
Chemical Sedimentary Rocks:
CARBONATES
a quick summary
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What are Carbonates?

- Carbonate rocks are chemical sedimentary rocks composed mainly or only by carbonate minerals
- Carbonate minerals include the ion CO_3^{2-} in their composition
- There are several carbonate minerals but only two are really common:
  - **Calcite**
  - **Dolomite**

Other carbonates

- Azurite
- Malachite
- Magnesite
- Rhodocrosite
- Siderite
- Cerussite
- Trona

Carbonate Rocks

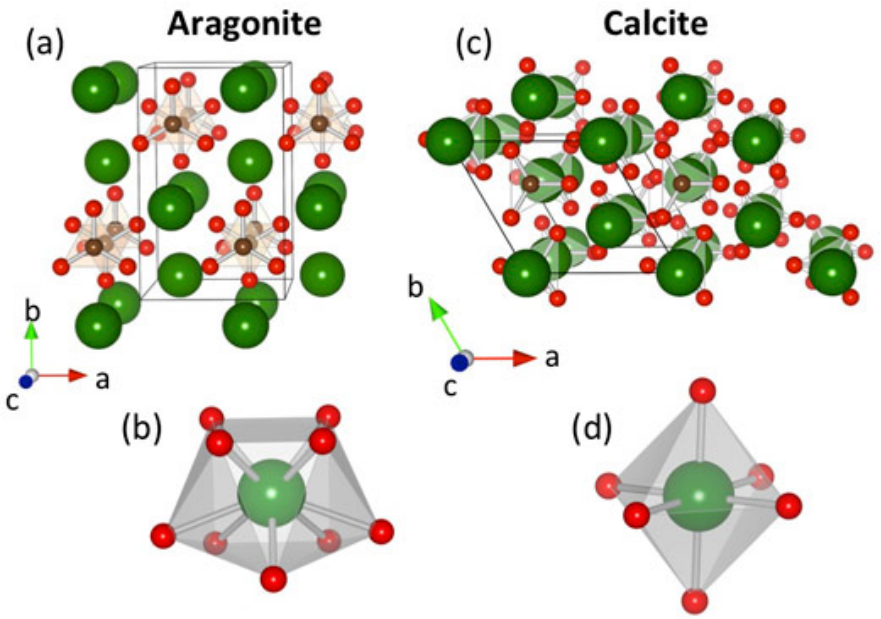
- Carbonate rocks include all rocks formed by carbonate minerals

- By far, the most common carbonate rocks are:
  - **Limestone** $CaCO_3$
    - Mostly calcite
    - Sometimes aragonite
  - **Dolostone** $(CaMg)[CO_3]_2$
    - Dolomite

Calcite vs. Aragonite

- Magnesium and its role in the formation of calcite

- **Calcite vs. aragonite**
  - Polymorphs!
  - Why do some organisms prefer aragonite to calcite?
  - What is the role of plate tectonics in the establishment of “calcite seas” vs. aragonite seas”?

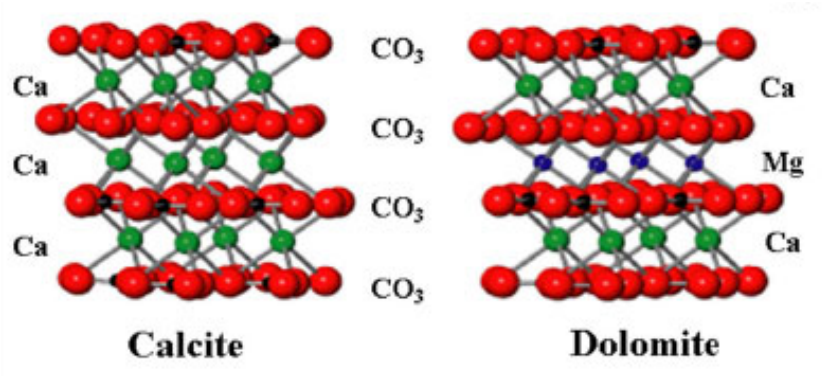


Schematic crystal structure of the $CaCO_3$ polymorphs aragonite and calcite

From: https://www.researchgate.net/figure/Schematic-crystal-structure-of-the-CaCO-3-polymorphs-aragonite-and-calcite-Aragonite-a_fig1_305654328

Calcite vs. Dolomite

- Calcite vs. dolomite
  - Where does magnesium go?
- Relative abundance of limestones and dolostones
  - Today: dolostones are rare
  - Geological record: dolostones almost as common as limestones in shallow-water deposits



