/simulation/sugar-and-salt-solution

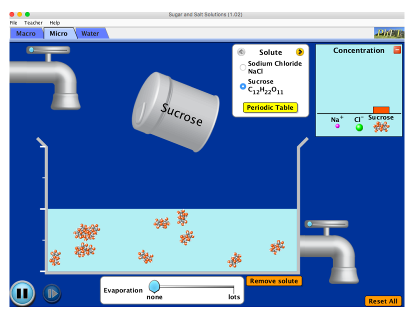
Part 1: Conductivity of salt vs. sugar in solution.

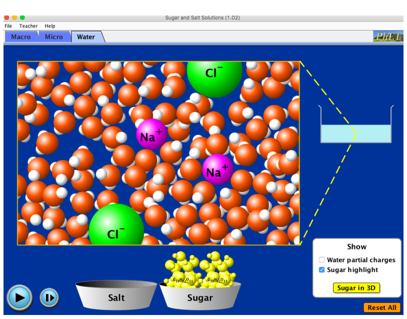


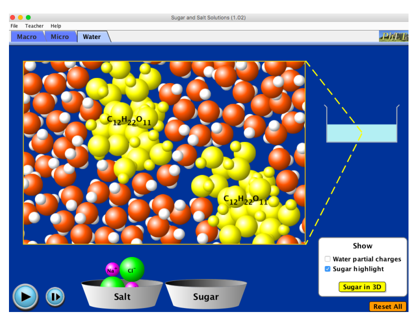


Parts 2 and 3 compare the dissolving of sugar in water at the molecular level.









An important observation in this activity.

Vinegar (acetic acid solution) conducted electricity. Like sugar, it is an organic molecule made of non-metals: hydrogen, oxygen, and carbon. Then like sugar, one would expect that it would not dissolve in a manner that releases ions.

Since it conducts electricity, vinegar must release ions into the solution. This is an important property of acids. We will examine this characteristic of acids like vinegar in the second part of this exploration into the chemistry of caves, in which "acidity" has a major role.

Follow up to: *Water, the "Universal Solvent"*

Water's ability as a solvent is without question one of its most impactful properties on our planet. Water's ability as an excellent solvent has led to the chemical weathering that has helped to shape our planet's surface. Approximately 70% of the Earth's surface is covered with a saltwater ocean, representing about 97% of the Earth's water. This is where life on Earth began. Would life have gotten its start if water hadn't washed over the rocky surface of an early Earth, and dissolved the minerals forming our saltwater ocean?

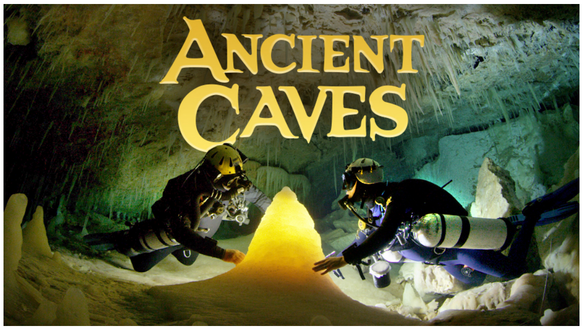
The scientific basis for the story behind *Ancient Caves,* is the record of Earth's ancient climate *written* in the mineral composition of water and the limestone layers within caves. Since water can dissolve a wide variety of materials as it passes through soil and bedrock, it can carry and leave behind a chemical record in cave deposits for the conditions at that period in time.

Organic molecules within limestone layers might hold clues as to the conditions outside the cave at that time, such as temperature, vegetation, and soil conditions. Water is able to dissolve trace amounts of Uranium from minerals in the bedrock above a cave system, which can become part of the materials deposited in each layer of a speleothem. Thus, scientists are able to take advantage of the ratio of radioactive Uranium to Thorium in order to determine the age of layers in the limestone deposits of caves.

Returning to our original question

With water's ability to dissolve so many materials it is not able to dissolve calcium carbonate, the mineral compound that makes up limestone. Then, how is calcium carbonate in bedrock able to get into the groundwater and then become deposited and form the limestone features caves?

In part 2 of our lesson: *The Chemistry of Caves,* we will investigate the answer to this question.



Exploring the Chemistry of Caves Part 2

Limestone, acidity, and pH
A question and a hypothesis

Introduction

The science behind the story in *Ancient Caves* is based on the chemical record in the limestone deposits in caves during different time periods. We know that these deposits are left behind as water drips into caves and evaporates, as shown in the lesson: *Speleothems and Paleoclimatology*.

To form these deposits, the calcium carbonate in soil and bedrock must be dissolved in the groundwater and seep into caves. However, in *Ancient Caves* the limestone features formed in caves do not dissolve when caves become flooded, as in the underwater cave system of Abaco Island shown below.

We also know that the limestone exoskeletons of corals, mollusks, and other aquatic creatures do not dissolve in water. Even when hard boiling an egg, its calcium carbonate shells do not dissolve. Thus we're left with a couple of questions.

Since calcium carbonate is not soluble in water, then how does it get into the groundwater, and become deposited to build the limestone formations in caves? Why don't the limestone formations "re-dissolve" in flooded caves?

In this second part of our investigation into the chemistry of caves, we will develop a hypothesis and learn the background information needed to answer these questions and gain a better understanding of the chemistry in limestone caves.

Class Discussion: Forming a hypothesis to the following question.

If calcium carbonate does not dissolve in water, then how is it able to get into the groundwater that seeps into caves?

Record any thoughts or ideas that you may have that might lead to an answer to this question.

____

____

____

____

We know that caves flooded with seawater do not dissolve limestone deposits. What is different about seawater and the water that must be dissolving calcium carbonate for cave deposits?

Does salt prevent water from dissolving limestone?

Think about a pot of boiling tap water, can that dissolve the calcium carbonate shell of an egg? ______

So can salt be a factor? _____

The water that must be dissolving calcium carbonate to form limestone deposits in caves is rainwater.

Maybe there is something chemically different about rainwater.

Let's look at a basic water quality measurement, pH. pH is a measure of the water's acidity.

Classroom Activity: Comparing the pH of rainwater, tap water, and seawater.

If possible, collect a sample of rainwater, tapwater, and seawater in a clean, dry, well rinsed container.

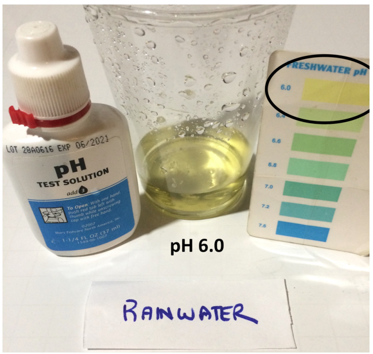
Test the pH of each sample using a pH meter, precision pH paper, or aquarium pH indicator solution and record the results below.

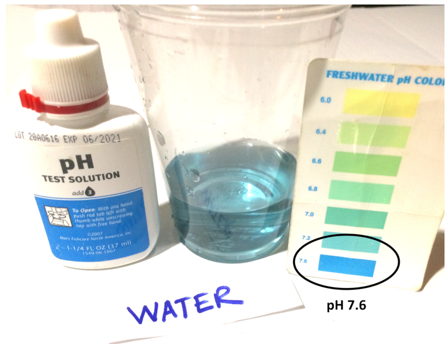
Rainwater	Tapwater	Seawater
pH = _____	pH = _____	pH= ______

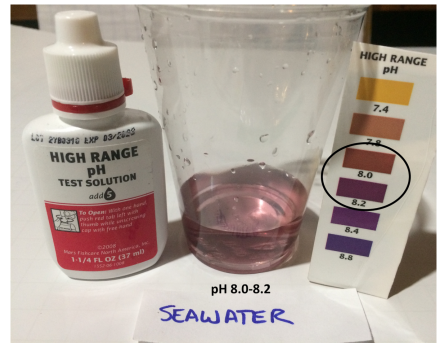
If unable to conduct this activity, there are the results for the pH of water samples on the next page

Results:

Pictured below is the acidity (pH) for actual samples of rainwater, tap water, and seawater using pH indicator solutions from “Aquarium Pharmaceuticals.”







Rainwater has a lower pH and is more **acidic** than either tap water or seawater. So perhaps being “**acidic”** gives rainwater the ability to dissolve calcium carbonate.

This is a hypothesis that we can and will test in Part 3 of this investigation into the chemistry of caves. However, before testing this hypothesis we should have a basic understanding of acidity and pH.

With an understanding of acidity, we can learn why rainwater is normally acidic. In addition we can understand how being acidic may give rainwater the ability to dissolve calcium carbonate ($CaCO_3$) which must happen in order to form limestone deposits in caves.

As we continue with Part 2 of our investigation into the chemistry of caves, we will examine acids, acidity, and pH.

What is an acid and acidity?

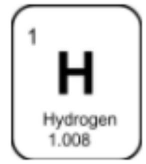
Acids are a large group of compounds known for their sour taste and corrosive properties. ***Corrosive*** *means that they chemically break down or “eat away” certain materials.* The word acid comes from the Latin name for sour which is *“acidus.”* Examples: vinegar and citric acid in citrus fruits.

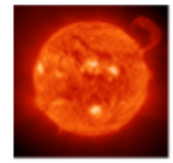
Here are a just a few common acids and their chemical formulas :

- Hydrochloric Acid (HCl)
- Nitric Acid (HNO_3)
- Sulfuric Acid (H_2SO_4)
- Carbonic Acid (H_2CO_3)

From their chemical formulas, it appears that hydrogen is the defining element in acids.

The Element Hydrogen




nasa.gov

With atoms of just one proton and one electron, hydrogen is made of the simplest atoms, but it is the element from which we owe our existence. Ninety percent of the visible universe is hydrogen. Our Sun and other stars are giant balls of hydrogen whose energy comes from the nuclear fusion of hydrogen atoms into atoms of helium. On Earth, hydrogen is a key element in all of the organic compounds that make up living things. It is in many of the compounds that form the Earth's crust, and of course without hydrogen we would not have water.


The Hindenburg explosion. May 6,1937. Lakehurst, NJ. *History.com*

Pure hydrogen exists as a gas which is too light to be held by Earth's gravity. It is very reactive with oxygen, making it dangerous and flammable. Since it is such a light gas, hydrogen was used to float airships until the Hindenburg disaster in 1937, which unfortunately exposed hydrogen's dangerous properties. Blimps and balloons are now filled with helium to float in the air.

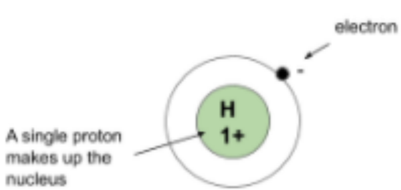
Dissolved Hydrogen in Acids

On the previous page we saw that hydrogen is the one element that all acids share and is a key part of their chemical makeup. Acids are very soluble in water dissolving a form of hydrogen into the solution. It is this dissolved form of hydrogen that gives acids their sour taste and corrosive properties.

