

# Geology Topics Through a Chemistry Lens

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## Topic #1: Acid Mine Drainage

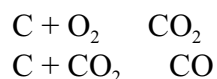
AMD is a common acronym used for acid mine drainage that is a major problem associated with the extractive mining of high sulfur coal beds that result in the disruption of the sedimentary shales and sandstones above and below them. If it wasn't for its sulfur content, coal would be a much cleaner, and preferred, source of energy. Since sulfur, along with carbon, hydrogen, oxygen, phosphorus, and nitrogen are the six elements required for life on Earth, the environmental goal is to reduce, not eliminate, sulfur emissions.

The sulfur found in coal and associated rocks originated in the plants that grew in the original coal-forming peat bogs hundreds of millions of years ago. A mire is a wetland in which peat accumulates. The sulfur in coal is primarily present in two major forms, as a component of the organic matrix or as the mineral pyrite,  $\text{FeS}_2$ . A third form, sulfate sulfur,  $\text{SO}_4^{2-}$ , is only associated with coal-associated rocks exposed to weathering for an extended period of time. While students will normally associate AMD with the surface mining process, rocks that have been newly exposed by surface mining are rarely left exposed to the atmosphere long enough to generate much sulfate sulfur. As a result, sulfate sulfur does not contribute a great deal to AMD.

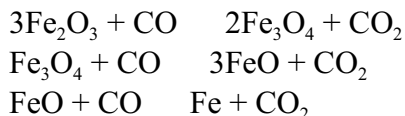
Coals mined throughout the southern Appalachian Coal Basin are considered high quality coals. High quality coals are those that contain less than 1% total sulfur and 10% ash. In this region most of the sulfur is tied up as part of the organic portion of the coal and associated rocks. Organic sulfur can only be removed by breaking down the organic components of which the coal is made. Because organic sulfur cannot be removed naturally upon exposure to the atmosphere, it is not considered an environmental problem. The mineral pyrite is the major contributor to AMD. The pyrite concentration of these southern coals is low because of the environmental climatic conditions that existed during the early part of the Pennsylvanian Period when the coal-forming peat was accumulating. Back then, while the regional climate was not quite tropical, it was nevertheless quite warm with abundant rainfall. As a result of the near daily rainfall events, most of the iron and sulfur were leached out of the peat by percolating acidic rainwater. As a result, little pyrite could form or be left behind to be incorporated into the coal that subsequently formed from the peat. Because of the very low concentration of pyrite, acid mine drainage is not a major environmental problem in the southern coal fields.

Historically, high quality coals such as those produced in the southern Appalachian Coal Basin were used to make coke. The requirements for coking coal are very stringent; less than 0.5% sulfur and 5% ash. During the time when Pittsburgh, Pennsylvania, was a major steel-producing center, the high quality southern Appalachian coals were roasted to form coke by removing the volatile components of the coal. We now know that many of the vapors released during coke production are carcinogenic. As a result, very little coke is currently produced in the United States. Most of the coke used in domestic steel mills is imported.

The carbon-rich coke is used in blast furnaces to reduce the iron contained in iron ore (solid rock containing some chemical type of iron oxide) to liquid iron. This is accomplished by first charging a blast furnace with a mixture of iron ore, limestone, and coke. Oxygen is then forced into the bottom of the furnace (hence the “blast” term) so that it can react with the coke (C) to produce CO<sub>2</sub> which is then reduced to CO:

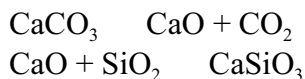


The CO then passed upward within the furnace into the iron ore where the CO reacts with the ore’s iron oxides to release iron in liquid form:



As an aside, we might add a comment about the formula for the oxide of iron produced in the first equation, Fe<sub>3</sub>O<sub>4</sub>. Students often comment on the lack of charge balance in the formula as written. The problem is best solved by rewriting the formula as Fe<sub>2</sub>O<sub>3</sub> • FeO. In mineral form, the combination of the two oxides is magnetite, another ore of iron.

The limestone, CaCO<sub>3</sub>, was added to the blast furnace to remove the silica impurities produced during the reduction of the iron ore. This process makes the uneconomical waste product called slag, CaSiO<sub>3</sub>:



In comparison to the older southern coal field coals, most of the geologically younger coals of the northern Appalachian Basin have sulfur contents in ranging from 1% to 3% total sulfur and are considered medium quality coals. Coals containing total sulfur content in excess of 1% are usually due to the presence of the mineral pyrite, FeS<sub>2</sub>. Once again, ancient environmental conditions play a role in this elevated content. Northern mires were accumulating peat during the latter part of the Pennsylvanian Period. By that time, the climate had changed to an environment with distinct wet and dry seasons. This seasonal climate reduced the amount of leaching by percolating acid rainwater. As a result, more pyritic sulfur was retained in the peat and eventually incorporated into the coal.

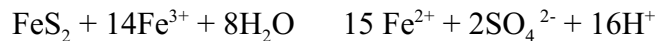
In the northern coal fields, the oxidation of pyrite is responsible for AMD. Production occurs in two phases. The first phase occurs when the rocks are exposed to the atmosphere by the mining process. This allows the pyrite to react with oxygen and water:



Oxidation of the sulfide ion to the sulfate ion solubilizes the ferrous iron,  $\text{Fe}^{2+}$ , which is subsequently oxidized to the ferric ion,  $\text{Fe}^{3+}$ :



Once formed during the second phase of the reaction, the ferric ion becomes the major oxidizer of pyrite, creating additional ferrous ions and more acid:



Note that the second reaction produces four times more hydrogen ions than was generated during the first reaction.

