Carbonate Rocks

The carbonate rocks make up 10 to 15% of sedimentary rocks. They largely consist of two types of rocks.

1. Limestones which are composed mostly of calcite (CaCO₃) or high Mg calcite \((\text{Ca},\text{Mg})\text{CO}_3\), and

2. Dolostones which are composed mostly of dolomite \([\text{CaMg(\text{CO}_3)_2}]\)

Because carbonate minerals in general are soluble in slightly acidic waters, they often have high porosity and permeability, making them ideal reservoirs for petroleum. For this reason they are well studied.

Limestone can be easily recognized in hand specimen or outcrop because of its high solubility in HCl. A drop of such acid placed on the rock will cause it to fizz due to the generation of CO₂ gas. A dolostone, on the other hand, will not fizz until a fine powder is made from the rock or mineral. Also, dolostones tend to weather to a brownish color rock, whereas limestones tend to weather to a white or gray colored rock. The brown color of dolostones is due to the fact that Fe occurs in small amounts replacing some of the Mg in dolomite.

Classification

Two classification schemes are in common use by those who work on carbonate rocks. Although you will use only the Folk classification in lab, you should also become familiar with the Dunham classification since it is widely used as well.

- **Folk Classification** - The Folk classification, which we will use in lab, is shown below. The classification divides carbonates into two groups. *Allochemical* rocks are those that contain grains brought in from elsewhere (i.e. similar to detrital grains in clastic rocks). *Orthochemical* rocks are those in which the carbonate crystallized in place. Allochemical rocks have grains that may consist of fossiliferous material, ooids, peloids, or intraclasts. These are embedded in a matrix consisting of microcrystalline carbonate (calcite or dolomite), called micrite, or larger visible crystals of carbonate, called sparite. Sparite is clear granular carbonate that has formed through recrystallization of micrite, or by crystallization within previously existing void spaces during diagenesis.
The Dunham classification is based on the concept of grain support. The classification divides carbonate rocks into two broad groups, those whose original components were not bound together during deposition and those whose original components formed in place and consist of intergrowths of skeletal material. The latter group are called boundstones (similar to biolithite of the Folk classification). The former group is further subdivided as to whether or not the grains are mud-supported or grain supported. If the rock consists of less than 10% grains it is called a mudstone (potentially confusing if taken out of context). If it is mud supported with greater than 10% grains it is called a wackstone. If the rock is grain supported, it is called a packstone, if the grains have shapes that allow for small amounts of mud to occur in the interstices, and a grainstone if there is no mud between the grains.

<table>
<thead>
<tr>
<th>Original components not bound together during deposition</th>
<th>Oroginal components bound together during deposition. Shows intergrown skeletal material, lamination contrary to gravity, or sediment-floored cavities that are roofed over by organic material and are too large to be interstices.</th>
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<tbody>
<tr>
<td>Contains mud (particles of clay and fine silt size)</td>
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<tr>
<td>Lacks mud</td>
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<tr>
<td>Mud-supported</td>
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<td>Grain-supported</td>
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<td>Less than 10% Grains</td>
<td>More than 10% Grains</td>
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<td>Mudstone</td>
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<tr>
<td>Packstone</td>
<td>Grainstone</td>
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<tr>
<td>Boundstone</td>
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*After Dunham, 1962, Am. Assoc. Petrol. Geol. Mem, 117*
Textures
Textures of carbonate rocks are extremely variable. Textures can vary from those similar to clastic sediments, showing characteristic grain sizes, sorting, and rounding, to those produced by chemical precipitation. In carbonates the matrix can range from fine grained carbonate mud to crystalline calcite or dolomite. But carbonates can also show textures derived from the growth of living organisms.