Perhaps it's the dissolved hydrogen that gives acidic rainwater the ability to break down limestone.

In water, dissolved hydrogen is in the form of positively charged particles called "hydrogen ions" (H^+), which are hydrogen atoms that have lost their electron, (see below). Remember, in part 1 of this investigation, we saw that a vinegar solution was able to conduct electricity (see image below). This provides evidence that acids release charged particles or ions in solution, namely hydrogen ions. It is these H^+ ions that give acids their properties. When you experience a sour taste, your taste buds are detecting H^+ ions. At high concentrations hydrogen ions are corrosive and harmful to living things.

The definition of an acid is a compound that when dissolved in water releases hydrogen ions (H^+).



A neutral Hydrogen atom *(1 proton and 1 electron)*

A hydrogen Ion is a charged hydrogen atom which has lost its electron giving it a net charge +1.

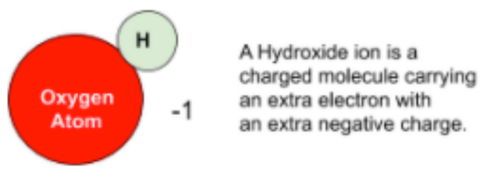
Vinegar solution conducts electricity with our conductivity tester.

To help us to better understand acidity it's worth discussing their "opposite" in the chemical world which are compounds known as **"bases."**

Here is a list of some common bases and their chemical formulas.

Common Bases: Sodium Hydroxide $NaOH$ Potassium Hydroxide KOH
Calcium Hydroxide $Ca(OH)_2$ Magnesium Hydroxide $Mg(OH)_2$

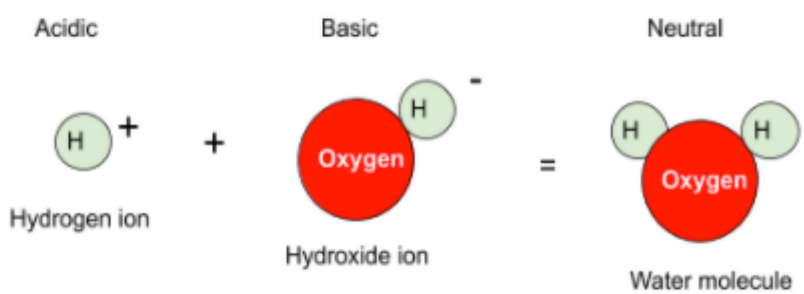
Like acids, bases are also easily dissolved water, *but* release Hydroxide ions (OH^-) when dissolved in water.



Hydroxide ions destroy organic molecules, such as proteins, fats, and oils. Cleaning agents are "basic" so they're good at removing stains from clothing and cleaning greasy oily messes. They have a bitter taste and slippery feel. Soaps, detergents, and shampoos are typically basic.

Acids can be neutralized by bases and bases are neutralized by acids.

The (H^+) ions in a solution from an acid are "neutralized" by hydroxide ions (OH^-) by bonding to form "neutral" molecules of water. Bases sort of "cancel out" the effects of acids.

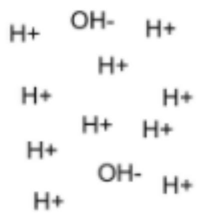


When the (H^+) ions in water is equal to the hydroxide ions (OH^-) you simply will have water.... a "neutral" solution... neither acidic or basic.

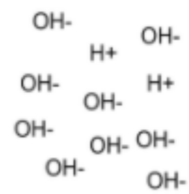
An everyday example of this process can be seen in our use of bases like calcium hydroxide or magnesium hydroxide which are found in medications called "antacids." We may use antacids to neutralize stomach acid and help bring relief to an upset stomach.

Acidity and pH.

"pH" stands for the *potential or power of hydrogen.* pH measures the concentration of H^+ ions in water which is a solution's **"acidity."** pH is only a characteristic of **"aqueous"** solutions, which are solutions of dissolved materials in water. pH is not a property measured in other liquids such as oils.



Acidic low pH
(higher concentration of H+ ions than OH- ions)



Basic or "Alkaline" high pH
(Higher concentration of OH- than H+ ions)

The pH scale

pH is measured on a scale from 0-14. Where a low pH represents an acidic solution in water and a high pH is basic. Pure water has a pH of 7 and is considered to have a neutral pH.

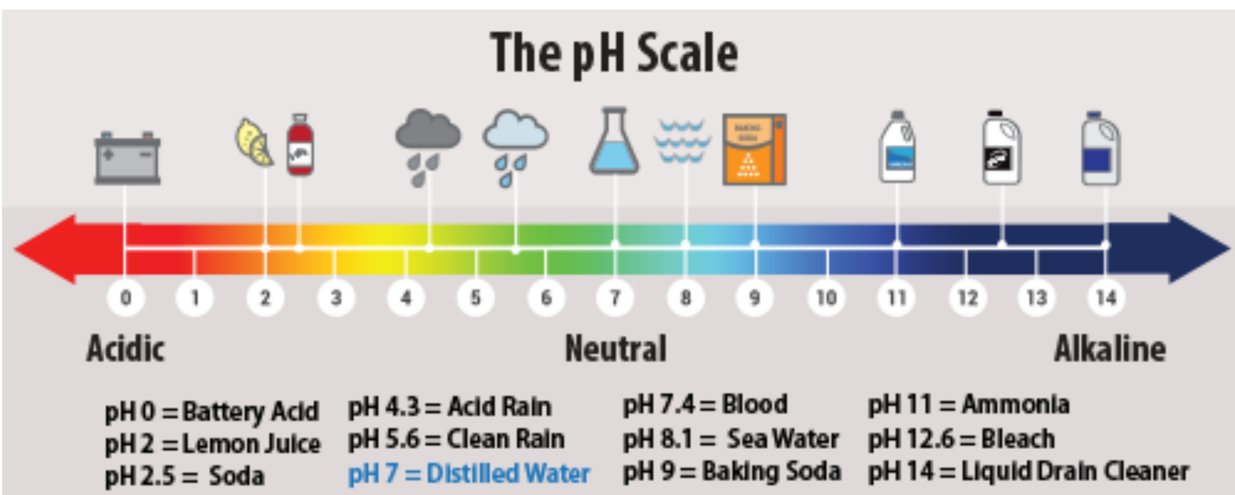


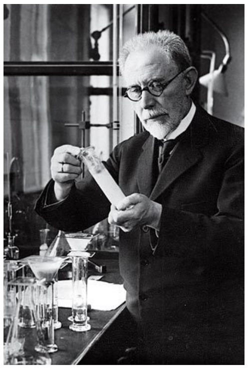
Diagram from: What is Acid Rain? United States Environmental Protection Agency. *https://www.epa.gov/acidrain/what-acid-rain*

The lower the pH the higher the acidity of a solution. This seems confusing so let's look at how the pH scale works.

How does the pH scale work? Why would a lower pH mean a <u>higher</u> acidity?

The pH scale is a **<u>logarithmic scale</u>**. Each step increase on the scale is ten times that of the previous step.

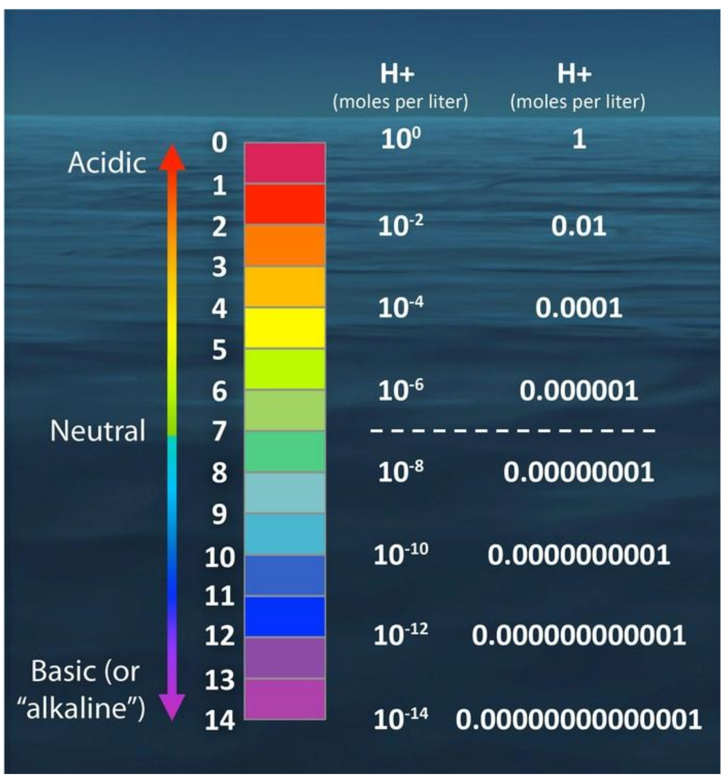
For example, a pH of 2 has an acidity that is a ten times stronger acid than that of a pH of 3. A solution with a pH of 2 is 100 times more acidic than a solution with a pH of 4. Thus a small change in pH is a big difference in acidity.



Danish scientist Dr. Søren Sørensen developed the pH scale in 1909.

A H^+ ion concentration of "1.0".. means that there is one **MOLE** of H+ ions per liter. *A "MOLE" is a standard quantity of particles..like a pair or dozen..except this quantity is huge..really huge .. a mole is 6.02 x 10^{23} particles (that's 6 hundred billion trillion particles!)*

The diagram below is from "The pH scale by numbers." PMEL Carbon Program. National Oceanic and Atmospheric Administration.
https://www.pmel.noaa.gov/co2/file/The+pH+scale+by+numbers



In the pH scale, **the pH number represents a decimal place** or a negative power of 10.

For example a pH of "4" is a H^+ ion concentration of 0.0001 (four decimal places) or 1 x 10^{-4}, which is weakly acid.

A pH of "3" is a H^+ ion concentration of 0.001 or 1 x10^{--3}… 10 times stronger acid than pH of 4.

A pH of "2" is a H^+ ion concentration of 0.01 or 1 x10^{-2}… 100 times stronger acid than pH of 4.

A pH of 0 has a H^+ ion concentration of 1.0 or 1 x10^0… 10,000 times stronger acid than pH of 4.

Thus, a STRONG acid has a LOW pH and one step on the pH scale is a big difference in acidity... a ten-fold difference

Follow up questions:

1. What are acids? ____

____

2. What is meant by "acidity"? ____

____

3 . The pH scale measures ____

4. Describe what happens to the concentration of H^+ ions for every step **<u>decrease</u>** on the pH scale.

____

5 a. What is the H+ ion concentration in a solution with:

a pH of 5? ________________ a pH of 2? ________________

b. So.. which is more acidic: a solution with a pH of 2 or a solution with a pH of 5 ? _______

c. How many times more acidic? ____________

6a. As pH **<u>increases</u>**: the acidity _________________ so the H+ ion concentration _____________________

b. As pH **<u>decreases</u>**: the acidity _________________ so the H+ ion concentration ____________________

7. A neutral solution means that the pH = _______ .

An H+ ion bonded to an OH- ion . would turn into a molecule of ________________________

8. Suppose a sample of rainwater has a pH of 6, and a sample of tap water has a pH of 7.

If there is only a difference of one step on the pH scale, then is rainwater really that chemically different from tap water?