It is assumed by many that oxygen is required to carry on the AMD reactions. This is not the case. Once the ferrous ion is oxidized to the ferric ion in the second reaction and becomes the major oxidizing agent, oxygen is no longer required. The chemistry clearly demonstrates that the idea of reducing AMD production by sealing old workings in high sulfur coal mines was doomed to failure.

As long as the water pH remains below 3, the ferric ion stays in solution. In fact, acid water with pH values less than 3 will be deceptively crystal clear and can be misinterpreted as clean, or even potable, water. However, when the pH rises above 3, either by treatment design or by natural ground water dilution processes, the ferric ion begins to precipitate as  $\text{Fe}(\text{OH})_3$ :



Ferric hydroxide is the commonly a bright yellow material called “yellow boy” that stains the bottoms of streams throughout the northern Appalachian coal basin.

## Topic #2: AMD Treatment

Acid mine drainage is commonly treated with strong bases such as NaOH, Na<sub>2</sub>CO<sub>3</sub>, or Ca(OH)<sub>2</sub> that readily ionize and go into solution. AMD neutralization is achieved as the hydroxyl ions, (OH<sup>-</sup>), and carbonate ions, (CO<sub>3</sub><sup>2-</sup>) combine with the hydrogen ions (H<sup>+</sup>) to create water and carbonic acid. Carbonic acid poses no environmental problems because it is a weak acid that breaks down into water and carbon dioxide:



While most individuals consider AMD to be the direct result of active mining operations, such is not the case. Companies that are involved in the mining of coal have learned from years of research how to control AMD production, how to neutralize that which is created, and how to conduct effective reclamation of soils, rock, and land associated with both surface and underground operations. The source of most of the AMD being generated within the northern coal fields comes from very old, long-abandoned deep, and often ill-mapped, underground mines that were in operation well before the 1970's Clean Water Act. If mine openings are not present or if maps of the old mine workings are unavailable to be used to locate the underground workings, the only alternative is to treat the acid once it comes to the surface. If the AMD surfaces as a single point effluent, a facility can be built to both contain and neutralize the acid and collect and dispose of precipitated waste products. Unfortunately, much of acid that is produced by old, abandoned underground mines comes to the surface as seeps which are difficult to both locate and contain. In many cases, these seeps are in or near stream beds, making them almost impossible to locate visually.

## Topic #3: Bowen's Crystallization Series

**Introduction:** A chemist would state that compounds precipitate from a solution. Solutions can exist in solid, liquid, or gaseous state. The component that determines the physical state of the solution is called the solvent. All the remaining components are called solutes. Usually, but not always, the solvent is the most abundant compound in the mixture. For example, consider air as a gaseous solution. Nitrogen is the most abundant component of the atmosphere (78%). As such, it is the solvent. At 21%, oxygen is the most abundant solute. An essential component of the atmosphere that is needed for life as we know it is water in the form of water vapor. For a compound to precipitate from solution, a change in either the physical or chemical properties of the solution is required. To precipitate water from the atmosphere requires the temperature of the atmosphere to decrease below the dew point; the temperature at which air becomes saturated with water vapor. If the temperature of the dew point is above the freezing point of water, ( $0^{\circ}\text{C}$  or  $32^{\circ}\text{F}$ ), the water vapor precipitates as liquid water or rain. On the other hand, if when reached the dew point is below the freezing point of water, it precipitates as a crystalline solid; most likely as snow. Note that ice is a mineral while water is not. The only mineral that readily precipitates from the air is ice. The freezing points of all the other gaseous solutes that naturally occur in Earth's atmosphere are far too low to ever be attained on Earth. What prevents rains of oxygen or carbon dioxide crystals? The freezing point of oxygen  $-218^{\circ}\text{C}$  and the freezing point of  $\text{CO}_2$  is  $-57^{\circ}\text{C}$ . We might add, however, that there is one place on Earth where temperatures have been low enough to cause the precipitation of  $\text{CO}_2$  and that was at the Soviet Vostok Station in the Antarctic when the temperature dropped to  $-89.2^{\circ}\text{C}$ . In passing, the temperatures at the Martian poles vary but often hit  $-127^{\circ}\text{C}$  ( $-195^{\circ}\text{F}$ ), easily low enough to produce the crystals of carbon dioxide that make up its polar ice caps. This short explanation may help you understand the seemingly strange phenomena of methane rain, and other such events that astronomers say may exist on other planets.

### Precipitating minerals and rocks from liquid solutions

Most of the minerals that make up Earth's crust precipitate from liquid solution; the great majority of them precipitate from the universal solvent we know as water. Halite,  $\text{NaCl}$ , precipitates from aqueous solution to form rock salt. Gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , precipitates from water solution to form layers of gypsum. Many of these minerals are important in of their own. Where would we be without salt ( $\text{NaCl}$ ); where would society be without hematite ( $\text{Fe}_2\text{O}_3$ ); where would our hi-tech computerized world be without cuprite ( $\text{Cu}_2\text{O}$ )? However, geologists do not regard any of these kinds of minerals as major rock-formers. In fact, the one mineral that does form a common rock is calcite,  $\text{CaCO}_3$ , the major mineral in limestone. Even then, however, limestones only account for 10% of all sedimentary rocks that, in turn, account for only 5% of the volume of Earth's crust.