Many limestones (carbonate rocks in general) show characteristics similar to those of clastic sediments, like sandstones. Sandstones are composed of sand grains, a mud or clay matrix, and a crystalline cement produced during diagenesis. Similarly carbonate rocks are composed of allochemical grains (grains produced by precipitation somewhere else and transported, usually short distances, to the depositional site), mud matrix, consisting of fine-grained carbonate minerals, and a crystalline cement of calcite (or dolomite) precipitated during diagenesis. From the figure shown here, one can see that the average sandstone and mudrock have similar proportions of analogous constituents to average sparry (crystalline) limestones and micritic (fine grained crystalline limestones. This suggests a similarity of processes involved in the formation of clastic sediments and carbonate rocks.

Grains in Carbonate Rocks - The grains that occur in carbonate rocks are called allochemical particles or allochems. They are grains often precipitated by organisms that formed elsewhere and became included in the carbonate sediment. Because calcite and aragonite, the main biochemical precipitates, are soft and soluble in water, the distance of transport is usually not very far. Unlike clastic sediments, the degree of rounding and sorting of the grains may not be a reflection of the energy of the transporting medium, but may be biologically determined. For example some organisms produce particles that already have a rounded shape. If many of the same size organisms die at the same place, then the grains may be well sorted. Grains found in carbonate rocks are as follows:

1. Whole or broken skeletons of organisms (fossils). These may range in size from gravel to fine sand, depending on the organism and the degree to which the grains are broken by waves or during transport.
2. Ooids. These are spherical sand sized particles that have a concentric or radial internal structure. The central part of each particle consists of a grain of quartz or other carbonate particle surrounded by thin concentric layers of chemically precipitated calcite. The layers or coatings are formed in agitated waters as the grain rolls around.

3. Peloids. These are spherical aggregates of microcrystalline calcite of coarse silt to fine sand size. Most appear to be fecal pellets from burrowing benthic organisms. As these organisms burrow through the muddy carbonate-rich sediment, they ingest material in search of nutritional organic compounds resulting in waste products containing microcrystalline calcite. The peloids are much easier seen in thin section than in hand specimen because of their small size.

4. Limeclasts. These are fragments of earlier formed limestone or partially lithified carbonate sediment. Most are intraclasts, originating within the basin of deposition. They may be pieces of partially cemented carbonate mud that were ripped from the seafloor by storms. Some appear to be fragments of partially cemented carbonate mud that originated in intertidal mudflats. Some may also be pieces of limestone carried into the basin from nearby carbonate outcrops.

- **Matrix**- The matrix of carbonate rocks consists of either fine grained carbonate mud, called *micrite*. Or coarser grained calcite crystals formed during diagenesis, called *sparite*.
  - The micrite results from recrystallization of carbonate mud during diagenesis or from direct precipitation of calcite, and causes lithification of the sediment. The micrite gives the dull opaque appearance of most limestones as seen in hand specimen. If the rock consists entirely of fine-grained mud matrix, it implies deposition in a low energy environment just like in siliclastic mudstones. Some of the mud may start out as aragonite needles 5 to 10 \( \mu \text{m} \) in length produced by calcareous algae. But, again this becomes recrystallized to a microspar 5 to 15 \( \mu \text{m} \) in diameter during diagenesis.
  - Larger sparry calcite matrix results from diagenesis in the same way that calcite cement originates in sandstones.

- **Insoluble Residues** - While minor amounts of clay minerals and quartz occur in limestones, most of the insoluble residues, (so called because they do not dissolve in HCl) are grains of nodules of chert. Such chert mostly originates from the shells of silica secreting organisms. These include diatoms, radiolarians, and some sponges. Individual grains of chert result from recrystallization of the shells of these organisms. Chert nodules can range in size from centimeters to meters in length. Many nodules are concentrated along bedding planes and probably resulted from dissolution of the siliceous debris and reprecipitation of the microcrystalline quartz at centers of nucleation located along zones of migration of the fluids, such as along bedding planes.
Structures
Since most limestones are formed by clastic processes, many of the same types of structures observed in siliciclastic rocks also occur in limestones.

