Chalk Rock: The Heart of KU

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Spooner Hall & Local Importance

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Spooner Hall was commissioned after a donation in 1891 of $91,000, which is approximately $2.4 million in 2017, from Boston leather merchant William B. Spooner. This donation was made for his great nephew, Francis Huntington Snow, who was chancellor of the University of Kansas at the time. Spooner’s donation was split into two to construct “the first permanent chancellor's residence on the corner of 14th street and Louisiana” and Spooner Hall. Henry Van Brunt, a distinguished Kansas City-area architect renowned for designing libraries, sketched a blueprint for the hall and it was built with Oread limestone and trimmed with imported red sandstone. Mount Oread is the first, and only place, Oread limestone is found, and is the hill on which the University of Kansas is situated. The abundance of limestone found on the hill gave the University of Kansas’ science club the idea of the “Rock Chalk Chant.” In 1889, they switched the word order from “chalk rock” to “Rock Chalk,” and replaced the old “Rah Rah” chant.

Contrary to popular belief, the Oread limestone formation is not exclusively made up of one type of sedimentary rock. It is made up of two divergent alignments - the Oread formation and the Lawrence formation, named after the city. Each formation is made up of several different types of rock; the Oread formation consists of the Toronto, Snyderville, Leavenworth, Heebner, and Plattsmouth Limestone and Shale Members. These differing rock sheets are due to the erosion process by the Pennsylvanian Sea that used to occupy the space where Mount Oread stands today during the Carboniferous geological time period. The limestone erosion
process is multi-step and is done completely from the pressure and movements of water currents. Erosion takes years before moving onto the next stage, which results in organic limestone taking millions of years to form; as the amount of skeletal pieces gather on the seafloor, the organism debris gradually compresses together by pushing out water occupying the space in between them. Next, the sediments are slowly bonded together, followed with continued compression. A more in-depth description of this process can be found in the “Limestone Cycle” section.

Shale is classified as a clastic sedimentary rock that forms near limestone deposits and develops from the compaction of finely-grained particles and silt. Due to their small size, these particles are inclined to remain suspended in bodies of water for long periods of time before depositing in shallow and slow moving water. Although shale is not formed with calcium carbonate, bits of CaCO₃ from nearby limestone formations may mix in with the shale particles; therefore, it may also react with acid, although less vigorously than limestone, making shale more weather resistant; weathering effects on limestone are shown in the “Industrial Uses” section.

These unlike rocks were deposited at different layers because of the Pennsylvanian Sea’s fluctuating sea levels, resulting in cyclic rock deposits. During the Carboniferous time, ice caps were regularly melting and reforming, causing the Pennsylvanian Sea’s water levels to fluctuate; when the Pennsylvanian’s water levels were low, shale was formed due to its particles depositing in shallow water. Conversely, limestone was formed when sea levels were high. This resulted in rock layers that alternate between limestone and shale, shown in the picture to the left, giving each rock type their own thickness and distinct colors; the Toronto limestone member is between 5 to 12 feet thick and is a brownish-gray color. The Snyderville Shale is usually 12 feet thick, varying from bluish-gray, to a red, to a green color. The Leavenworth Limestone is a dark bluish-gray and quite thin, only being between 1 to 2 feet thick. The Heebner Shale comes in four different shades: gray, dark bluish-gray, black, or yellow; it’s thickness ranges from 5 to 8 feet. The Plattsmouth Limestone is a light bluish-gray and fluctuates from 15 to 30 feet in thickness.
When Spooner Hall was commissioned, Oread limestone had just been recently discovered and the first layer of it, the Plattsmouth limestone member, was chosen to build the hall. This specific type of chalk rock was found to be one of the most dense forms, making it the most durable type within the Oread formation. As it also had bits of shale within itself, the Plattsmouth limestone was even more durable than originally thought, against the effects of weather, than other nearby limestone types, such as Cottonwood limestone from the Flint Hills. Cottonwood limestone does not have other heavy-duty rock types placed throughout and had been used to construct buildings at Kansas State University for decades. It is believed that architect Van Brunt refused to utilize the more common, therefore “less special,” Cottonwood limestone when he saw Plattsmouth limestone for the first time. The light bluish-gray sedimentary rock had bits of shale coloring within, offsetting nicely with the red sandstone trimming. This gave a more unique and blended facade to Spooner Hall, setting Van Brunt’s design apart from rival university Kansas State’s designs. This specific layer of rock was also extremely close in proximity to the actual building site, taking only three years from the building commission to the grand unveiling of the University of Kansas’ first library, solidifying Van Brunt’s reputation and legacy.