The dozen or so major rock forming minerals that mix together to become Earth's most abundant crustal rocks are all silicate minerals whose composition and structure are based on the silicate anion,  $\text{SiO}_4^{4-}$ . Silicate minerals are not water soluble and thus could not have formed from some naturally existing aqueous solution or solutions. Instead, the major rock forming silicate minerals crystallized from the natural-occurring liquid solvent, molten rock, either magma or lava. Note

that we have changed the process by which the minerals form from solution from precipitation to crystallization. While some geochemists would use the terms interchangeably, most would reserve the process of precipitation to describe the creation of solids from an aqueous solution while using the term crystallization to refer to a similar process by which minerals form during the cooling of molten rock. Molten rock originates below Earth's surface as magma. Once the molten rock reaches Earth's surface, even the seafloor, it is called lava.

Just as was the case with ice crystals, mineral crystals begin to crystallize when the molten rock temperature drops below their individual freezing points. Keep in mind that freezing/melting points are physical properties and, as is the case with the physical properties of all compounds, are determined by the combination of composition and crystal structure. In the early 1900s, Norman L. Bowen set out to determine the order in which the major rock-forming silicate minerals crystallized from cooling liquid rock. His initial goal was to explain why certain silicate minerals were associated with each other while others were not. For example, while olivine and anorthite are commonly associated in the rock called basalt, olivine and quartz are never found together in the same rock. Bowen prepared mixtures of various powdered minerals and heated them to their melting points. He then slowly cooled the melt and noted the temperatures at which certain mineral crystals crystallized.

The unexpected outcome of his work was the development of an order of crystallization of the nine most abundant minerals found in igneous rocks. Within these nine minerals, he chemically recognized two distinct groups. One group of four became known as the ferro-magnesian minerals because they contained iron and magnesium. The other group, in which iron-magnesium were lacking and had been replaced with aluminum, he called the non-ferromagnesian minerals. Because of their content of iron, all of the ferro-magnesian minerals are dark in color, ranging from a dark green in olivine to black biotite. The non-ferromagnesian minerals, on the other hand are all light in color ranging from quartz and muscovite which are clear and colorless to the whites, creams, oranges, and reds of the feldspars.

When further arranged by crystallization temperature, the following chart emerged. In his original paper reporting his data, Bowen referred to the chart as his "Reaction Series". However, as my mentor pointed out in class, it is simply an order of crystallization as I have indicated in the following chart.

**Table 1: Bowen's Order of Crystallization**

	<b>Ferro-Magnesian Minerals</b>	<b>Non-Ferromagnesian Minerals</b>
<b>High Temp</b>	<b>Olivine</b> $(\text{Fe,Mg})_2\text{SiO}_4$ <b>Augite</b> $(\text{Ca,Na})(\text{Mg,Fe,Al})(\text{Si,Al})_2\text{O}$ <b>Hornblende</b> $\text{Ca}_2\text{Na}(\text{Mg,Fe}^{2+})_4 -$ $(\text{AlFe}^{3+}, \text{Ti})_3\text{Si}_8\text{O}_{22}(\text{O,OH})_2$ <b>Biotite</b> $\text{K}(\text{Mg,Fe})_3(\text{Al,Si}_3\text{O}_{10})(\text{OH})_2$ Potash Feldspar	<b>Feldspars</b> <i>(Plagioclase Feldspars)</i> <b>Anorthite</b> $\text{CaAl}_2\text{Si}_2\text{O}_8$  <b>Albite</b> $\text{NaAlSi}_3\text{O}_8$  <b>Orthoclase</b> $\text{KAlSi}_3\text{O}_8$ <b>Muscovite</b> $\text{KAl}_2(\text{Al,Si}_3\text{O}_{10})(\text{OH})_2$ <b>Quartz</b> $\text{SiO}_2$

## Low Temp

Since the process deals with molten rock, the temperatures are out of our normal experience range. The crystallization temperatures range from a high of 1,300°C for olivine to a low of 600°C for quartz. Thus, the use of high versus low temperature mineral crystallization are relative terms. The most abundant of the major rock-forming silicate minerals are the feldspars. Their abundance can be seen graphically in how much of the chart that occupy. The feldspars are separated into two groups, the plagioclase feldspars and the potash feldspars. The plagioclase feldspars represent an isomorphous series with anorthite and albite as the end members. In the series, the relative abundance of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  progressively changes from calcium-rich anorthite to sodium-rich albite as the temperatures decrease. Between these two end members are a series of plagioclase feldspars that vary in the relative abundance of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  with names like bytownite, labradorite, andesine, and oligoclase. Orthoclase feldspar represents the potash series of feldspars. Orthoclase is listed in a separate series from the plagioclase feldspars because the atomic radii of its potassium ion is too large to allow it to substitute for either the calcium or sodium ion found in other feldspars. The substitution rule states that for one ion to substitute for another of the same charge, the radii of two ions must be within 15% of each other in order.