- **Current-Generated Structures.** Structures like cross-bedding, ripple marks, dunes, graded bedding, and imbricate bedding are common in carbonate rocks, although they may not be as evident as in siliciclastic rocks because of the lack of contrasting colors of individual beds in carbonates. Since many shells of organisms have curved outlines in cross-section (brachipods, pelecypods, ostracods, and trilobites, especially), when the organism dies it may settle to the bottom with the outline being concave downward, and latter become filled with carbonate mud. When such features occur they can be used as top/bottom indicators.

- **Lamination.** The most common type of lamination in carbonate rocks is produced by organisms, in particular blue-green algae that grow in the tidal environment. These organism grow as filaments and produce mats by trapping and binding microcrystalline carbonates, as incoming tides sweep over the sand. This leads to the formation of laminated layers that consist of layers of organic tissue interbedded with mud. In ancient limestones, the organic matter has usually been removed as a result of decay, leaving cavities in the rock separated by layers of material that was once mud. These cavities are called *fenestrae* (for a photo, see Figure 16-14, page 305, in Blatt & Tracy).

Another type of lamination occurs as bulbous structures, termed **Stomatolites** (for photo, see Figure 16-15, p. 306, in Blatt & Tracy). These are produced in a similar fashion, i.e. by filamentous blue-green algae, but represent mounds rather than mats.

- **Stylolites.** Stylolites are irregular surfaces that result from pressure solution of large amounts of carbonate. In cross-section they have a saw tooth appearance with the stylolites themselves being made of insoluble residues or insoluble organic material. Some studies have suggested that the stylolites represent anywhere from 25% to as much as 90% of missing rock that has been dissolved and carried away by dissolution (for a photo, see Figure 16-22, page 314, in Blatt & Tracy).

Carbonate Depositional Environments
Most modern, and probably most ancient, carbonates are predominantly shallow water (depths <10-20 m) deposits. This is because the organisms that produce carbonate are either photosynthetic or require the presence of photosynthetic organisms. Since photosynthesis requires light from the Sun, and such light cannot penetrate to great depths in the oceans, the organisms thrive only at shallow depths. Furthermore, carbonate deposition in general only occurs in environments where there is a lack of siliciclastic input into the water. Siliciclastic input increases the turbidity of the water and prevents light from penetrating, and silicate minerals have a hardness much greater than carbonate minerals, and would tend to mechanically abrade the carbonates. Most carbonate deposition also requires relatively warm waters which also enhance the abundance of carbonate secreting organisms and decrease the solubility of calcium carbonate in seawater. Nevertheless, carbonate rocks form in the deep...
ocean basins and in colder environments if other conditions are right.

For this course, our discussion of carbonate depositional environments will be brief. See your text for more detailed discussion. The principal carbonate depositional environments are as follows:

- **Carbonate Platforms and Shelves.** Warm shallow seas attached the continents, or in the case of epiric seas, partially covering the continents, are ideal places for carbonate deposition. Other shelves occur surrounding oceanic islands after volcanism has ceased and the island has been eroded (these are called **atolls**). Carbonate platforms are buildups of carbonate rocks in the deeper parts of the oceans on top of continental blocks left behind during continent - continent separation.

  Reef building organisms from the framework of most of these carbonate buildups.

- **Tidal Flats.** Tidal flats are areas that flood during high tides and are exposed during low tides. Carbonate sands carried in by the tides are cemented together by carbonate secreting organisms, forming algal mats and stromatolites.

