How Limestone Saved the World!

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What is Limestone?

Sedimentary rock composed of Calcium Carbonate (CaCO$_3$)

Two minerals:
- Aragonite
  - Unstable under almost any conditions on Earth
- Calcite (unique chemical properties)
  - Supersaturated, saturated AND undersaturated in surface and subsurface waters
  - Calcite is the third most common mineral in Earth’s crust (behind feldspar and quartz)
  - It is relatively soft with a hardness of 3 out of 10.
How does limestone form?

Sediment that is born from water and life – not made from magma! – then chemical properties harden it to rock.
Shallow Water Tropical Paradise - Bahamas
Cross section of CaCO$_3$ sediment-producing environments

Subtidal Carbonate Factory

Shoreward Transport

Fallout of Calcareous Plankton

Basinward Transport

After James
Modern Sediment Exercise

• Ooid grains
• Lime Mud
• Corals
• Mollusc Shells
Ooid Shoal at Low Tide
Ooids in Cross Section

After Scholle, 2003
Mud in Tidal Flat

Abu Dhabi - Subtidal Part of Channel
Favorite Coral Reefs

Rat cay blue hole porities
Favorite Coral Reefs
Western Australia Shell Beach
Ancient Rock Exercise

Look at your rock and discuss what you see in it. Use the magnifiers to help. Think about the environment in which the sediment was deposited. The answer is underneath. No peaking until the end.

OK, now you know a bit about where CaCO$_3$ sediment is produced, how it is produced, and where it is deposited.

So, how did it save the world?
Experiment

• Put a drop of the liquid on crystal (don’t touch the liquid)
• What happens?

• $\text{CaCO}_3(s) + 2 \text{HCl}_{(aq)} \rightarrow \text{CaCl}_2(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$

• So how did limestone save the world?
Early in Earth History

- \( \text{CO}_2 + \text{CaSiO}_3 = \text{CaCO}_3 + \text{SiO}_2 \) Combined weathering and precipitation reaction shows that calcite holds \( \text{CO}_2 \)
- Over 4 Billion years ago, Earth’s early atmosphere came from comets and what comes out of volcanoes, including water, \( \text{CO}_2 \), sulfur, and nitrogen compounds.
- There was no limestone yet, only igneous silicate rocks solidified from magma and lava.
- Today, most of the Earth’s \( \text{CO}_2 \) is tied up in the crystal structure of limestone. Before limestone existed, much of it would have been in the atmosphere. If all or some of the \( 10^{23} \) g of C was in the atmosphere, estimates range from 10- 80 bars of \( \text{CO}_2 \) in Earth’s atmosphere for first few hundred million years of Earth history (.000372 bars out of 1 bar today)
- That is a good thing for an Earth with liquided water hospitable to life, as solar luminosity was 30% lower then.
- \( \text{CO}_2 \) is a greenhouse gas and what little heat we recieved from the young weak sun was retained, keeping the oceans from freezing solid.
- In this case, the absence of limestone temporarily saved our bacon and allowed life to show up on the planet 3.8-3.5 billion years ago.
As Solar Luminosity Increased, Limestone Saved Us Again!

- Solar intensity increased significantly over time and would have heated up the Earth.
- It did not because limestone formed.
- CO$_2$ dissolves in the water, falling into the ocean.
- CO$_2$ is locked into CaCO$_3$ as it forms limestone.
- This removed most of the greenhouse gas from the atmosphere.

(a) Earth: H$_2$O, CO$_2$, and SO$_2$ are recycled.
Without Limestone, Earth Would Have Been Like Venus

- Mostly carbon dioxide atmosphere, 96.5%
- Surface Temperature: 460°C
- 90 bars at the surface
- All of the water has long since boiled away because of this runaway greenhouse effect
- Dead, hot, dry!
Removal of CO$_2$ to Make Limestone Cooled the Temperature and Saved the Oceans

A planet conducive to life
Limestone provided Shelter - Caves

Carbon dioxide in air and soil combines with water to form weak carbonic acid and dissolves caves in limestone – Limestone is the dominant rock that forms caves – Not only does Calcite precipitate at the surface, it dissolves too!
Limestone provided Shelter - Caves

- Human’s occupied cave entrances at least temporarily in the Paleolithic period and after (Homo antecessor, Homo neanderthalensis (Neanderthals), Homo erectus and Homo heidelbergensis. Early humans, Homo sapiens)
- Harsh cold climate in Europe so caves worked as shelter from time to time, helping humans to survive during ice ages

Chauvet cave, France – 30-32,000 years old
Limestone provided shelter – building stone

• Calcite has hardness of 3 (out of 10); its softness makes it easily quarried and shaped by harder tools including copper pickaxes, chisels, granite hammers (quartz is 7; iron is 4-5; copper is 3)