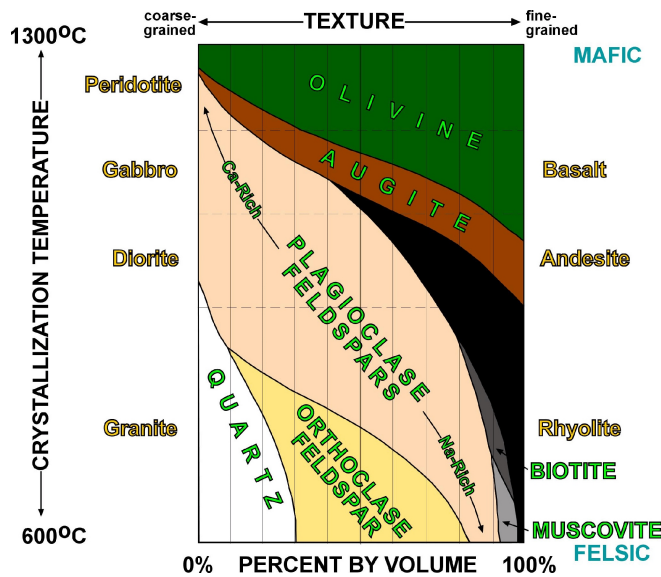
You will note that muscovite and biotite belong to a group of silicate minerals called the micas. The micas are the only mineral group found in both the ferro-magnesian and non-ferromagnesian columns. We might point out that before the advent of tempered glass that could be heated to high temperatures without melting, clear sheets of muscovite were used as the windows in items such as the original Franklin stoves and early lanterns.

Another way to illustrate Bowen's results is shown in Figure 1. The golden colored names represent igneous rock names and the various colored fields within the chart itself illustrate the crystallization temperatures of the nine major rock-forming silicate minerals. By comparing the arrangement of the minerals in Table 1 and Figure 1, the first thing you should notice is that the arrangement of the individual minerals in Table 1 implies that each mineral has a specific freezing/melting point while in Figure 1, each of the minerals crystallize over a range of temperatures. Which scheme is a more accurate portrayal of the cooling-crystallization history of the silicate minerals? If a compound has a specific combination of composition and crystal structure, it will have a specific freezing/melting point. If, on the other hand, the composition and/or crystal structure for a particular compound varies, it will have a variable freezing/melting point. A simple perusal of the formulae included in the chart illustrating Bowen's Crystallization Series clearly points out the compositional variability of nearly all of the major rock-forming silicate minerals except for quartz and orthoclase. The inclusion of bracketed elemental symbols illustrates the composition variability within each mineral. As a result, the chart in Figure 1 is therefore a more accurate portrayal of the crystallization history of the silicate minerals.

To utilize the chart in Figure 1, cover it with a piece of paper (or your hand) and move the edge of the paper from the top of the chart to the bottom. Note that the minerals will appear from under the edge of the paper in the order in which they reach their freezing points and begin to crystallize. Note also that as the paper is drawn downward, combinations of minerals may be crystallizing simultaneously. Note that eventually the field representing a specific mineral will come to an end as the components required to create the minerals have been consumed. We have also included on the chart the combinations of minerals that make up the major types of igneous

rocks. The columns identified as coarse-grained and fine grained refer to the crystallite sizes that formed as the molten rock cooled. Coarse-grained rocks such as granite form by the slow cooling of magma below Earth's surface while fine-grained rocks such as basalt form by fast cooling of lava on Earth's surface where it may be exposed to the atmosphere, water, or ice.

Since the chart in Figure 1 clearly shows crystallization temperatures, it should also be understood that some combinations of minerals will not occur. Thus, the disparate temperatures at which olivine and quartz precipitate explains why they would not naturally occur together in any igneous rock. On the other hand, olivine, anorthite and augite should be commonly associated with each other in rocks such as basalt and gabbro because of their common crystallization temperatures.



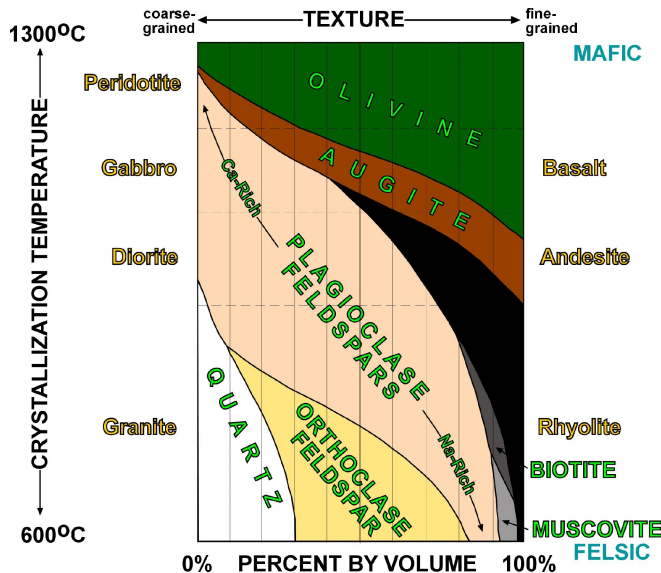
Did you recognize the anomaly? Quartz ( $\text{SiO}_2$ ) and orthoclase ( $\text{KAlSi}_3\text{O}_8$ ) have fixed chemical compositions but both precipitate over a range of temperatures. Bowen was unable to explain this and eventually stated that “The matter is really too complex to be presented in such simple form. Nevertheless the simplicity, while somewhat misleading, may prove of service in presenting the subject in concrete form.” His best suggestion to explain the discrepancy was that there must be some reaction occurring between the remaining molten rock and the minerals that were beginning to form, giving rise to his original reference to his “Reaction Series”.