_________ Explain your answer. ____

____

Reviewing student responses in this lesson.

From page 3. Here are a just a few common acids and their chemical formulas :

- Hydrochloric Acid (HCl)
- Sulfuric Acid (H_2SO_4)
- Nitric Acid (HNO_3)
- Carbonic Acid (H_2CO_3)

From their chemical formulas what do they all have in common ?

From their chemical formulas, acids have the element hydrogen in their makeup.

Follow up questions from pp. 7-8.

1. What are acids? *Acids are compounds that when dissolved in water, release hydrogen ions in solution.*

2. What is meant by "acidity"? *Acidity is the concentration of hydrogen ions in solution.*

3 . The pH scale measures *The pH scale measures acidity or the concentration of hydrogen ions in solution.*

4. Describe what happens to the concentration of H^+ ions for every step **decrease** on the pH scale.

The concentration of hydrogen ions increases by a factor of ten for every step decrease on the pH scale.

5 a. What is the H+ ion concentration in a solution with:

a pH of 5? *1/100,000* a pH of 2? *1/100* .

b. So.. which is more acidic: a solution with a pH of 2 or a solution with a pH of 5 ? *a pH of 2* .

c. How many times more acidic? *1000 times more acidic .*

6a. As pH **increases**: the acidity *decreases* so the H+ ion concentration *also decreases* .

b. As pH **decreases**: the acidity *increases* so the H+ ion concentration *also increases* .

7. A neutral solution means that the pH = _7_.

An H+ ion bonded to an OH- ion . would turn into a molecule of _water (H_2O)_.

8. Suppose a sample of rainwater has a pH of 6, and a sample of tap water has a pH of 7.

If there is only a difference of one step on the pH scale, then is rainwater really that chemically different from tap water?

Yes Explain your answer. _A difference in pH from 7 to 6 is means that this sample of rainwater is ten times more acidic than the tap water which would make the rainwater very different chemically._

Resources used for the background text and images in this lesson.

"Acids and Bases are Everywhere." Chem4Kids.com. Andrew Rader Studios. http://www.chem4kids.com/files/react_acidbase.html

"Ancient Caves." MacGillivray Freeman Films. Produced by Oceanic Research Group, Inc. 2020.

"pH and Water." Water Science School. United States Geological Service. https://www.usgs.gov/special-topic/water-science-school/science/ph-and-water?qt-science_center_objects=0#qt-scien

"The Hindenburg Disaster." History.com. Updated: May4, 2020. https://www.history.com/this-day-in-history/the-hindenburg-disaster

"The pH scale by numbers." PMEL Carbon Program. National Oceanic and Atmospheric Administration. https://www.pmel.noaa.gov/co2/file/The+pH+scale+by+numbers

"What is Acid Rain?" United States Environmental Protection Agency. Updated: May 12, 2020. https://www.epa.gov/acidrain/what-acid-rain

"Where Does the Sun's Energy Come From?" NASA Science Space Place. Updated: September 10, 2020. https://spaceplace.nasa.gov/sun-heat/en/

The Chemistry of Caves Part 2.
Limestone, acidity, and pH.

Follow up activity: Visualizing pH and acidity with food dye

Acids are compounds that release H^+ ions when dissolved in water and give acids their properties. With a pH less than 7.0, rainwater is acidic and has hydrogen ions in solution. it may be that its lower pH is responsible for its ability to dissolve calcium carbonate which would lead to the formation of limestone deposits in caves.

A measurement of acidity is represented on the pH scale, but this can be confusing because the lower the number on the pH scale, the greater or stronger the acidity. A low pH = high acidity? .. how is that explained?

In this activity we will visualize how acidity and the pH scale work by diluting food dye in a series of spoons representing steps on the acidic part of the pH scale 1-6. The food dye will represent hydrogen ions at a pH of "0."

Materials for each lab group:

• food dye (representing "H^+ ions") • 6 plastic spoons labeled with their pH (see photo below)

• a cup of water • a separate "rinse cup" used for waste when rinsing pipettes

• two droppers or small pipettes : one for transferring water to spoons and one for colored water

Procedure:
1. Line up six plastic spoons with increasing pH 1-6 as shown in the photo .

Before continuing, study the diagram on next page to get an idea of how you will dilute water with food dye in a step by step (spoon to spoon) manner, to demonstrate changes to acidity as pH increases.

Now begin the series of dilutions.

2. Place one drop of food dye from its bottle into the first spoon. **The food dye will represent H^+ ions.**

With the dropper designated FOR WATER ONLY.... dilute the dye by adding nine drops of water to the dye in that spoon.

• What will be the concentration of dye " (H^+) ions " in this first spoon? ... one part in _____.

The concentration of dye in this first spoon will represent the concentration of H^+ ions at a pH of 1.

A pH of " 1 " represents an acidity "1/10th" that of the highest concentration of H^+ ions.

3. Next, with the dropper designated FOR COLORED WATER, add one drop of the dye/water solution from the first spoon (pH 1) to the next spoon in the series (pH 2).

Dilute this drop of colored water in the second spoon by adding nine drops of clean water .

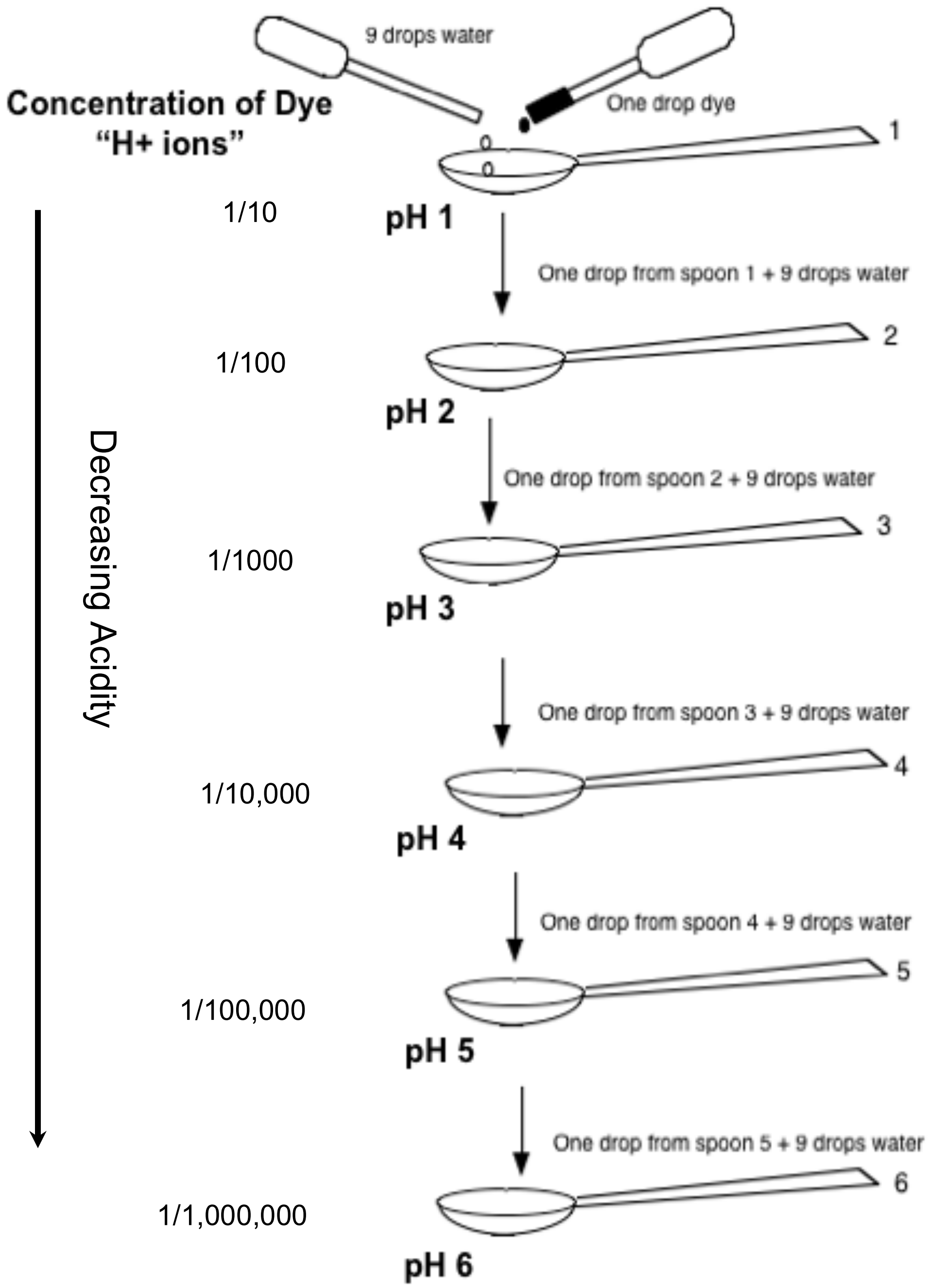
• What will be the concentration of dye " (H^+) ions " in this second spoon? . one part in ________.

The concentration of dye in this second spoon will represent the concentration of H^+ ions at a pH of 2.

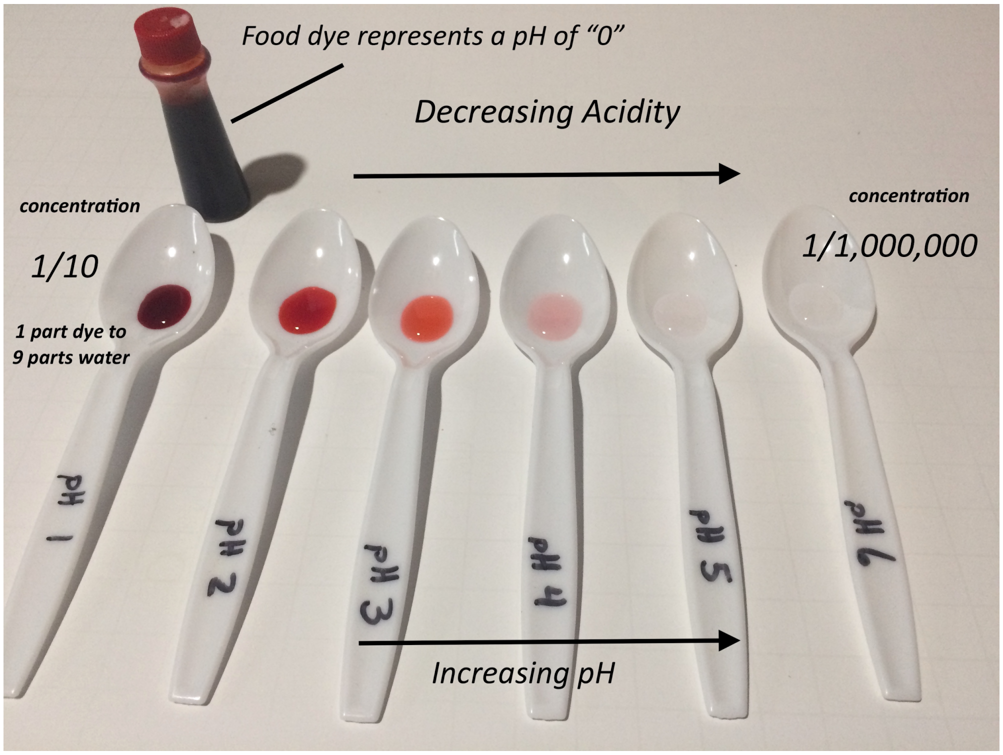
A pH of " 2 " represents an acidity "1/100th" that of the highest concentration of H^+ ions.