- **Deep Ocean.** Carbonate deposition can only occur in the shallower parts of the deep ocean unless organic productivity is so high that the remains of organisms are quickly buried. This is because at depths between 3,000 and 5,000 m (largely dependent on latitude - deeper near the equator and shallower nearer the poles) in the deep oceans the rate of dissolution of carbonate is so high and the water so undersaturated with respect to calcium carbonate, that carbonates cannot accumulate. This depth is called the **carbonate compensation depth (CCD)**. The main type of carbonate deposition in the deep oceans consists of the accumulation of the remains of planktonic foraminifera to form a carbonate ooze. Upon burial, this ooze undergoes diagenetic recrystallization to form micritic limestones. Since most oceanic ridges are at a depth shallower than the CCD, carbonate oozes can accumulate on the flanks of the ridges and can be buried as the oceanic crust moves away from the ridge to deeper levels in the ocean. Since most oceanic crust and overlying sediment are eventually subducted, the preservation of such deep sea carbonates in the geologic record is rare, although some have been identified in areas where sediment has been scraped off the top of the subducting oceanic crust and added to the continents, such as in the Franciscan Formation of Jurassic age in California.

- **Non-marine Lakes.** Carbonate deposition can occur in non-marine lakes as a result of evaporation, in which case the carbonates are associated with other evaporite deposits, and as a result of organisms that remove CO$_2$ from the water causing it to become oversaturated with respect to calcite.

- **Hot Springs.** When hot water saturated with calcium carbonate reaches the surface of the Earth at hot springs, the water evaporates and cools resulting in the precipitation of calcite to form a type of limestone called **travertine**.
**Dolostones**

Dolostones are carbonate rocks composed almost entirely of dolomite - \((\text{Ca,Mg})\text{CO}_3\).

Although there used to be a common perception that the abundance of dolostones increased with age of the rock, it is now recognized that although no primary dolomite bearing rocks are being directly precipitated in modern times, dolostones have formed throughout geologic time. This is true despite the fact that modern sea water is saturated with respect to dolomite. Still, most dolostones appear to result from diagenetic conversion of calcite or high-Mg calcite to dolomite, after primary deposition of the original calcium carbonate bearing minerals.

Dolomite, and therefore rocks containing large amounts of dolomite, like dolostones, is easily distinguished by the fact that it only fizzes in dilute HCl if broken down to a fine powder. Also, dolostones tend to weather to a brownish color rock, whereas limestones tend to weather to a white or gray colored rock. The brown color of dolostones is due to the fact that Fe occurs in small amounts replacing some of the Mg in dolomite.

In thin section it is more difficult to distinguish from calcite, unless it is twined. Unfortunately, sedimentary dolomite is rarely twinned. In order to facilitate its identification in thin section, the sections are often stained with alizarin red S. This turns calcite pink, but leaves the dolomite unstained.

Dolostones are almost entirely composed of euhedral and subhedral rhombs of dolomite. Although dolostones contain allochems, like limestones, the allochems are generally recrystallized to dolomite, and rhombs of dolomite can be seen to cut across the boundaries of allochemical particles. Some dolostones show no evidence of allochems, but only contain rhombs of dolomite. These could either represent limestones that have completely recrystallized to dolomite, leaving no trace of the original fragments that made up the limestone, or could represent primary crystals of dolomite.

Two mechanisms of dolomitization of limestones have been proposed based on field and laboratory studies.

- **Evaporative Reflux.** This mechanism involves the evaporation of seawater to form a brine that precipitates gypsum. After precipitation of gypsum, the brine is both enriched in Mg relative to Ca and has a higher density. If the brine then enters the groundwater system and moves downward into buried limestones, this Mg-rich brine then reacts with the calcite in the limestone to produce dolomite.

- **Mixing of Seawater and Meteoric Water.** This mechanism involves the mixing of groundwater derived from the surface with saline groundwater beneath the oceans. Dolomitization is thought to occur where the two groundwater compositions mix with each in the porous and permeable limestone within a few meters of the surface.