## Topic #4: Chemical Decomposition of Igneous Rocks

Another aspect of the major types of igneous rocks was their varying rates of chemical decomposition. In 1938, Samuel Goldich published a paper in which showed that the order in which the major rock forming silicate minerals chemically decomposed was the same order in which Bowen stated they crystallized from molten rock. Stated another way, those minerals that crystallized first at the highest temperatures chemically decomposed first and at the highest rates. Conversely, those that precipitated last at the lowest temperatures were the most chemically resistant to decomposition and decomposed at the slowest rates.

Actually this is a good teachable moment for some students. If asked, without even using the term “thermodynamics”, they should be able to determine that minerals that crystallize at high temperature would not be expected to be stable at low temperature. Likewise, a mineral that crystallizes at a low temperature would not be stable at a high temperature. In addition, they might also be able to surmise the greater the difference between the temperature of crystallization and atmospheric temperature, the higher the rate of decomposition. The following examples may



be used to demonstrate the relationship. Figure 1 shows Bowen’s Crystallization Series. Note that the igneous rock basalt, at the top of the diagram, consists of minerals that crystallize at high temperature. According to Goldich, these minerals, and the basalt their mixture forms, should weather chemically at a relatively fast rate. This is clearly the case on the Big Island of Hawaii where it is not uncommon to see, only fifty years after a lava flow cooled, small plants already beginning to take root in soils formed from the decomposing basaltic rock. In contrast, find granite’s position on the illustration. It is a mixture containing extensive amounts of quartz and orthoclase feldspar, both of which crystallize at low

temperatures I should not be so surprising that granite it very resistant to decomposition. In fact, of all the major igneous rocks, granite is the most resistant to chemical attack. Thus its preferred use as a building and ornamental stone. It also explains why the name “Rock of Ages” was given to a commercial brand of granite tombstones.

There is one sedimentary rock that is highly resistant to chemical attack. Can you suggest which one? Sandstone is a good guess but not quite right. The sedimentary rock quartzite is a sandstone with the quartz grains are cemented together by quartz. Of all the sedimentary rocks, quartzites are the most resistant to chemical attack. If you have been to Seneca Rocks or the crest of North Fork Mountain you have seen how this resistance rock contributes to the rugged landscape of that area. Geologically, the sand at your favorite beach is more than likely to consist of sand-sized grains of quartz. In fact, about 400 million years ago, the quartz one now sees exposed at Seneca Rocks was part of a quartz-rich beach.

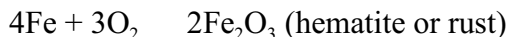
## Topic #5: Introduction to Weathering

While some rocks do seem to last for a very long time, geologically, no rock will last very long. Once exposed to the atmosphere, the minerals of which they are made will succumb to processes that will either break them apart or will attack them chemically. The processes by which rocks and minerals disintegrate or decompose are called weathering. Weathering is of two kinds; physical and chemical. Physical weathering includes any process by which rocks particles are physically reduced in size. You see the results of physical weathering as you drive along and observe the piles of rock debris at the base of roadcuts or cliffs. A major agent of physical weathering in temperate climates is the freezing and thawing of ice, a process called frost wedging. Much of the rock debris that we see along the base of road cuts and cliffs was generated by the process of frost wedging. In the case of shales, the debris consists primarily of relatively small rock fragments that may have been the result of freeze/thaw cycles within a single winter while large boulders of sandstone lying along the roadside may have taken decades of winters to be broken from the sandstone beds of which it was originally a part. Considering that all chemical reactions involving solids are surface reactions, the reduction in particle size and the subsequent increase in surface area resulting from physical weathering is essentially preparing rocks and minerals for the second type of attack, namely, chemical weathering.

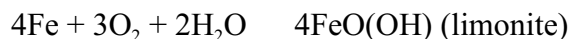
### Chemical Weathering

Oxygen and carbon dioxide are the two major chemical weathering agents. It is important to understand, however, that for either to be an effective agent of chemical weathering, they must be dissolved in water. Most individuals assume that the mere mention of oxygen as an agent of oxidation is a reference to gaseous oxygen at atmospheric temperatures. Thus, you should be specific. Fortunately for carbon units, such as you, your students, and all living things, oxygen gas is a relatively ineffective oxidizing agent at atmospheric temperatures. In truth, for oxygen gas to be an effective oxidation agent, it must be heated to high temperatures, such as in the flame of a burning log or an acetylene torch.