Spooner Library was first opened in 1894 as the sixth building on campus with state of the art accommodations, such as “cast-iron book stacks and incandescent electric lamps.” However, after years of increasing enrollment, the library became terribly overcrowded. In order to accommodate the growing student body, Watson library was built and it opened in 1924 on Jayhawk Boulevard. Spooner Library was then converted into the Spooner-Thayer Art Museum, displaying artworks for over fifty years; it was converted again in 1978 into an anthropology museum when the Spencer Museum of Art opened. The hall is currently the oldest academia building on campus and was added to the National Register of Historic Places in 1973. Today, it continues to house over a million various anthropology pieces for students and researchers.
Limestone Cycle

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Limestone is a sedimentary rock formed from calcium carbonate originating from both organic and inorganic sources. In biological sedimentation, fragments of calcium carbonate systems are deposited, compressed, and pressurized to form the rock known as limestone. The sediments for biological limestone formation are frequently derived from the shells of marine organisms. Many organisms such as oysters, coral, and clams with delicate tissues living in marine environments are able to utilize calcium carbonate dissolved in water to form hard exoskeletons and protect themselves; when the organism dies, its shell can be fractured and deposited on the ocean floor. The pressure of the shell fragments on each other and the pressure from the water above slowly drives water out from the spaces between sediments and replaces it with a carbonate precipitate.¹ Over many years, with appropriate sedimentation and pressure, limestone can be formed through this way. Limestone formed through biological sedimentation can have variable composition based upon the type of organism from which sediments were derived and the pressure and turbulence that the sample underwent, as discussed more fully in the “Limestone Chemical Structure and Composition” section. This biological sedimentation also provides the opportunity for the appearance of marine fossils within the limestone itself, which can be used as evidence for Kansas’ oceanic past, discussed in “Spooner Hall and Local Importance”.

Limestone can also be formed through chemical means. One of the most common sources of chemical limestone is the precipitation of calcium carbonate directly from water in the reaction between calcium ions and carbonic acids.²⁶ This precipitation of calcium carbonate creates small crystal systems that can be deposited to form the white sand beaches frequently encountered in the Caribbean.⁴ Chemical limestone can also occur through the evaporation of water containing dissolved CaCO₃, leaving behind only solid calcium carbonate.⁵ This type of CaCO₃ deposition can be encountered in the stalactite and stalagmite formations of caves. When water moves through a cave, it can pick up minerals such as calcium carbonate and carry them until it reaches cracks or imperfections in the cave ceiling.²⁷ At that point, the water drips through the ceiling and either deposits the calcium carbonate on the ceiling as it evaporates, or carries the calcium carbonate as it drips to the floor and later evaporates to leave limestone behind, eventually forming a cone-shaped limestone system.⁵ The deposition of
CaCO₃ on the ceiling forms stalactites; the deposition on the floor forms stalagmites. The formation of both biological and chemical limestone deposits requires a great amount of time. Though limestone is formed through complex processes that require many years to form only a small amount of stone, limestone can be broken down and changed through a number of reactions and processes. One of the most notable characteristics of limestone is that it reacts readily with acids to produce carbon dioxide, water, and calcium salts—compounds containing calcium along with a negatively charged anion. These calcium salts can be cycled through the environment if they are taken up by plants and animals or fixed into the soil; they can also be transported to large bodies of water where they can once again dissolve and react with carbonic acid to form calcium carbonate. The reaction of limestone with acids is also particularly hazardous for industrial limestones exposed to acid rain, as shown in “Industrial Uses”.