IMPORTANT: Rinse the dropper that is used for transferring colored water with clean water and squirting it into the rinse cup.

4. While referring to the diagram on the next page, repeat the step by step dilution of colored water until a concentration of food dye is at a pH of 6.


9 drops water
One drop dye
Concentration of Dye
“H+ ions”
1
1/10
pH 1
One drop from spoon 1 + 9 drops water
2
1/100
pH 2
One drop from spoon 2 + 9 drops water
3
1/1000
pH 3
Decreasing Acidity
One drop from spoon 3 + 9 drops water
4
1/10,000
pH 4
One drop from spoon 4 + 9 drops water
5
1/100,000
pH 5
One drop from spoon 5 + 9 drops water
6
1/1,000,000
pH 6

Reviewing the results



With this activity we can visualize how an <u>increase</u> in pH is actually a <u>decrease</u> in acidity.

From the second page of this activity.

- What will be the concentration of dye " (H^+) ions " in this first spoon? ... one part in **10 .**

- What will be the concentration of dye " (H^+) ions " in this second spoon? . one part in **100 .**

We can see that as we go from one spoon to the next, the concentration of the dye gets ten times weaker. In this way we're representing the pH scale . With each step increase in pH, acidity becomes ten times weaker than the previous step.

So, a solution with a pH of 1 is :

• 10 times more acidic than a solution with a pH of 2.

• 100 times more acidic than a solution with a pH of 3.

• 1000 times more acidic than a solution with a pH of 4.

and so on.

Reflection.

Why might understanding pH be important to our investigation into the chemistry of caves ?

Without being able to dissolve calcium carbonate, limestone deposits would not have formed in caves. Since seawater is unable to dissolve calcium carbonate, limestone formations in flooded caves remain intact and a record of Earth's climate can be preserved and studied.

We believe that rainwater having a lower pH than tap water or seawater may give rainwater the ability to dissolve calcium carbonate, whereas tap water and seawater cannot. But does rainwater's pH of 6.0 make it all that different from tap water or seawater? Can a slightly lower pH really make that much of a difference to rainwater's chemistry?

Since each step lower on the pH scale is a ten fold increase in acidity, rainwater with a pH of just 6 is at least 10 times more acidic than tap water and over 100 times more acidic than seawater! Thus, rainwater is not "slightly" more acidic than tap water or seawater and having a pH of just 6.0, can make rainwater very different chemically from tap water or seawater.

The relevance of understanding pH around a major environmental concern for our ocean… ocean acidification.

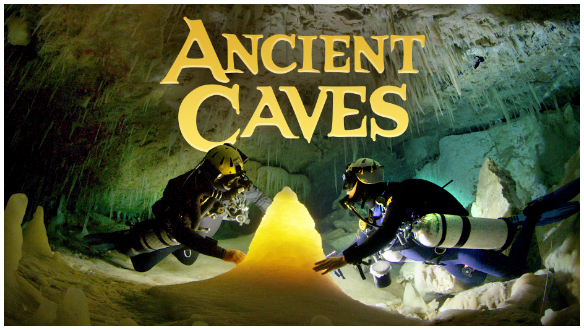
Our oceans are increasing in acidity due to the burning of fossil fuels. Since the industrial revolution the oceans average pH has dropped from a pH of 8.2 to 8.1 which doesn't seem like much but this represents a 30 percent increase in the ocean's acidity!

If this trend continues the ocean may have a pH of 7.8-7.9 by the end of this century, representing an increase in acidity which would have devastating effects on much of our marine life.

"If we continue on the expected trajectory for fossil-fuel use and rising atmospheric CO_2, pH is likely to drop by 0.3-0.4 units by the end of the 21st century and increase ocean hydrogen ion concentration (or acidity) by 100-150% above what it was in preindustrial times."— Scott Doney, Senior Scientist, Woods Hole Oceanographic Institution, USA.

Resource: "FAQ's about Ocean Acidification." Woods Hole Oceanographic Institution.
https://www.whoi.edu/know-your-ocean/ocean-topics/ocean-chemistry/ocean-acidification/faqs-about-ocean-acidification/

Hopefully this activity has helped you to have a better understanding of pH and that even small changes to pH can have significant effects. In part 3 of our investigation into the chemistry of caves, we will test to see if acidity is a factor in dissolving calcium carbonate and look at how rainwater becomes acidic.



Exploring the Chemistry of Caves Part 3

Experimentation:
Testing our hypothesis

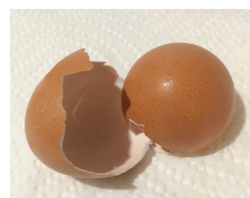
Introduction

Whether it's the exoskeletons of marine creatures or stalactites and stalagmites, we know that limestone is not soluble in tap water or seawater. Then how is calcium carbonate able to dissolve to form limestone deposits in caves? In part 2 of this investigation, we developed a hypothesis that claimed the acidity of rainwater may give it the ability to breakdown calcium carbonate and deposit its dissolved materials in caves to form limestone deposits.

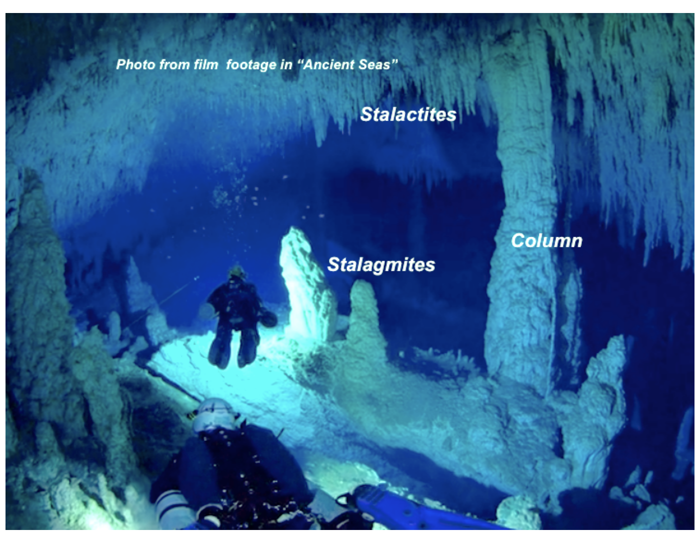
In this part of our investigation, we will test to see if acidity is a factor in dissolving calcium carbonate and look at how rainwater becomes acidic. Our results will either prove or disprove our hypothesis and hopefully help us gain a better understanding of cave chemistry.

Activity 1: An Egg in Vinegar
Dissolving Limestone in Acid vs. Water

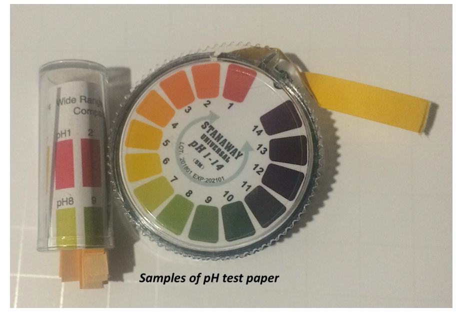
In nature, limestone or calcium carbonate can come in many forms such as a seashell, piece of coral, a rock of limestone, or even the shell of chicken egg.



We've seen that rainwater can be acidic whereas seawater and freshwater from other sources are not. Perhaps being **acidic** can give rainwater the ability to dissolve calcium carbonate. In this activity we will test this idea by examining the ability of an acidic solution, household vinegar, to dissolve the calcium carbonate or limestone shell of a chicken egg.



Materials:


Samples of pH test paper

•Two clear plastic cups or beakers *(large enough to hold a submerged egg).*

• Two chicken eggs • White Vinegar (Acetic Acid) • Tap Water

• Tweezers • Paper Towels • pH test paper with color chart

Procedure:

Fill a cup or beaker about two thirds with water and one with an equal amount of vinegar.

Measuring the pH of vinegar and tap water.

1. Test the pH of the tap water and vinegar at the start of this experiment using two small strips of pH paper, 1 inch / 3cm in length.

2. In each liquid and using tweezers, dip and QUICKLY REMOVE one of these strips of pH paper.

3. While holding the pH paper strip outside the cup, let the color of the paper develop for 30 seconds.

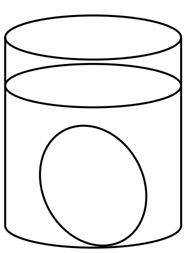
4. Next, match this color to that on the pH color scale for that paper.

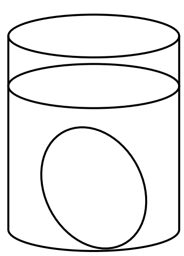
5. From the color of the strip, record the pH of the tap water and vinegar in the data table on the next page.

Comparing the ability of calcium carbonate (limestone) to dissolve in water and vinegar.

1. Carefully place one chicken egg in the cup with water and one in the cup with vinegar.

2. Watch each egg for several minutes and record your observations in the data table.


Egg in water


Egg in vinegar

3. Let the eggs sit in the two cups overnight, and examine each set up the next day.

The next day.

1. Once again, determine the pH of the water and vinegar using pH test paper strips and record the pH of each liquid in the data table.

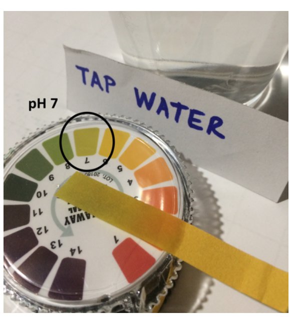
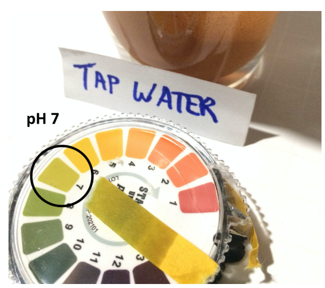
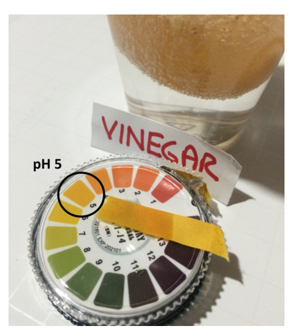
2. Gently remove the eggs from each cup and dry them with a paper towel. Place each on a paper towel and carefully examine the condition of the shell for each egg. Record your observations in the data table.