This leads to another point requiring clarification. Many textbooks present the following reaction to explain the rusting of an iron nail:



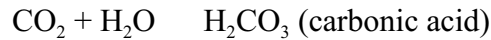
In fact, in the absence of water, such as in a very dry desert, iron tools can survive for very long periods of time. However, in West Virginia's more humid, temperate climate, the reaction should be presented by two reactions:



When exposed to the warming of the Sun, limonite dehydrates, creating hematite or rust:



By volume, carbon dioxide only represents 0.035% of Earth's atmosphere. The major natural sources of atmospheric carbon dioxide are the decay of once living tissues and volcanic eruptions. All living forms are made primarily of carbon which will eventually oxidize and return to the atmosphere. Of all the gases erupted during volcanic eruptions, carbon dioxide is second only to water vapor in abundance. As was the case with gaseous oxygen, carbon dioxide must also be dissolved in water to become an effective agent of chemical weathering. However, the process is not straight forward. First, carbon dioxide reacts with water to produce carbonic acid:



You should note that, as written in the above equation, carbonic acid has no acidic properties. It must first dissociate to produce the acidic hydrogen ion,  $\text{H}^+$ , or the hydronium ion,  $\text{H}_3\text{O}^+$ :



or



Because carbonic acid has a very low dissociation constant, it is a very weak acid, explaining why we can drink a very dilute solution of it, bathe in it, and cook our food in it. It is worth pointing out that the first reaction between water and carbon dioxide occurs in the atmosphere, meaning that acid rain has been falling on Earth in the form of a dilute solution of carbonic acid since the first drop of rain fell some three billion years ago.

## Chemical Weathering of Igneous Rocks

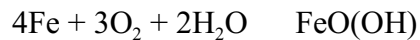
The nine major minerals making up the igneous rocks of Earth's crust were mentioned in Topic #3: Bowen's Crystallization Series. Table 1 from that topic is repeated here.

**Table 1: Bowen's Order of Crystallization**

	<b>Ferro-Magnesian Minerals</b>	<b>Non-Ferromagnesian Minerals</b>
<b>High Temp</b>	<b>Olivine</b> $(\text{Fe,Mg})_2\text{SiO}_4$ <b>Augite</b> $(\text{Ca,Na})(\text{Mg,Fe,Al})(\text{Si,Al})_2\text{O}$ <b>Hornblende</b> $\text{Ca}_2\text{Na}(\text{Mg,Fe}^{2+})_4 -$ $(\text{AlFe}^{3+},\text{Ti})_3\text{Si}_8\text{O}_{22}(\text{O,OH})_2$ <b>Biotite</b> $\text{K}(\text{Mg,Fe})_3(\text{Al,Si}_3\text{O}_{10})(\text{OH})_2$ Potash Feldspar	<b>Feldspars</b> <i>(Plagioclase Feldspars)</i> <b>Anorthite</b> $\text{CaAl}_2\text{Si}_2\text{O}_8$  <b>Albite</b> $\text{NaAlSi}_3\text{O}_8$  <b>Orthoclase</b> $\text{KAlSi}_3\text{O}_8$ <b>Muscovite</b> $\text{KAl}_2(\text{Al,Si}_3\text{O}_{10})(\text{OH})_2$ <b>Quartz</b> $\text{SiO}_2$

## Low Temp

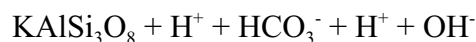
Note that their major ionic components are ferrous iron ( $\text{Fe}^{2+}$ ), ferric iron ( $\text{Fe}^{3+}$ ), aluminum ( $\text{Al}^{3+}$ ), the alkali elements sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ), the alkaline earth elements calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ), and silica ( $\text{SiO}_4^{4-}$ ). If the rocks are in a region where water is available, the iron is removed from the exposed surfaces of the ferro-magnesian minerals by first creating the oxy-hydroxide which in turn dehydrates to form the oxide:



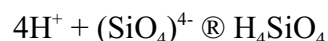
The yellow limonite and the red hematite created by the oxidation of the ferro-magnesian minerals along with black organic matter generated by the decay of once living tissues are the three major coloring agents of sediments, sedimentary rocks, and soils. When blended together in various proportions, they provide the wide range of colors one sees from red to brown to black.

The process of carbonation involves the reaction between the bicarbonate ion and the alkali and alkaline earth elements to form the water-soluble bicarbonates of sodium,  $\text{Na}^+$ , potassium,  $\text{K}^+$ , calcium,  $\text{Ca}^{2+}$ , and magnesium,  $\text{Mg}^{2+}$ , which are subsequently carried off by streams and groundwater, eventually to the ocean. Because all gases, including  $\text{CO}_2$ , are more soluble in cold water than in warm, the concentration of carbonic acid in cold water is higher than in warm water. As a result, rocks such as limestone are more soluble in cold water than in warm. Conversely, in warm waters such as those that exist over the continental shelves between the Tropics of Cancer and Capricorn,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  ions react to precipitate as calcite,  $\text{CaCO}_3$ , either chemically to form carbonate mud or biochemically to form the shells of animals such as coral, snails, and clams. As either the carbonate mud or the remains of shells are lithified, they are converted into the third most abundant sedimentary rock type, limestone (10%).

Perhaps the most important reaction is one called carbonation/hydrolysis. Hydrolysis refers to the reaction with the dissociated form of water,  $\text{H}^+ + \text{OH}^-$ . As an example, consider the reaction involving orthoclase feldspar, carbonic acid, and water:



With the potassium ions removed from the exposed silicate minerals by reacting with the bicarbonate ion and being carried off to the ocean as a water soluble bicarbonate, ( $\text{KHCO}_3$ ) what remains of the original minerals are the aluminum and the silica. Some of the silica reacts with the hydrogen ions from the carbonic acid and water to form silicic acid:



Silicic acid is even weaker than carbonic acid and is taken into molecular solution and carried off, eventually to the ocean. Under conditions not exactly understood, the silicic acid precipitates first in warm ocean waters as a gel which subsequently dehydrates and crystallizes into cryptocrystalline (microscopic) crystals of quartz,  $\text{SiO}_2$ :



The quartz crystals then lithify into a sedimentary rock called chert. Chert is commonly associated with limestone which suggests that the chemical environment that favors the formation of calcite also favors the precipitation of crypto-crystalline quartz. However, a recent theory indicates that a major source of the quartz that forms chert is derived from wind-blown, wind-rounded quartz sand grains from coastal deserts. While chert is not a familiar rock type to most individuals, a variety of chert called flint is well known as the major material used by paleo-people to make tools.