Through a series of hydration and heat reactions as well as reactions with carbon dioxide, the calcium carbonate forming limestone can decompose and reform. The heating of limestone can cause the thermal decomposition of calcium carbonate into CaO—commonly known as quicklime—and carbon dioxide. The quicklime resulting from thermal decomposition readily reacts with water to form Ca(OH)₂ or slaked lime, a calcium salt made up of a calcium cation and two hydroxide anions. Ca(OH)₂ is capable of undergoing a double replacement reaction with carbon dioxide to produce water and calcium carbonate. Through this series of reactions it is possible for limestone to be broken down into various products and eventually reformed once again; however, this specific sequence of reactions is infrequent in nature for a number of reasons. As stated in “Limestone Chemical Structure and Composition”, the least stable form of calcium carbonate has a minimum melting point of 400°C and some forms only melt at temperatures upwards of 1300 °C. These temperatures are unlikely to be encountered in most places on Earth, and therefore the initial thermal decomposition of limestone to begin the cycle is unfavorable outside of industrial settings.

Limestone can be broken down and reformed through chemical processes involving heat, carbon dioxide, and water. However, limestone can also be transformed into new types of rock through processes involving heat and pressure. Most notably, limestone can be formed into marble—a metamorphic rock—by being subjected to extreme heat and pressure conditions. The subjection of limestone to high pressure causes the individual, disorderly collections of calcium carbonate to interlock with each other and recrystallize to form a rock with higher uniformity in both composition and appearance.

Some scholars argue that limestone is capable of forming another type of rock—the igneous carbonatite. Igneous rocks are those formed from the cooling of magma or lava and typically contain a high concentration of silicon compounds. However, carbonatites are unusual
in that they have a notably low silicate concentration and instead have upwards of 50% carbonate materials, unlike other igneous rocks formed from lava and magma. The origin of carbonatites is highly debated; some believe that they are essentially “igneous limestones” and are formed through the cooling of magma or lava containing a high concentration of calcium carbonates.\textsuperscript{31} Others believe that carbonatites are formed through the cooling of secondary lavas derived from natrocarbonatite lavas with a high concentration of sodium.\textsuperscript{32} In any case, the continued cycling of limestone—or more specifically, calcium carbonate and carbonate compounds—may be possible through compression and temperature changes to form new rocks that can be broken down to form new sediments that may eventually reform into limestone itself.
Limestone Chemical Structure and Composition

Limestone is by definition a rock that contains at least 50% calcium carbonate in the form of calcite by weight. All limestones contain at least a few percent other materials. These can be small particles of quartz, feldspar, clay minerals, pyrite, siderite, and other minerals. It can also contain large nodules of chert, pyrite, or siderite. The calcium carbonate content of limestone gives it a property that is often used in rock identification - it effervesces in contact with a cold solution of 5% hydrochloric acid. Limestone is a sedimentary rock containing calcite and aragonite, both made up of calcium carbonate, and is primarily made up of the skeletal fragments of marine organisms, thus proof of Kansas’ oceanic past. Calcium Carbonate can be found in the form of three variants found in rocks and minerals: calcite, aragonite, and vaterite.

To delve into these three types, first, let’s cover crystal systems. Space groups and crystals are divided into seven crystal systems according to their point groups, and into seven lattice systems according to their Bravais lattices. Five of the crystal systems are essentially the same as five of the lattice systems, but the hexagonal and trigonal crystal systems differ from the hexagonal and rhombohedral lattice systems. The six crystal families are formed by combining the hexagonal and trigonal crystal systems into one hexagonal family, in order to eliminate this confusion.

Calcite has a trigonal System which means it consists of the five point groups that have seven corresponding space groups associated with the rhombohedral lattice system (and 18 corresponding space groups associated with the hexagonal lattice system). Aragonite has an orthorhombic system comprised of orthorhombic lattices, which result from stretching a cubic lattice along two of its orthogonal pairs by two different factors, resulting in a rectangular prism with a rectangular base (a by b) and height (c), such that a, b, and c are distinct. All three bases intersect at 90° angles, so the three lattice vectors remain mutually orthogonal. Finally, vaterite has a hexagonal system consisting of 27 space groups such that all space groups with the same point group are in the hexagonal lattice system.