• Yet it has high compressive strength:
  – Modern brickwork 1000 psi
  – Concrete 2000 psi
  – Limestone 9000 psi
  – Granite 19000 psi
  – Steel 32,000 psi
Limestone provided shelter – building stone
Limestone Provides Shelter – Portland Cement

• Limestone is heated at 1500°F to produce CaO
  \[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]

• Old style cement - mixed with water CaO + H\textsubscript{2}O → \text{Ca(OH)}\textsubscript{2} and hardens

• Modern Portland cement - in furnace CaO reacts with other minerals (clay, gypsum, sand iron oxide, aluminum oxide)

• It hardens to \(3,2\text{CaO} \cdot \text{SiO}_2\) and \(3\text{CaO} \cdot \text{Al}_2\text{O}_3\) to make most of the mortar, cement and concrete products that we know today
Energy!

- Oil and gas is found in small-scale pore systems in rocks.
- Typical limestone has less than 5% pore space.
- But when corrosive water contacts it in nature, it dissolves.
- Pores in limestone (or dolomite) hold more than 60% of the oil and gas in the World.
Energy!

- Most oil in the Middle East is in limestone and dolomite reservoirs
- Let’s talk a little about Texas

Permian Basin of west Texas and southeast New Mexico contains an estimated 30 billion barrels of mobile oil

Eagle Ford Shale play in your neighborhood contains 7-10 Billion barrels. It can be fracked because it is limestone. Calcite makes it brittle
Limestone and Groundwater

- Groundwater is easily the most important ... source of freshwater and constitutes about two thirds of the freshwater resources of the world (World Health Org/Unesco)
- Limestone aquifers are among the best – Why do you think that is?

### Relative hydraulic conductivity

<table>
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<th>Very high</th>
<th>High</th>
<th>Moderate</th>
<th>Low</th>
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#### Consolidated rocks
- Massive igneous and metamorphic rocks (unfractured)
- Shales
- Laminated sandstones
- Cemented, unjointed sandstones
- Crystalline, unjointed sandstones
- Volcanic tuffs
- Fractured and/or weathered granites and gneisses
- Jointed sandstones
- Dolomites
- Vesicular basalts
- Karst limestones
San Antonio is semi-arid and exists because of abundant groundwater in the Edwards Aquifer.

http://www.edwardsaquifer.net/geology.html
Limestone and Groundwater

95% of water storage is in the rock matrix

95% of water movement occurs in conduits

- approx. 3500 feet
- Edwards and associated limestones
- formations older than Edwards
- fresh water
- saline water
- barrier fault
- formations younger than Edwards
- faults

Flow
Limestone and Groundwater

19th Century San Pedro Springs

http://www.edwardsaquifer.net/spspring.html
Abundant water played a major part in the Spanish building permanent settlements here, the nucleus of San Antonio in the early 1700s.
Will limestone save the world again – In the future?

- We know that enhanced CO₂ in the atmosphere could lead to climate change. Just think about 100 million years ago, the hot and steamy Cretaceous, when atmospheric CO₂ was quite high - a good time to be a Dinosaur at least.
- High CO₂ in atmosphere today leads to more carbonic acid in oceans which makes dissolution of CaCO₃ more widespread in oceans CO₂+H₂O+CaCO₃ = Ca²⁺+2HCO₃⁻ 60-70% of the excess atmosphere CO₂ would be removed in just 5-6 thousand years and end up dissolved in the oceans.

Archer et al. model assumes we stop adding CO₂ to atmosphere in 2100.
Will limestone save the world again – In the future?

- Higher surface temperatures with higher levels of greenhouse gas increase the rate of rocks weathering on the surface of the earth
  \[ 2\text{CO}_2 + \text{H}_2\text{O} + \text{CaSiO}_3 = \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{SiO}_2 \]
- Much of remaining excess \( \text{CO}_2 \) is removed on a time scale of 100s of thousands of years to 1 million years.

Ridgewell and Zeebe, 2005
How did limestone save the world?

- Removed carbon dioxide from the atmosphere which kept Earth’s oceans from boiling – oceans resulted in life
- Shelter for humans – caves, building stone, cement
- Energy in the World’s major oil and gas reservoirs
- The best aquifers for fresh water
- Why did it do this? Unique properties that allow CaCO$_3$ to both precipitate as the mineral calcite and to dissolve at the surface and below it – and its ability to react with CO$_2$
- Is it done doing its job of saving the world? Absolutely not! It will mostly erase the effects of addition of CO$_2$ to atmosphere
Most Importantly – What does limestone have to do with KU basketball?

The rock *chalk*, is a type of limestone