Following the removal of the potassium and some of the silica, All that remains of the silicate minerals is the aluminum and the remaining silica along with hydroxyl ions which combine to form the clay minerals,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . The formula just cited is that of kaolinite, often referred to as the “pure clay material”. There are however, a wide variety of clay mineral types, each with their own characteristics. The importance of the clay minerals is that they are the major component of soils, without which the land surface of Earth would look like a non-life supportive moonscape.

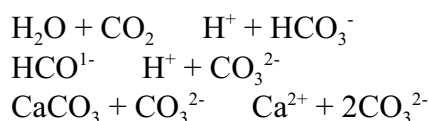
Clay minerals are also the major component of shales that make up 70% of all sedimentary rocks. With the clay minerals being created by the carbonation/hydrolysis of all of the major silicate minerals except olivine (olivine has no aluminum) and quartz which doesn't react with either dissolved oxygen or carbon dioxide, it should come as no surprise that the most abundant type of sedimentary rocks is shale. The remaining 20% of all sedimentary rocks are sandstones composed primarily of quartz, the most chemically resistant of all the silicate minerals. The remaining 10% of sedimentary rocks are limestones, the most abundant of which are of biochemical origin.

## Topic #6: The Formation of Caves and Caverns



Although caves and caverns do form in regions underlain by gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , by far, most caves and caverns form in limestone. All rocks possess irregular fracture systems but most also contain two sets of more regular, near vertical, intersecting, open fractures called joints (Figure 1).

Joints in limestones can be exploited by moving groundwater and become increasingly larger passageways as the dilute solution of carbonic acid (groundwater) dissolves the limestone exposed in the fracture walls by the process of carbonation:

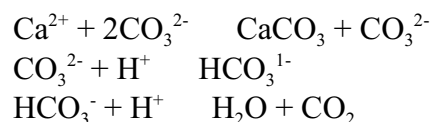


While this dissolution process is very slow because of the weakness of carbonic acid, there is another dissolution reaction that most students have been made aware of and that is the common “fizz” test used to identify a mineral as calcite:



Because of the rectangular arrangement of the joints, the passageways of caves and caverns commonly follow the same rectangular pattern. The presence of weathered limestone bedrock often results in the formation of a particular landscape called karst topography containing extensive underground cave systems and surface sinkholes. Karst topography is a common feature throughout the Great Valley (or Shenandoah Valley) of Appalachia and can be easily seen in Greenbrier and Monroe counties, West Virginia.

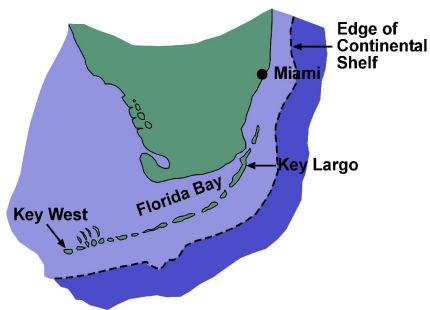
A source of great interest in limestone cave systems are speleothems such as stalactites and stalagmites produced from precipitated calcite. Because calcite is more soluble in cold water than in warm, as the percolating water moves downward through a cave system and is warmed, the following occurs:



Warm water speleothem reactions are the reverse sequence of the cold water karst reactions. The warm water reactions also describe bioengineered shells developed by coral, clams, oysters, and snails. These animals have body mechanisms that allow them to remove  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  directly from ocean water and precipitate it in the form of shells. Once again, the requirement of warm water applies with most shelled animals living in the waters between the Tropic of Cancer in the

north and the Tropic of Capricorn in the south. A particular ideal site is where the cold, ocean waters rise from the abyssal depths and spread out over a shallow portion of the coastline. The area adjacent to the Florida Keys is an excellent example.

Cold ( $\sim 3^{\circ}\text{C}$ ) carbonate-rich waters rise from the abyssal depths of the Gulf of Mexico and are driven by the prevailing winds into Florida Bay where the water averages only about 10 feet deep. Located about 80 miles north of the Tropic of Cancer, the shallow bay water is significantly warmer. This makes the site an ideal natural carbonate chemical factory. Tiny crystals of calcite precipitate out of the water and eventually cover the floor of the bay with a carbonate mud that, ultimately, will become a chemical limestone. The elevated temperatures and



the levels of evaporation make the bay too warm and too salty for most animal life. As a result, limestones that would form in such environments will be basically fossil free. Interestingly, to the immediate Gulf side of the Keys, literally a walk across the road, the waters are the ideal habitat for shell-bearing coral and gastropods whose shell material will eventually be turned into fossiliferous, biochemical limestones. West Virginia road cuts and outcrops contain examples of both kinds of limestones formed by the same processes over 300,000,000 years ago.