We will focus more on Calcite and Aragonite, being the main components of limestone. Aragonite and calcite have the same chemical formula, CaCO₃, but their atoms are stacked in different configurations. That is, they are polymorphs, which is the ability of a solid material to
exist in more than one form or crystal structure. Aragonite has an orthorhombic structure and calcite a trigonal structure (the Mindat site can help you visualize these for aragonite and for calcite).\textsuperscript{16}

Calcite is more stable in general than aragonite, although as temperatures and pressures change one of the two minerals may convert to the other. At surface conditions, aragonite spontaneously turns into calcite over geologic time, but at higher pressures aragonite, the denser of the two, is the preferred structure. High temperatures work in the favor of calcite. At surface pressure, aragonite can't endure temperatures above around 400°C for long.\textsuperscript{16}

Calcium carbonate chemistry is more complicated when it comes to understanding which polymorph will crystallize out of solution. This process is common in nature, because neither mineral is highly soluble, and the presence of dissolved carbon dioxide (CO\textsubscript{2}) in water pushes them toward precipitating. In water, CO\textsubscript{2} exists in balance with the bicarbonate ion, HCO\textsubscript{3}\textsuperscript{-}, and carbonic acid, H\textsubscript{2}CO\textsubscript{3}, all of which are highly soluble. Changing the level of CO\textsubscript{2} affects the levels of these other compounds, but the CaCO\textsubscript{3} in the middle of this chemical chain pretty much has no choice but to precipitate as a mineral that can't dissolve quickly and return to the water. This one-way process is a major driver of the geological carbon cycle.\textsuperscript{16}

The chemical formula of calcium carbonate is CaCO\textsubscript{3} and its molar mass is 100.1 g/mol. It is a salt made of the bivalent calcium cation (Ca\textsuperscript{2+}) and the bidentate carbonate anion (CO\textsubscript{3}\textsuperscript{2-}), in which the carbon is attached to two oxygen atoms through single bonds and one oxygen atom through a double bond.\textsuperscript{17}

Calcium carbonate occurs naturally in several mineral forms including the pure calcite, aragonite and vaterite minerals as well as the impure minerals-limestone, chalk, marble and travertine. It is also the main chemical constituent of egg shells, sea shells, oyster shells, snail shells, corals, etc. Pure CaCO\textsubscript{3} is an odorless, fine white powder. It has a density of 2.71 g/mL and melting point of 1,339 °C, as its calcite form. The other common mineral form, aragonite, has a density of 2.83 g/mL and melting point of 825 °C.\textsuperscript{17}

As far as chemical properties are concerned, calcium carbonate is insoluble in water and stable at normal temperatures. When heated to high temperatures, it decomposes to form calcium oxide with the release of carbon dioxide (shown below).\textsuperscript{17}

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2
\]

CaCO\textsubscript{3} also releases carbon dioxide when it is reacted with acids. Calcium carbonate reacts with water containing carbon dioxide to form the water soluble calcium bicarbonate salt (Ca(HCO\textsubscript{3})\textsubscript{2}). There are many different names used for limestone. These names are based upon how the rock formed, its appearance or its composition, and other factors. Here are some of the more commonly found varieties:\textsuperscript{16}
Chalk: A soft limestone with a very fine texture that is usually white or light gray in color. It is formed mainly from the calcareous shell remains of microscopic marine organisms such as foraminifera, or the calcareous remains from numerous types of marine algae. This is what is used in the multitudinous classrooms of the University.

Fossiliferous Limestone: A limestone that contains obvious and abundant fossils. These are normally shell and skeletal fossils of the organisms that produced the limestone.

Lithographic Limestone: A dense limestone with a very fine and very uniform grain size that occurs in thin beds which separate easily to form a very smooth surface. In the late 1700s, a printing process (lithography) was developed to reproduce images by drawing them on the stone with an oil-based ink and then using that stone to press multiple copies of the image.
Industrial Uses