3-D structure of calcite and dolomite

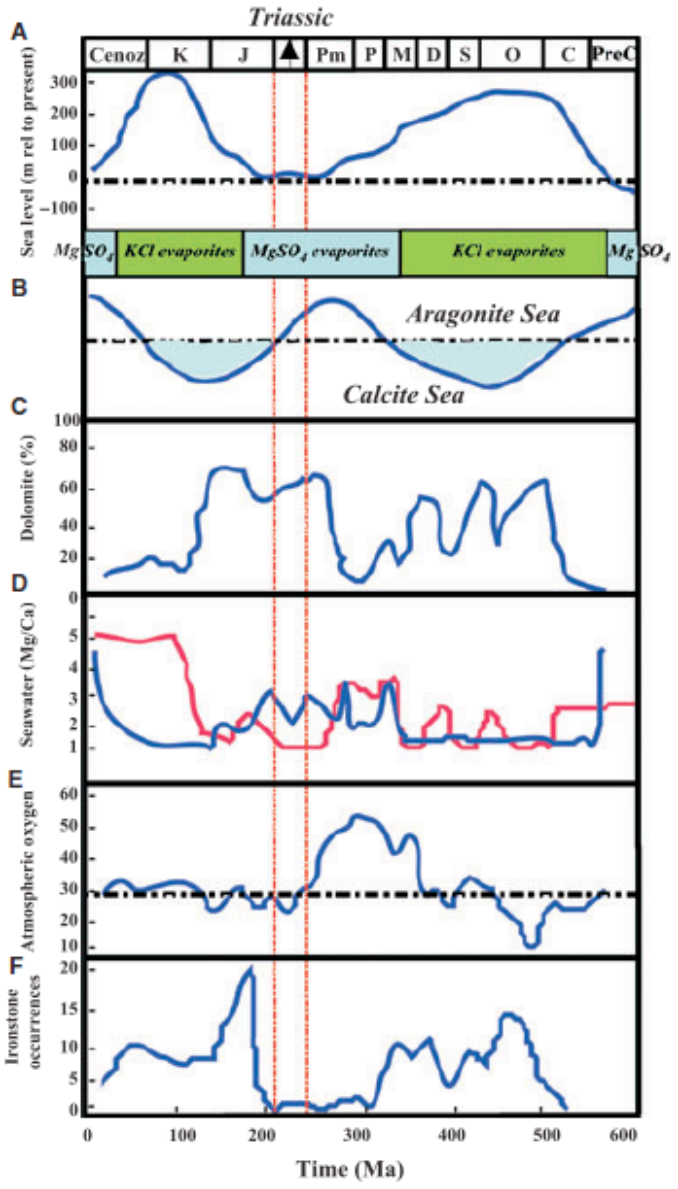
Both crystals consist of alternating sheets of carbonate ions but in calcite carbonate sheets can only alternate with calcium ions. In calcite, magnesium can disturb the calcium sheets, originating impurities. In dolomite instead, magnesium forms its own separated, alternating sheets.

Modified from http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0103-50532013000200018

Carbonate changes through Geologic Time

- Most dolomite is not a primary precipitate but forms as a slow alteration of original calcite

- Ocean conditions that favor dolomite replacement for calcite are;
  - High salinity
  - High pH
  - Low Ca^{2}+/Mg^{2+} ratio
  - High temperature



Relative variation of dolomite (and other parameters) over geologic time

The Dolomites of Italy

Tre Cime (Three Peaks) di Lavaredo
Dolomiti region of Belluno and Bolzano, Italy

Dolomites as rocks were first investigated and described in northern Italy by the French geologist Deodat de Dolomieu. The mineral (dolomite), the rock (dolostone), and this whole geological region (Dolomiti) are named after him.

Calcite

- Calcite is the most common carbonate mineral in nature
- Calcite can form either inorganically or because of the biological action of organisms

- Equilibrium reaction of calcite in water:

$$\mathbf{CaCO_3 + H_2O + CO_2 \leftrightarrow Ca^{2+} + 2HCO_3^-}$$

- Adding CO_2 to solution dissolves calcite into its component ions
- Removing CO_2 from solution will cause precipitation of calcite

- High pressure and low temperature keep CO_2 in solution
- Low pressure and high temperature remove CO_2 from solution