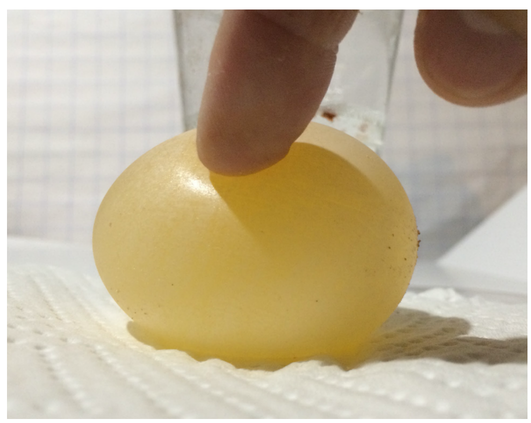
Data table showing the results of our experiment comparing an egg in vinegar and in tap water as well a record of the acidity (pH) for the tap water and vinegar solution over a 24 hour period.

Egg	Start of Experiment	Next Day
Egg in Tap Water	pH ______ Observations: ______________________ __________________________________ __________________________________	pH ______ Observations: __________________________ ______________________________________ ______________________________________
Egg in Vinegar	pH ______ Observations: ______________________ _________________________________ __________________________________	pH ______ Observations: __________________________ ______________________________________ ______________________________________

Review of the results
(instructor's copy)

Egg	Start of Experiment	Next Day
Egg in Tap Water	pH 7 Observations: *There are no changes taking place to the egg.*	pH 7 *no change* Observations: *After removing the egg from the water, it appears that there has been no change to the shell*
Egg in Vinegar	pH 2 *acidic* Observations: *Bubbles are forming all over the eggshell. The egg floats as bubbles collect on the eggshell.*	pH 5 *pH increased* Observations: *Bubbles cover the egg. After removing the egg from the cup and wiping it off, it no longer has a shell. The Egg is like a rubber ball.*

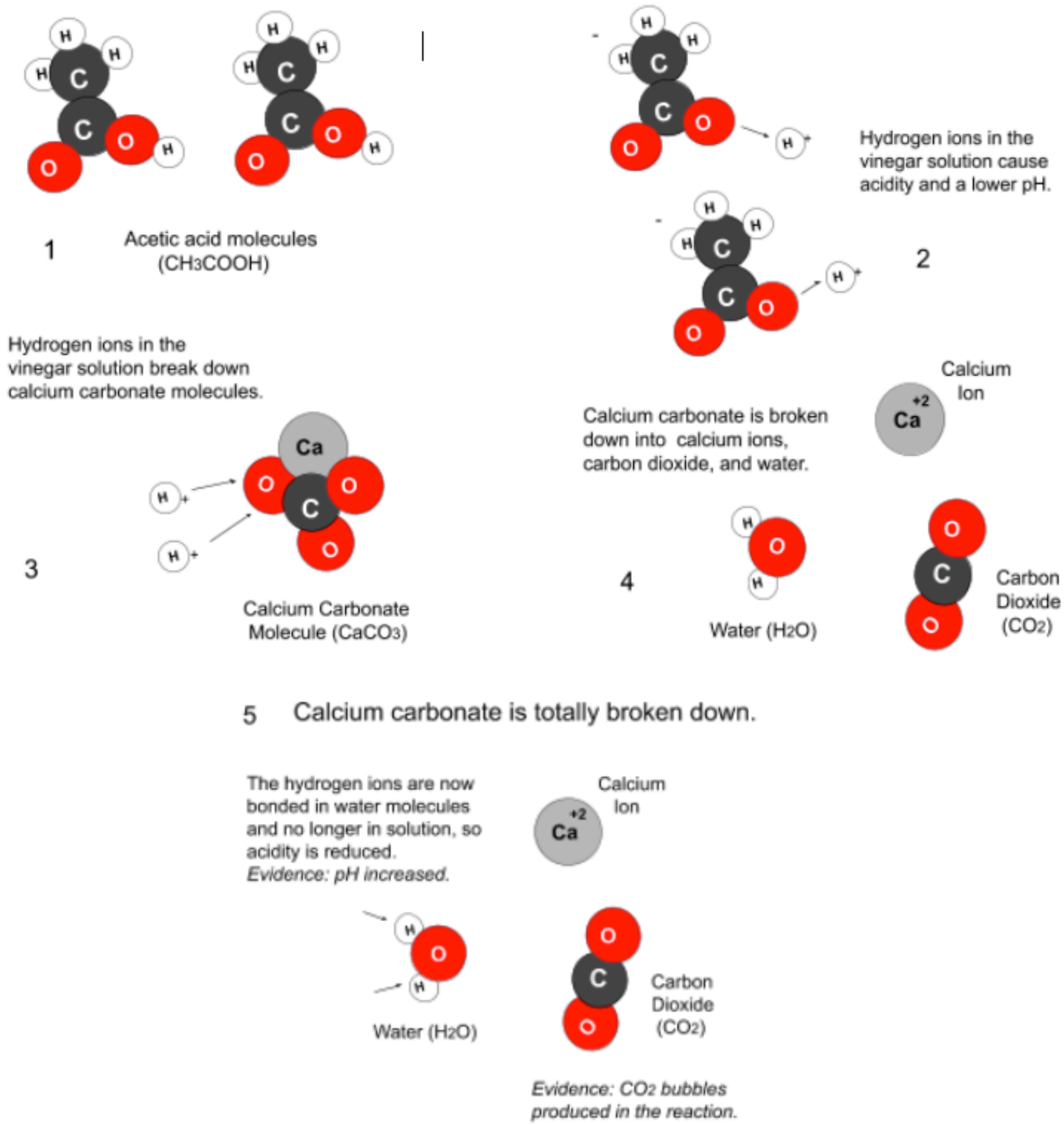
Acidity of the solutions. Based on color change to pH paper.	
Start of Experiment	Next Day
 	
 	

Observations of a chicken egg placed in tap water and vinegar solution over a 24 hour period.	
Start of Experiment	Next Day
	Egg shell is unchanged 
	Egg shell has been chemically broken down. 

Analysis and Conclusions. *The diagrams below describe the chemical reaction at the molecular level.*

Since the eggshell was destroyed in acetic acid and unchanged in tap water, we can conclude that calcium carbonate is broken down in acidic conditions. But how? All acids release hydrogen ions in solutions (step 2 below). The presence of hydrogen ions in the vinegar solution is confirmed by its low pH.

Next, the hydrogen ions in vinegar breakdown calcium carbonate molecules by removing oxygen atoms to form water molecules (steps 3-4), resulting in calcium ions and carbon dioxide bubbles (steps 4-5). This reaction removes hydrogen ions from the vinegar solution to form water molecules, so acidity was lowered. This was confirmed by an increase to the pH when the calcium carbonate egg shell was broken down.



A slide presentation describing this explanation and analysis can be reviewed at the following link:
Calcium Carbonate and Acetic Acid Reaction. Explanation and Analysis

Conclusion. Writing activity: writing an evidence-based explanation

After stating the evidence from the activity that supports our claim, write an evidence based explanation that uses scientific principles and any background knowledge to explain why the evidence supports our claim.

Original Question:

If calcium carbonate is not able to be dissolved in water or seawater, then how can calcium carbonate get into the groundwater in order to form limestone deposits in caves?

Our claim or hypothesis.

Rainwater has a low pH and is acidic. We feel that acidity gives rainwater the ability to breakdown and dissolve calcium carbonate.

Evidence.

From the results of activities in this activity, state two pieces of evidence that supported our claim.

*1.*____

____

2. ____

____

Evidence based explanation. *Use scientific principles and your background knowledge to explain why the evidence (above) supports our claim.*

____

____

____

____

____

____

Sample of responses.

Original Question:

If calcium carbonate is not able to be dissolved in water or seawater, then how can calcium carbonate get into the groundwater in order to form limestone deposits in caves?

Our claim or hypothesis.

Since rainwater is acidic it has the ability to breakdown and dissolve calcium carbonate.

Evidence.

From the results of activities in this lesson, state two pieces of evidence that supported our claim.

1. *After one day, the calcium carbonate shell of a chicken egg was completely broken down in acetic acid (vinegar) but did not change in tap water.*
2. *The pH of vinegar increased from 2 to 5 after the egg shell was broken down. The vinegar was 1000 times less acidic after the egg shell was broken down.*

Evidence based Explanation. *Use scientific principles and your background knowledge to explain why the evidence (above) supports our claim.*

We believe that because rain water is acidic, it has the ability to breakdown and dissolve calcium carbonate.

When an egg was placed in vinegar the egg shell was completely broken down whereas the shell of an egg in tap water was unchanged. This showed us that acidity was needed to breakdown calcium carbonate. Furthermore, the pH of the vinegar solution increased after the egg shell was broken down, thus hydrogen ions from the vinegar were used in breaking down calcium carbonate.

Since acidity of the vinegar was needed to breakdown calcium carbonate, acidic rainwater may have the ability to breakdown and dissolve limestone which can then lead to the formation of cave deposits that hold a record of Earth's past climate.

Conclusion. Writing activity: writing an evidence-based explanation (Modified version)

After stating the evidence from the activity that supports our claim, write an evidence based explanation that uses scientific principles and any background knowledge to explain why the evidence supports our claim.

Original Question:

If calcium carbonate is not able to be dissolved in water or seawater, then how can calcium carbonate get into the groundwater in order to form limestone deposits in caves?

Our claim or hypothesis.

Rainwater has a low pH and is acidic. We feel that acidity gives rainwater the ability to breakdown and dissolve calcium carbonate.

Evidence. *Which of the following would be a form of evidence from this activity that supports our claim.*

a) A low pH represents a high acidity and high pH is a low acidity.

b) The limestone shell of a chicken egg was completely broken down in acetic acid (vinegar), but did not change in tap water.

c) Vinegar has a pH of 2 whereas the pH of water has a pH of 7, thus vinegar is acidic.

Evidence based explanation. *Use scientific principles and your background knowledge to explain why the evidence (above) supports our claim.*

First, write a topic sentence that restates the claim.

____

____

Next, write one or two sentences that explain how the evidence selected above supports the claim.

____

____

____

____

Conclusion. Give this some thought. Explain why the information above is important.

____

____

Sample of responses.

Conclusion. Writing activity: writing an evidence based explanation. (Modified version).

After stating the evidence from the activity that supports our claim, write an evidence based explanation that uses scientific principles and any background knowledge to explain why the evidence supports our claim.

Original Question:

If calcium carbonate is not able to be dissolved in water or seawater, then how can calcium carbonate get into the groundwater in order to form limestone deposits in caves?

Our claim or hypothesis.

Rainwater has a low pH and is acidic. We feel that acidity gives rainwater the ability to breakdown and dissolve calcium carbonate.