Limestone, the “chalk rock,” is used in so many industrial projects, of mineral raw materials it is ranked third in volume produced—coming in behind coal and sand and gravel. While a bit outdated, table 2 from the “Industrial Uses of Limestone and Dolomite” accessible online at lib.ku.edu, provides an accurate list of limestone uses and how much of it is used. Despite its widespread and varying uses, when most people think of limestone, they think of its use in structures; on KU’s campus the campanile is most notable, while in the world some may point to the Great Pyramids of Giza. These monuments are of great importance and were chosen as the material most likely due to limestone’s ability to withstand weathering and corrosion more than other materials. Corrosion is the process of breaking down a material into a more stable chemical form. Limestone’s chemical makeup as it is used in these monuments is already in a very stable state, as discussed in “Limestone Cycle,” so very little impacts it on a day-to-day basis. However, acid rain can cause limestone to react and seemingly deteriorate. While all rain is slightly acid with the average rainfall having a pH of around 5.6, the acid rain the truly does damage is a bit different. Acid rain only becomes more prevalent through the years due to pollution and it involves rains containing sulfuric or nitric acid but for our purposes we will look at how sulfuric acid reacts to then damage limestone. Sulfuric acid, written as $\text{H}_2\text{SO}_4$, converts into ions, as seen in the chemical equation: $\text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-}$. The sulfur dioxide lowers the pH of the rainwater even further, causing a much more acidic form of water to fall. Since limestone is largely composed of calcium carbonate the following reaction takes place upon rainfall making contact with the structures: $\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{CO}_2 + \text{H}_2\text{O}$. The reaction causes the limestone to turn into an aqueous state, calcium sulfate, a gas, carbon dioxide, and a liquid, water.

When used as a construction material, limestone is crushed and sometimes combined with concrete to make cement. It can also be combined with clay and when fired in a kiln at around 2,640 °F, almost 83 times hotter than standard conditions, forms “Portland cement.”
Portland cement is a very common general-use cement as it is used for roads, floors, roofs, pipes, etc. However, as referenced before, table 2 shows that limestone has many other uses in today’s world.

The fourth largest use of limestone, coming in at 2.8 percent of the total use of limestone, is calcium carbonate’s presence in paper. There are two different forms of calcium carbonate that the paper industry utilizes: ground calcium carbonate and precipitated calcium carbonate. The ground calcium carbonate, GCC, refers to the more chalky form of limestone, made from concentrated and finely ground calcium carbonate. It is used to make cardboard packaging, fine paper and pulp-based paper. As for the precipitated calcium carbonate, PCC, it is made from quicklime. Quicklime is produced industrially using something called a lime kiln. The heat in the kiln, ranging from 620.33°F to 2240.33°F, as converted from the diagram speed up the decomposition of calcium carbonate for the reaction to yield calcium oxide, quicklime, and carbon dioxide. By using the kiln air is kept from mixing with the limestone in order to avoid an unwanted reaction between the two. The PCC quicklime is then used as a filler in fine paper like copy paper to make it brighter and more opaque.

Sixth on the list is limestone’s role in glass. The simplified version of making glass is just melting sand and then letting it cool to form glass. However, this version leaves out the important role limestone plays. During the melting process sodium carbonate is added to form carbon dioxide and sodium oxide, yet these two products are soluble, meaning if a liquid were added at this stage, the glass would dissolve. Adding limestone to the mix prevents this from happening as once again the limestone reacts with the heat to form calcium oxide and carbon dioxide. Calcium oxide being very sparingly soluble allows the glass to be used for almost any glass product, as about 90 percent of glass in the world is made using limestone.

Water purification appears on the list as a prevalent use of limestone and it used to be a large part of the process but has fallen out of favor as a way to completely “purify” water. It started to be used in the process because limestone is an alkaline agent, giving it the ability to neutralize acids. Hydrochloric acid, a relatively common strong acid, can be neutralized with calcium carbonate through this reaction: \( \text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O} \). Reactions like these and the presence of other calcium products in limestone lead people to believe that the alkaline would have an impact on wastewater with higher pH levels. A typical “limestone
treatment system” would have involved a tank of limestone chips where wastewater is added at the bottom and then flows through the limestone and then hopefully as it exits the tank at the top, the acidic qualities of the water would have been decreased. The problem with this assumption lies in that the reaction is not instantaneous and requires a long amount of time to take place as well the fact the surface area of the limestone would then become coated with the debris from the reaction. Since the surface area of the limestone is what reacts with the water, if it is easily coated by what it is reacting with, it will only stay effective for so long and then the wastewater is just flowing through, what is essentially, more waste. Chemistry wise it makes sense that limestone will neutralize strong acids but in practice the formation of calcium salts on the rocks render the process ineffective.

Even if water purification by limestone isn’t the most effective, limestone is still used in many other processes today. The smallest use on the list being 2,530 tons or 5,060,000 pounds, it makes sense that it is the third most produced raw mineral every year.
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