## Topic #7: Hard and Soft Water

Hard water is, in one sense, a reference to calcium and/or magnesium content. It is particularly prevalent in regions directly underlain by limestones where dissolution of the bedrock limestone increases the calcium content of both the surface and groundwaters. Another carbonate rock commonly associated with limestones are dolomites that consist of the mineral dolomite,  $\text{CaMg}(\text{CO}_3)_2$  that provides additional  $\text{Ca}^{2+}$  as well as  $\text{Mg}^{2+}$  into the waters. When these waters are mixed with soap, an insoluble precipitate forms that is the all too familiar ring around the basin or bath tub or found adhering to clothes or dishes. Where did the scum come from?

The definition of water hardness is “the ability to precipitate soap”. Soap is sodium stearate. The stearate ion is a long chain of seventeen carbons and associated hydrogens that ends with a carbon atom to which is attached a double-bonded oxygen and a single-bonded oxygen ion. Sodium stearate is water soluble and dissolves to produce suds. If the water is “hard” due to its content of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, the stearate ion reacts with  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions and produces scum that consists of either the highly insoluble precipitate of calcium or magnesium stearate or both.

One solution to the problem is to react the hard water with “salt”,  $\text{Na}_2\text{CO}_3$ , which will precipitate all of the  $\text{Ca}^{2+}$  as  $\text{CaCO}_3$  and with  $\text{Ca}(\text{OH})_2$  which will precipitate the  $\text{Mg}^{2+}$  as the hydroxide. Perhaps an easier solution, however, is to use a commercial water softener consisting of a tank filled with tiny resin beads designed to preferentially adsorb  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  ions. Before being installed, the resin has been charged with  $\text{Na}^+$  by flushing the tank with brine ( $\text{NaCl}$ ). During use, the hard water passes through the resin bed exchanging its load of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  for the  $\text{Na}^+$  that goes into solution, rendering the water soft. Because sodium stearate is water soluble, there will be no scum precipitated. Of course, in time, all of the  $\text{Na}^+$  ions originally present on the resin will have been replaced with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. At that point, the resin will no longer be effective and the resin tank must be replaced with a new tank of resin that has been flushed with brine or recharged in situ by re-flushing it with a solution of  $\text{NaCl}$  to remove the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and replace them with  $\text{Na}^+$  ions.



## Topic #8: Soils, Clay Minerals, and Cation Exchange

The most important components of soil are the clay minerals. Part of the discussion in Topic #5: Introduction to Weathering Topic, addressed the production of clay minerals as the end product of the carbonation/hydrolysis chemical weathering process acting upon all but two of the nine major rock-forming silicate minerals

One learns in an introductory chemistry class that all compounds are electrically neutral. The fact is that clay minerals are never electrically neutral. While some may be positively-charged the great majority are negatively charged. The reason for the negative charge is because the crystal structures of the clay minerals rarely have the necessary number of cations within the structure needed to neutralize the anionic charge. But the rule that compounds must be electrically neutral still stands. As a result, if the charge deficiency cannot be taken care of within the crystal structure, it must be taken care of on the outside of the structure. This is accomplished through the adsorption of cations onto the surface of the clay minerals particles. The number of adsorbed cations depends on the magnitude of the charge on the clay particle and the charge on the adsorbed cation. An important aspect of the process is that whatever cations may be in the cation exchange positions, they may be replaced with other cations brought in proximity to the clay particles by percolating soil water. This process is called cation exchange. The cation exchange process is so important to agronomists that they have a laboratory test to determine the cation exchange capacity, the CEC, of any clay-rich soil material. The importance of the CEC lies in the fact that the clay minerals store and provide nutrients for the plants. I'm certain you have seen lawns and gardens covered with a white powder during the Spring of the year. Perhaps you may have even wondered what the white powder was. The material is agricultural lime which is simply limestone that has been ground into a fine powder. The reason for grinding the limestone into a fine powder is to increase the surface area which, in turn, increases the rate at which the limestone dissolves and provides  $\text{Ca}^{2+}$  ions to the percolating soil water and subsequently to the cation exchange sites on the clay minerals. The goal of this process is to neutralize acid soils that characterize most of the soils in the United States east of the 100<sup>th</sup> meridian. Because the soils have been naturally leached with a dilute solution of carbonic acid to which other anthropogenic acids have been added via air pollution, the cation exchange sites are all occupied by hydrogen ions. Once the acid soils have been treated with ag-lime, the hydrogen ions are replaced with a calcium ions. Not only has the acid soil been neutralized by replacing the  $\text{H}^+$  ion with the  $\text{Ca}^{2+}$  ion, but the soil is now able to provide the  $\text{Ca}^{2+}$  nutrient many plants such as grass desire. In contrast, the soils throughout the semi-arid interior of the continent that are subjected to periods of rain and drought are self-neutralized by extracting  $\text{Ca}^{2+}$  ions from the rising groundwater during the dryer parts of the year.

How do the plants acquire the essential nutrients the clay minerals hold by cation adsorption? The answer is that plants also employ cation exchange to derive nutrients from the soil. Their roots secrete carbonic acid. Once the acid dissociates, the hydrogen ions are exchanged for whatever nutrient the soil has in the cation exchange positions. However, because this process will eventually re-saturate the clay mineral particles with  $\text{H}^+$  ions, returning the soil to its original acid condition, the treatment of the soil with agricultural must be repeated, to the point it becomes a seasonal ritual.