Evidence. *Which of the following would be a form of evidence from this activity that supports our claim.*

b) The limestone shell of a chicken egg was completely broken down in acetic acid (vinegar), but did not change in tap water.

Evidence based explanation. *Use scientific principles and your background knowledge to explain why the evidence (above) supports our claim.*

First, write a topic sentence that restates the claim.

We believe that because rain water is acidic, it has the ability to breakdown and dissolve calcium carbonate.

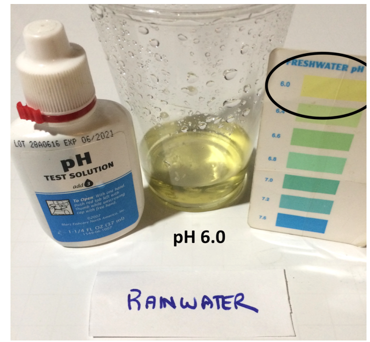
Next, write one or two sentences that explain how the evidence selected above supports the claim.

When an egg was placed in vinegar the egg shell was completely broken down whereas the shell of an egg in tap water was unchanged. This showed us that acidity was needed to breakdown calcium carbonate.

Conclusion. Give this some thought. Explain why the information above is important.

Since acidity of the vinegar was needed to breakdown calcium carbonate, acidic rainwater may have the ability to breakdown and dissolve limestone which can then lead to the formation of cave deposits that hold a record of Earth's past climate.

Next steps:



From its pH, we know that rainwater is acidic, and has hydrogen ions in solution.

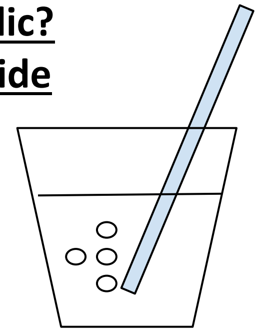
With these hydrogen ions, we can infer that rainwater (like vinegar) can break down calcium carbonate, and carry the components into caves to be deposited and build limestone formations.

Thus, it appears that rainwater being acidic is important to the chemistry behind limestone cave formations.

So why is rainwater acidic? And can we demonstrate that acidic rainwater is able to break down calcium carbonate?

We will answer these questions in the next two activities.

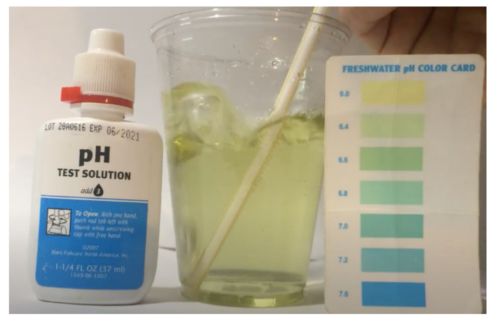
Activity 2: How does rainwater become acidic? Lowering the pH of water with Carbon Dioxide



Introduction:

In order for rainwater to become acidic, water droplets in the air must be acidified by something in the atmosphere. Remember, water is the universal solvent. Could water in the atmosphere dissolve a gas in our air to become acidic? In this experiment we will add carbon dioxide gas to water by exhaling into a sample of water to test its ability to make water acidic.

Materials:



- tap water
- beaker, or clear plastic cup
- drinking straw
- an aquarium pH indicator solution.

(The pH test solution picture here is the Low Range Test Solution from "Aquarium Pharmaceuticals.")

Procedure:

1. Fill a clear plastic cup or small beaker about half way with tap water .

2. Next, add about 20 drops of pH indicator solution to the water and mix it with a straw.

3. Record the color and pH of the solution.
   color: _______________

   From the pH color chart in the test kit determine the pH of this solution
   pH = _____

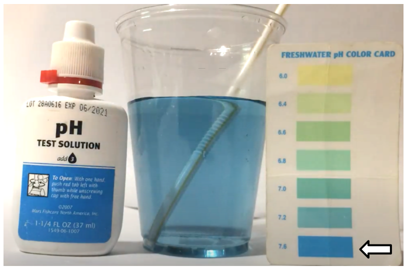
4. For at least 1 minute, **<u>slowly</u>** exhale through the straw into the water with pH indicator solution. You should notice a color change.

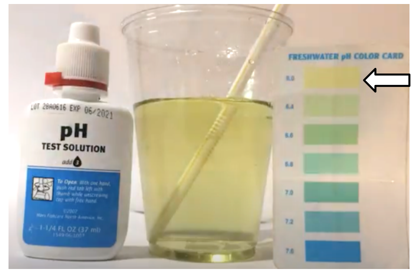
   Describe the color change to the solution

   ____

   From the new color of this solution, determine the new pH of the solution ______

Results and Analysis.





Before exhaling CO_2 into water. With a pH indicator solution.   After exhaling exhaling CO_2 into the water.

What does the addition of carbon dioxide gas do to the pH of water? ________________________________

Reasoning.

Rainwater becomes acidic by absorbing carbon dioxide gas from the atmosphere. When this happens, water and carbon dioxide molecules bond to form **carbonic acid** (H_2CO_3).

CO_2 Carbon Dioxide	+	H_2O Water	=	H_2CO_3 Carbonic Acid

Like all acids, carbonic acid then releases hydrogen ions (H^+) when dissolved in water, lowering the pH.

When dissolved in water:	H_2CO_3 Carbonic Acid	*breaks up into*	H^+ Hydrogen ion	+	HCO_3^{-1} Bicarbonate ion

It's the hydrogen ions that define acids and give them their chemical properties. The greater the concentration of hydrogen ions in water the greater the acidity and lower the pH.

The link below is to a presentation showing a video of this activity along with a stop motion animation of the chemical reaction involved in changing water to carbonic acid .

[***Acidification of water to carbonic acid.***] *is also found in the presentation to review.*

Activity 3: Dissolving limestone (calcium carbonate) in acidic water
Can rainwater dissolve calcium carbonate?

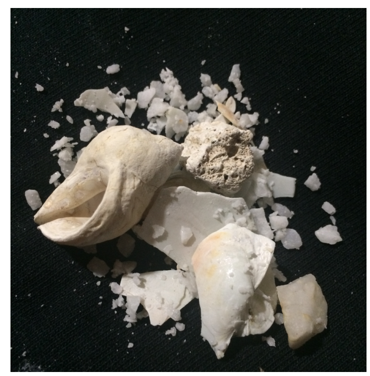
Introduction:

We know that calcium carbonate cannot be dissolved in water but can be broken down in acids like vinegar. Therefore, this may also happen in rainwater, which is often acidic. In the previous activity, we showed how rainwater can become acidic through the addition of carbon dioxide from the air.

In part 2 of this activity, we will try to break down calcium carbonate (limestone shells of marine creatures) in this acidic water. If this acidic rainwater breaks down these shells, then we can conclude that it is the acidification of rainwater that allows calcium carbonate to be broken down and carried in groundwater in order to seep into caves and create limestone formations.

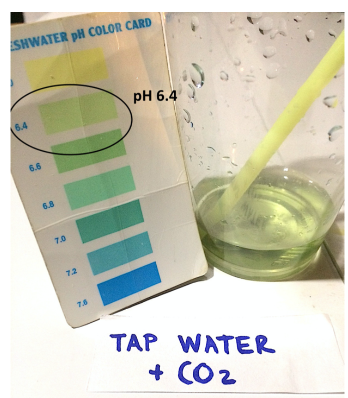
In addition, it explains why these limestone formations are not re-dissolved in submerged caves by water and seawater having a higher pH.

Materials:



In addition to the materials used in the previous demonstration, you need a handful of limestone fragments, such as bits of broken seashells or coral.

Procedure:



Repeat the previous activity using a smaller amount of tap water (about 20ml) and add only 10 drops of pH indicator solution to the tap water.

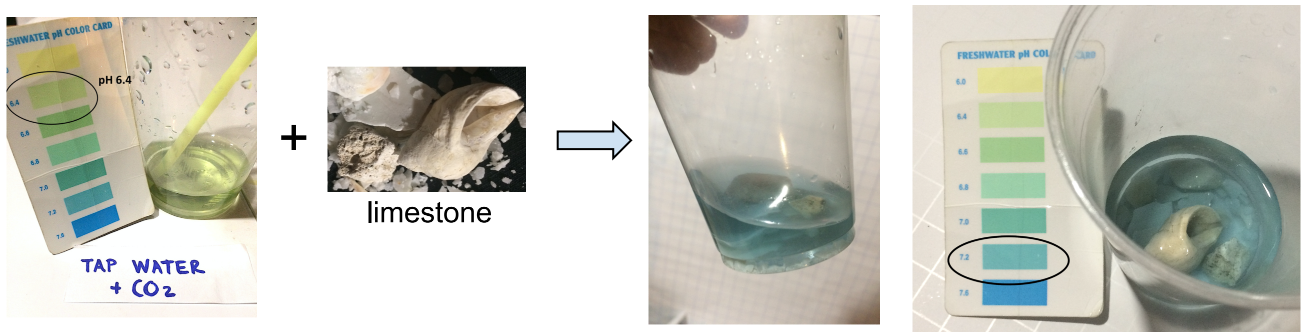
As in the previous demonstration, exhale through the straw until the pH of the solution is lowered to a pH of about 6.0 -6.4.

Next, add the pieces of limestone to the acidic water and swirl the mixture for about a minute or two.

Describe what happens. ____

____

Review and analysis of the results.



After adding limestone (calcium carbonate) and mixing it in the acidic water, the pH of the water rose to a neutral level. This means that the hydrogen ions must have reacted with the calcium carbonate and were taken out of the solution in the process.

Remember, in acidic rainwater:

H_2CO_3 Carbonic Acid	*dissolves into*	H^+ Hydrogen ions	+	HCO_3^{-1} Bicarbonate ions

When we added limestone to the acidic water the acidic pH became neutral. Here's how:

H^+ Hydrogen ion	+	$CaCO_3$ Calcium Carbonate	=	Ca^{+2} Calcium ion	+	HCO_3^{-1} Bicarbonate ion

The hydrogen ions are used to break down calcium carbonate and form bicarbonate and calcium ions.
As H+ ions form bicarbonate, the solution is neutralized and some of the calcium carbonate (limestone) must have been broken down. Now calcium and bicarbonate are dissolved in the water.

This chemical reaction can be visualized at the molecular level with this stop motion animation:
[Acidic water breaks down calcium carbonate]
From this last activity it appears that acidic rainwater, like vinegar, has the ability to dissolve calcium carbonate.

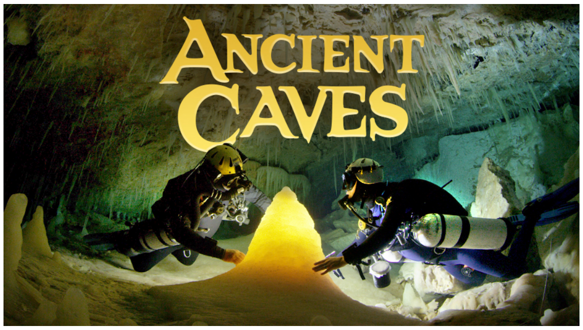
Conclusion

We clearly saw that the limestone shell of a chicken egg was totally broken down in vinegar accompanied by a rise in pH. It was not dissolved in tap water and we learned that the hydrogen ions from the acid were used in this reaction, breaking down the eggshell.