**Other Sedimentary Rocks**

**Evaporites**

Evaporite minerals are those minerals produced by extensive or total evaporation of a saline solution. Because such minerals dissolve readily in less saline rich solutions, like most groundwater and surface water, evaporite rocks rarely outcrop at the surface except in aid regions. Evaporite rocks are common, however, in the subsurface. Three different environments result in the deposition of evaporites.
1. **Basins of internal drainage.** In arid regions with basins of internal drainage, rainfall in the adjacent areas is carried into the basin by ephemeral streams carrying water and dissolved ions. The water fills the low points in the basin to form a **playa lake**. These lakes eventually evaporate, resulting in the precipitation of salts such as halite, gypsum, anhydrite, and a variety of other salts not commonly found in marine evaporite deposits, such as trona \((\text{NaHCO}_3\cdot\text{Na}_2\text{CO}_3\cdot2\text{H}_2\text{O})\), natron \((\text{Na}_2\text{CO}_3\cdot10\text{H}_2\text{O})\), nahcolite \((\text{NaHCO}_3)\), mirabilite \((\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O})\), borax \((\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4\cdot8\text{H}_2\text{O})\), kernite \([\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2\cdot3\text{H}_2\text{O}]\), and colemanite \((\text{CaB}_3\text{O}_4(\text{OH})_3\cdot\text{H}_2\text{O})\).

2. **Restricted bays or seas.** In areas where there is restricted input of fresh or marine waters into a basin, coupled with extensive evaporation within the basin, dissolved ion concentrations may increase to the point where a dense concentrated solution is formed near the surface. These dense saline waters then sink within the basin, become oversaturated with respect to salts like gypsum and halite, and precipitate the salts on the floor of the basin.

3. **Shallow arid coasts or sabkhas.** Along shallow arid coastlines where input of fresh water is rare and evaporation increases the salinity of the marine water, evaporation may increase the salinity of the water to a point where evaporite minerals like halite and gypsum are precipitated.

**Cherts**

Chert is a mineralogically simple rock consisting of microcrystalline quartz. There are three common occurrences of chert.

1. **As nodules and silt-sized grains in carbonate rocks.** Chert nodules, as discussed previously, occur as structureless dense masses within carbonate rocks. They range in size from a few centimeters to many meters in length. The source of silica is likely silica secreting organisms that include diatoms (Jurassic to Holocene), radiolaria (Ordovician to Holocene), and sponges (Cambrian to Holocene). But, these organisms are not preserved in the chert nodules. Instead, the remains of these organisms were likely dissolved by fluids flowing through the rock during diagenesis. Most chert nodules are found along bedding planes in the carbonate rocks, likely because these were zones along which fluids that precipitated the microcrystalline quartz were able to move.
2. **As bedded cherts that formed along tectonically active continental margins.** Bedded cherts occur in association turbidites, ophiolites, and mélanges (oceanic trench deposits scraped off the seafloor at subduction zones). The beds range in thickness from a few centimeters to several meters, and are interbedded with siliceous shales. Although thought to represent deep water accumulations of silica secreting organisms, they may also form in warm nutrient rich shallow water environments. Sometimes the remains of silica secreting organisms, like radiolaria, sponge spicules, or diatoms are preserved in the cherts, but most show a microcrystalline texture that results from recrystallization during diagenesis.

3. **Associated with hypersaline-lacustrine deposits.** Although less common than the previously discussed occurrences of chert, some cherts appear to form in a hypersaline environment where they are associated with evaporite deposits. Such cherts may in fact form as a result of replacement of sodium silicate evaporite minerals like magadiite by the following chemical reaction:

$$\text{NaSi}_7\text{O}_{13}(\text{OH})_3\cdot3\text{H}_2\text{O} \rightarrow 7\text{SiO}_2 + 4\text{H}_2\text{O} + \text{Na}^+ + \text{OH}^-$$

magadiite \hspace{1cm} quartz

Since mechanisms 1 and 2 generally require the presence of silica secreting organisms in order to form chert, the occurrence of chert in Precambrian rocks is problematical because no such organisms existed prior to the early Paleozoic. Such Precambrian cherts may have actually formed by direct chemical precipitation from silica oversaturated seawater.