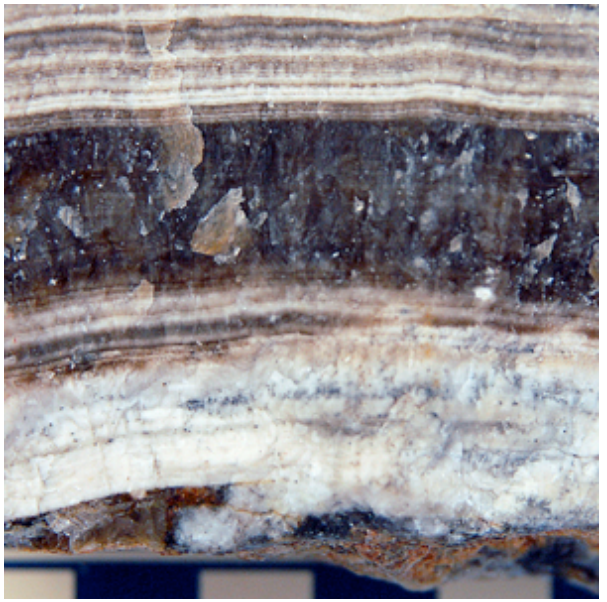
Types of **Limestones**

- Inorganic
  - form directly in water because of changing chemical equilibrium in solution
    - Travertine, Tufa, Oolitic Limestone
- Biochemical/Bioclastic
  - form because of the biological activity of an organism (biochemical) and successive mechanical weathering of remains (bioclastic)
    - Coral Reefs and Stromatolites, Fossiliferous Limestone, Coquina, Chalk, Micrite

Travertine

- Travertine is calcium carbonate that forms directly in the physical environment upon loss of CO_2 from water

- Terrestrial environments: waterfall, springs, hot springs, caves and caverns



Above: fossil leaf in Italian travertine,
Getty Center, Los Angeles, CA
Below: banded travertine
SMC rock collection, Santa Monica, Ca

Travertine actively forming (and immediately covered by moss) at a spring, creating its own waterfall.
Carbon dioxide leaves the solution upon water leaving a close environment (groundwater) and spraying at the waterfall

Aneva River, Labante di Castel D'Aiano, Bologna, Italy

Upon coming to the surface, hot water can quickly lose carbon dioxide, favoring the precipitation of calcite
Travertine terraces, Yellowstone National Park, Wyoming, USA

Water dripping from the ceiling of a cave quickly loses carbon dioxide to the atmosphere, favoring the formation of travertine. In this case “dripstones” are expressed as stalactites hanging from above
Mitchell Caverns, Mojave National Preserve, Kelso, California, USA

Tufa

- Tufa is a variety of travertine that forms in a few playa lakes of the American West, where different water chemistries mix

- A present day-example is Mono Lake
- An extinct system is at Searles Lake (Trona)

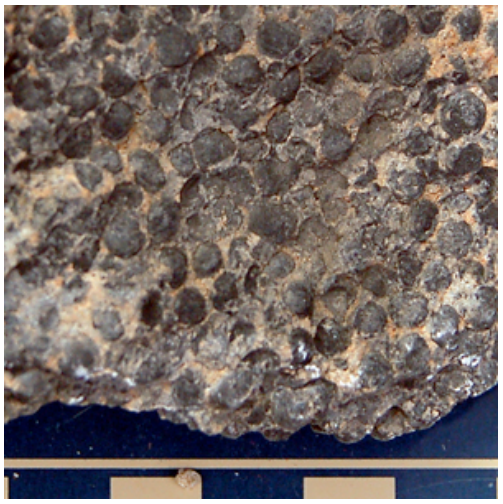
Above: Mono Lake, Lee Vining California
Below: Trona pinnacles, at dry Searles Lake, Tron, California

Oolites (oolitic limestones)

- Inorganic limestone formed by the cementation of sand-sized ooids
- Ooids are small spheres of calcite precipitated in warm, shallow seawater
- Tidal currents and sea-waves move grains, particles, small fossils, that coat themselves in calcium carbonate upon growing on a tropical carbonate shelf

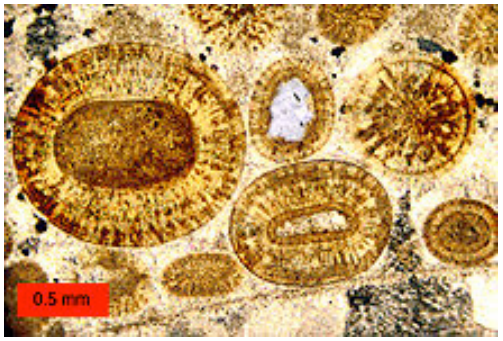
White oolite

SMC rock collection



Black oolite

SMC rock collection



Thin section of an oolite, showing both concentric and radial growth

Biochemical and Bioclastic Limestones

- Biochemical limestones are those produced by the activity of organisms
  - Mostly marine organisms
  - Also freshwater organisms

- Bioclastic limestones are those formed by the cementation of broken shells, pieces of coral reef, etc.

- Coral reefs
- Fossiliferous limestones
- Coquina
- Chalk
- Micrite (and Sparite)