In acidic water (simulating rainwater), we could not see the fragments of limestone dissolve enough to be noticeable. However, we did see a rise in pH when the shell fragments were mixed into the acidic water. Thus, the hydrogen ions were used to form other materials from the shell fragments.

We can conclude that acidic rainwater is capable of chemically breaking down calcium carbonate, and carrying the dissolved products from this reaction.

We're left with one final question. How can calcium and bicarbonate in groundwater form limestone deposits in caves?



Exploring the Chemistry of Caves Part 4

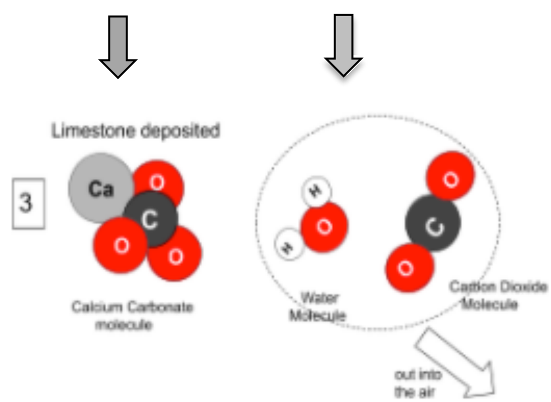
Conclusion and Summary
The deposition of limestone

In part 3 of this investigation, we concluded that because it's acidic, rainwater is capable of chemically breaking down calcium carbonate. The products from this reaction, calcium and bicarbonate, are then dissolved into groundwater which seeps into caves.

How can calcium and bicarbonate in groundwater form limestone deposits in caves?

We know that limestone stalactites and stalagmites form as the water with dissolved materials drips into caves and evaporates. So as the water evaporates into the air of the cave, calcium and bicarbonate will become "undissolved" and **precipitate** as calcium carbonate.

The process for depositing limestone basically reverses the process which broke down calcium carbonate. As calcium carbonate forms, water molecules and carbon dioxide are released. The process at the molecular level is summarized below.

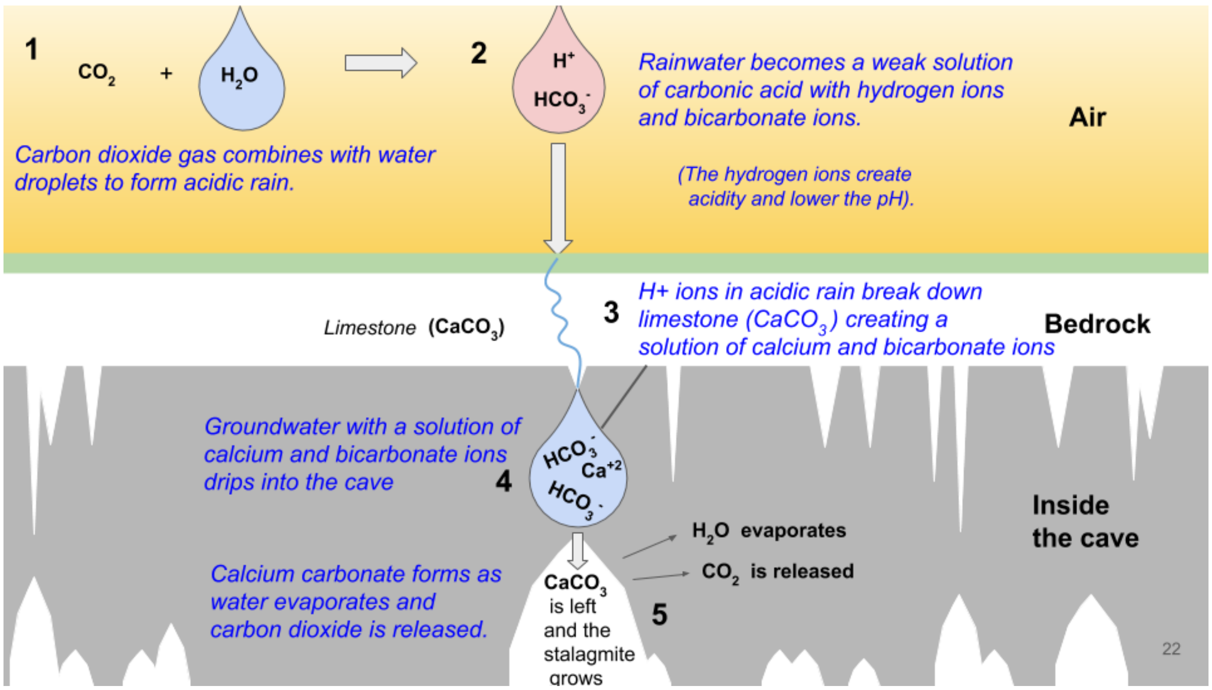


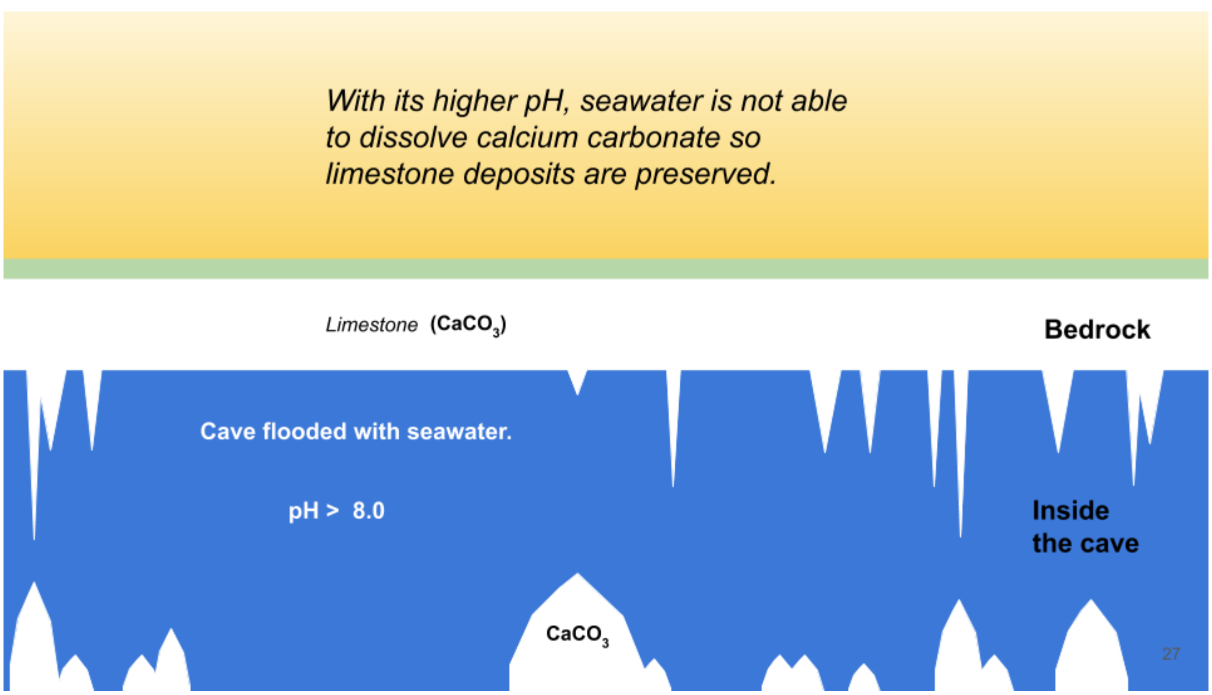
1. *Calcium and bicarbonate ions are dissolved in the groundwater seeping into caves.*
2. *As the groundwater evaporates bicarbonate ions breakdown and calcium bonds to carbonate.*
3. *Limestone is deposited, water evaporates, and carbon dioxide is released.*

Background for this lesson was provided by : Science Learning Hub. Pokapu Akoranga Putaiao. *Carbonate Chemistry.* Published Oct 10, 2012. New Zealand science education resources. https://www.sciencelearn.org.nz/resources/469-carbonate-chemistry

The link below is to a slide presentation summarizing the chemical changes that lead to the formation of limestone deposits or features in caves. Slides from the presentation summarizing important steps in the chemistry of caves are shown below

Link: *The process of limestone deposition*

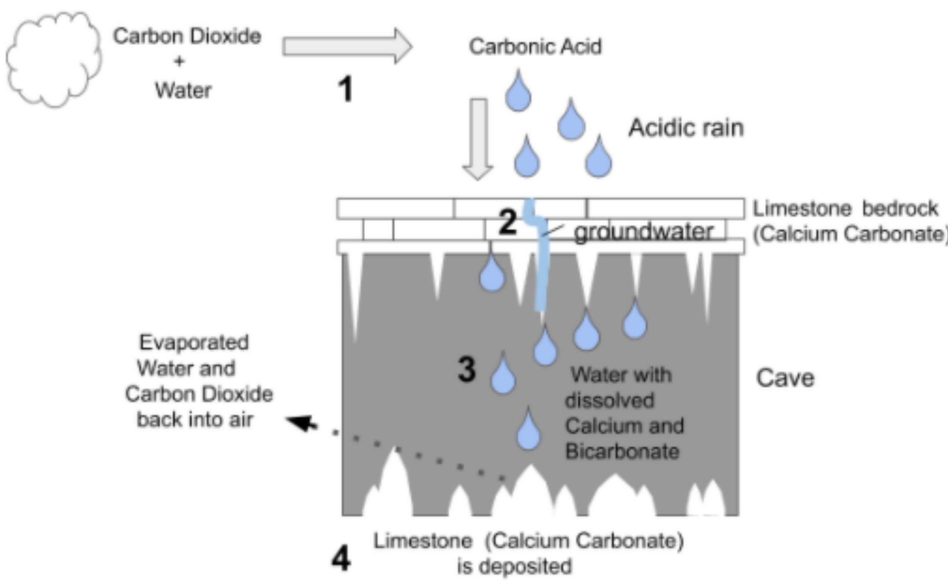




Culminating Activities: Options: Writing Activity or “One Pager”

Option One: Writing activity.

Using the information in the slide presentation, the informational text in this section, and the diagram below summarize (step by step) the chemical changes involved in forming limestone deposits in caves.



Step 1: ____

____

Step 2: ____

____

Step 3: ____

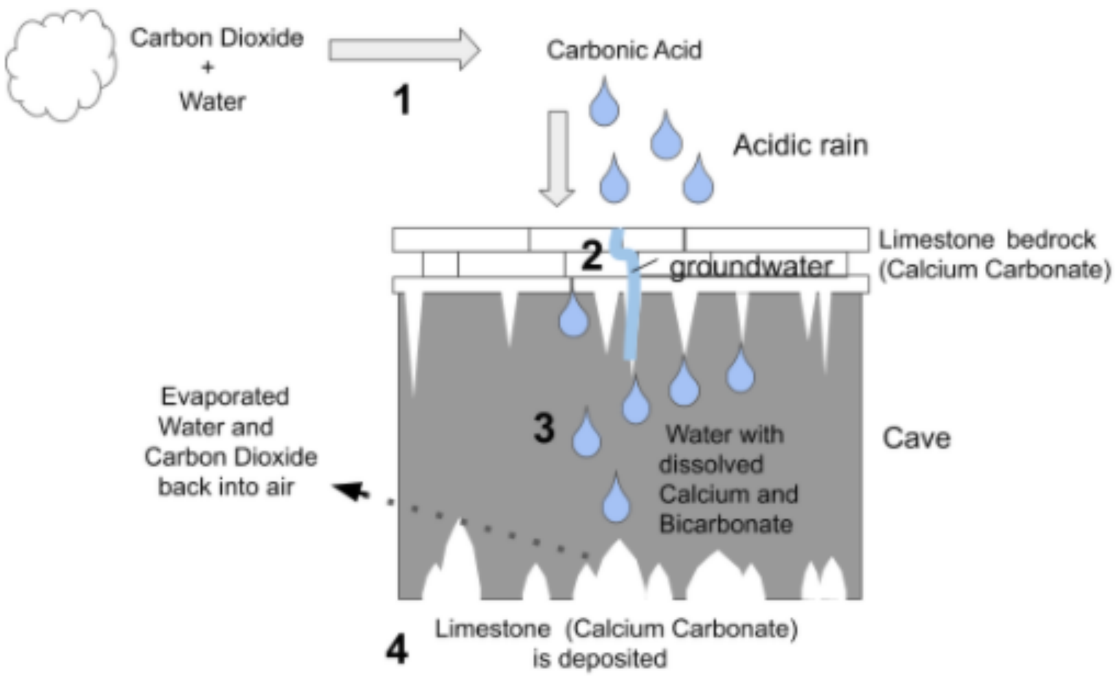
____

Step 4: ____

____

Answer key for responses.

The chemical changes leading to the formation of limestone features in caves is summarized in the diagram below.



Writing activity: Using the above diagram, and the text in this section, summarize the chemical changes involved in forming limestone deposits in caves.

Step 1: *Water droplets in the air dissolve carbon dioxide gas to form carbonic acid. As the drops grow, they fall to the ground as acidic rain.*

Step 2: *Acidic rainwater contains hydrogen ions which break down calcium carbonate in the limestone bedrock into calcium and bicarbonate ions.*

Step 3: *Groundwater with dissolved calcium and bicarbonate drips into caves.*

Step 4: *As the groundwater evaporates, calcium and bicarbonate become calcium carbonate, carbon dioxide, and water. The water evaporates and carbon dioxide is released leaving deposits of limestone.*

Option 2: A "One-Pager."

Prepare a "one pager" which summarizes the chemistry of caves. In a "one pager" you can summarize the important "takeaways" from this lesson on a single sheet of paper in a creative way. Instead of the usual written options, a one-pager allows you to mix images and information. We tend to remember more when we have mixed language and imagery.

For this assignment produce a colorful and visually appealing one pager that summarizes the steps to forming limestone features such as stalagmites and stalactites in caves.

Required Elements in your one-pager.

- *Include the major steps in the chemical changes from forming acidic rain to the deposition of limestone in caves on a single page of paper.*

- *The explanation should have a sufficient number of images used along with written annotations to tell this story.*

- *The information should be accurate, sufficient, and clear. Thus, the story should be understood by its audience and stand on its own, without needing additional explanation.*

Visual appeal

- *There should be an appropriate use of color in images and labels. Colored pencils and fine point markers.*

- *Neatness, time, care, and craftsmanship is evident*

- *Annotations and labels are clearly visible and accurate, with correct spelling.*

- *Images are appropriately placed in a way that makes the story in the one pager clear and easy to follow.*

If you are not familiar with one-pagers and would like to learn more about how to use them to effectively and creatively share what you have learned, check out the following resource:

"A Simple Trick for Success with One-Pagers." Betsy Potash. May 26, 2019. Cult of Pedagogy. https://www.cultofpedagogy.com/one-pagers/

Takeaways from this investigation into the chemistry of caves.

The importance of water as the universal solvent

Ultimately, the chemistry of caves is about water's ability to dissolve materials. This is shown as water dissolves carbon dioxide to form carbonic acid. Water then dissolves this acid to release the hydrogen ions that can break down calcium carbonate and then dissolve those materials into the groundwater. The groundwater can then enter caves and form the limestone deposits that hold a record of Earth's climate.

The importance of acidity and pH.

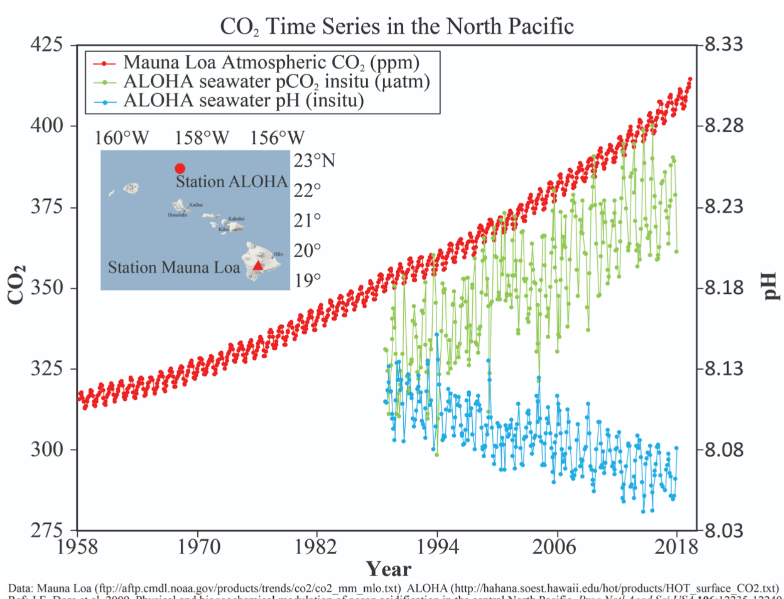
Without rain being acidic, limestone bedrock could not have been dissolved into the groundwater and thus limestone deposits and even caves themselves would not have formed.

Going further: Carbon dioxide, acidity, and ocean acidification.

A more relevant topic connected to the chemistry of caves, is that the acidity of our ocean is increasing. Like global warming, ocean acidification is a result of increasing carbon dioxide levels in our atmosphere from the burning of fossil fuel. Levels of CO_2 have climbed to well over 400 parts per million, the highest ever in human history.

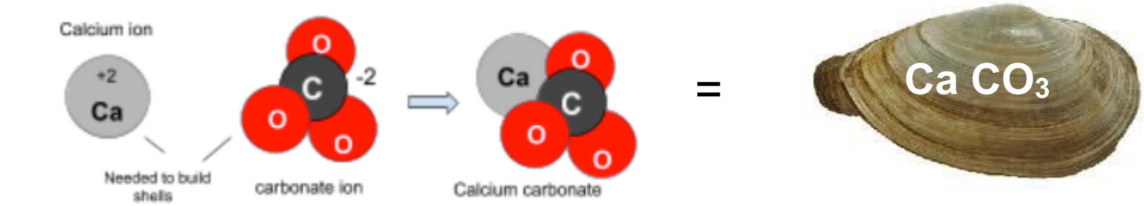
The ocean absorbs about 30% of atmospheric CO_2 and as demonstrated in part three of this investigation, when water dissolves CO_2 it becomes carbonic acid, and this lowers the pH of the ocean.

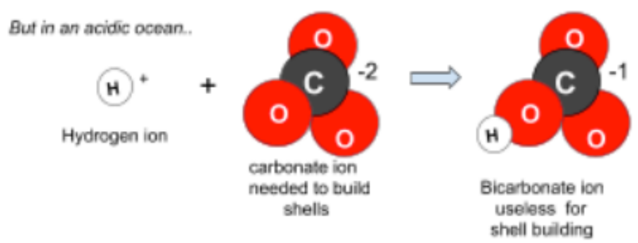
This graph from "*The Carbon Dioxide Time Series in the North Pacific.*" shows the direct relationship between the increase in atmospheric carbon dioxide and the lowering of pH to the ocean.



Source: *OA Observations and Data.* PMEL Carbon Program. National Oceanic and Atmospheric Administration. *https://www.pmel.noaa.gov/co2/story/OA+Observations+and+Data*

Many aquatic creatures from corals to mollusks evolved and depend on exoskeletons of calcium carbonate for their survival. However, with the acidification of our ocean, the levels of dissolved carbonate (CO_3^{-2}) needed to build these exoskeletons are decreasing in the ocean as hydrogen ions are changing it into bicarbonate (HCO_3^{-1}).

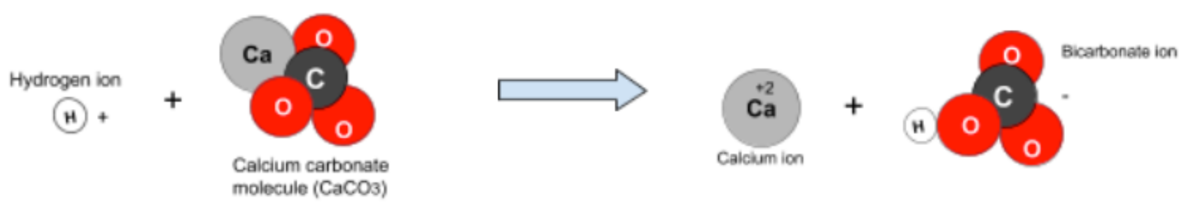




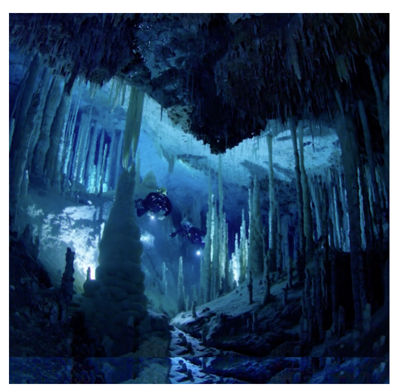
With less carbonate to build their shells many marine creatures will struggle to grow shell and survive.

An increase in hydrogen ions in the ocean can chemically breakdown calcium carbonate shells of marine animals, especially in their larval stages. *We saw this in part 3 of our exploration into the chemistry of caves.*

H^+	+	$CaCO_3$	=	Ca^{+2}	+	HCO_3^{-1}
Hydrogen ion		Calcium Carbonate		Calcium ion		Bicarbonate ion



One must also wonder if the limestone stalactites and stalagmites in submerged caves will be impacted by the acidification of the ocean.



Hopefully the lessons and activities around the chemistry of caves can help improve our understanding of other relevant and important phenomena, such as ocean acidification.