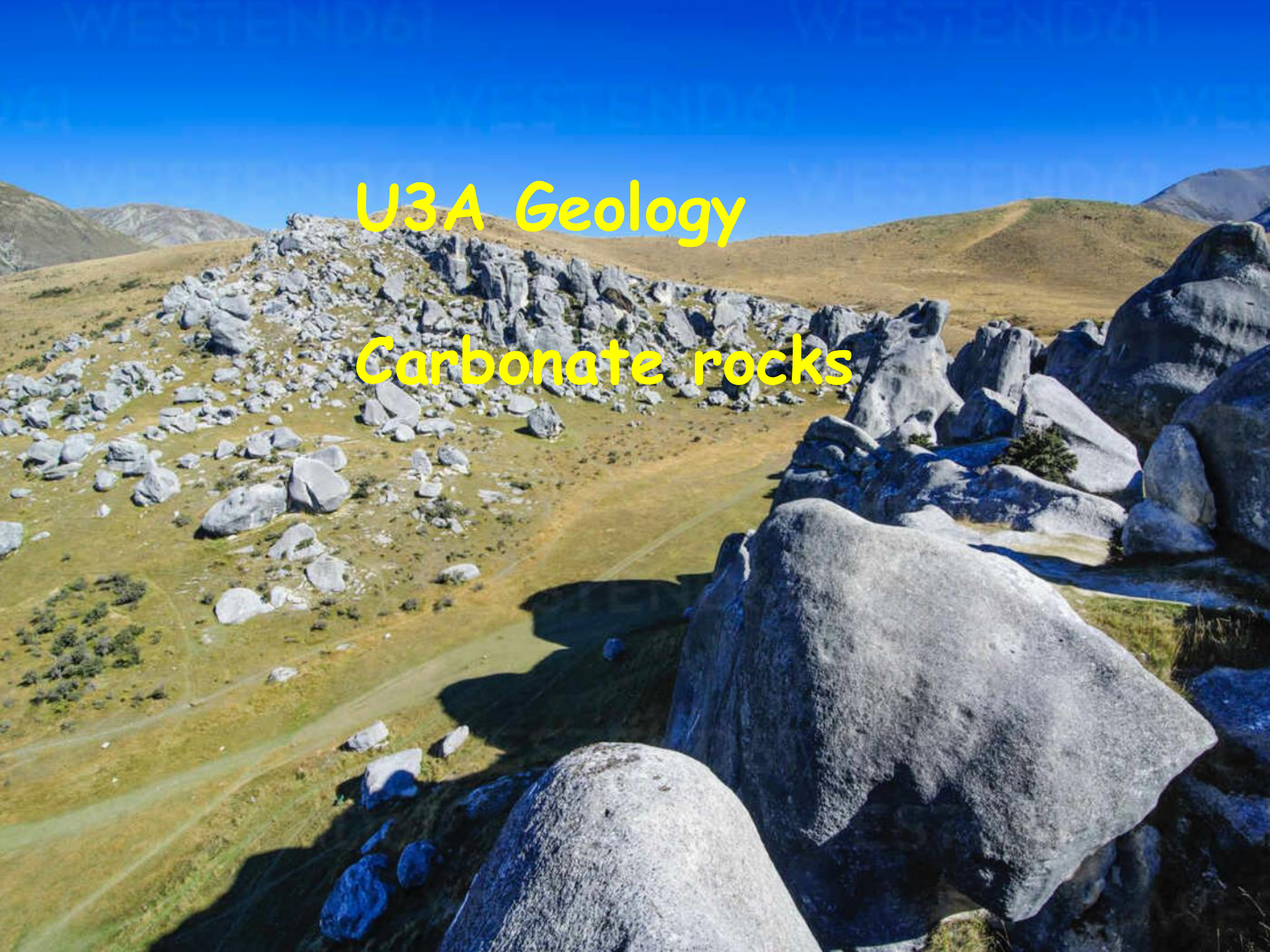


U3A Geology

Carbonate rocks

Introduction

- Carbonate rocks → sedimentary rocks consisting of carbonate minerals
- the most common carbonates in these rocks → $CaCO_3$ polymorphs calcite and aragonite and dolomite $CaMg(CO_3)_2$
- carbonate rocks consisting of calcite are called limestone
- carbonate rocks composed mainly of dolomite are called dolostone
- carbonate rocks containing a mixture of fine-grained calcite and terrigenous mud are called marl

Carbonate rocks

- Sedimentary carbonate rocks are composed predominantly of calcite, aragonite and dolomite
- however, a rock consisting of 40% detrital quartz, 25% calcite fossil fragments and 35% calcite cement is considered a fossiliferous sandstone even though it contains 60% carbonate
- carbonates form ~10% of the exposed sedimentary rock record and are known from rocks as old as 2.7billion years

Carbonate mineralogy

- Approximately 60 minerals occur in nature that contain the CO_3 group
- calcite and aragonite ($CaCO_3$) are the most common carbonates in modern sedimentary rocks
- in ancient carbonate rocks, calcite and dolomite are the most common comprising almost 100% of carbonate minerals in carbonate rocks
- aragonite because of its greater solubility is essentially absent in ancient rocks → removed by dissolution or replaced by other minerals
- magnesite $MgCO_3$, natron $Na_2CO_3.10H_2O$ and trona $Na_3H(CO_3).2H_2O$ are common in evaporites and siderite $FeCO_3$ occurs in peat

Carbonate minerals

- Dominant minerals in carbonate rocks → calcite, dolomite, aragonite
- calcite of limestones is both primary or diagenetic (secondary)
- several generations of calcite are present in many limestones, some as shelly debris, some as crystallization of aragonite, some as precipitated cement
- dolomite is not commonly primary, in most cases → replacement of calcite or aragonite, no shell structures originally dolomitic
- aragonite is the chief component of pelycopod and gastropod shells and some corals. Aragonite shells are largely free of $MgCO_3$
- siderite ($FeCO_3$) is a rare and minor component of some limestones

Carbonate minerals

Calcite $CaCO_3$

Aragonite $CaCO_3$

Dolomite $CaMg(CO_3)_2$

Magnesite $MgCO_3$

Origin of carbonate sediments

- $CaCO_3$ dissolves in seawater and freshwater with Ca derived from weathering of Ca-bearing minerals e.g. plagioclase

- atmospheric CO_2 dissolves in water producing the weak acid H_2CO_3 (carbonic acid)

$$CO_2 + H_2O \longleftrightarrow H_2CO_3$$

- H_2CO_3 dissociates in water as carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions

- precipitation of $CaCO_3$ from water is balanced by the reaction:

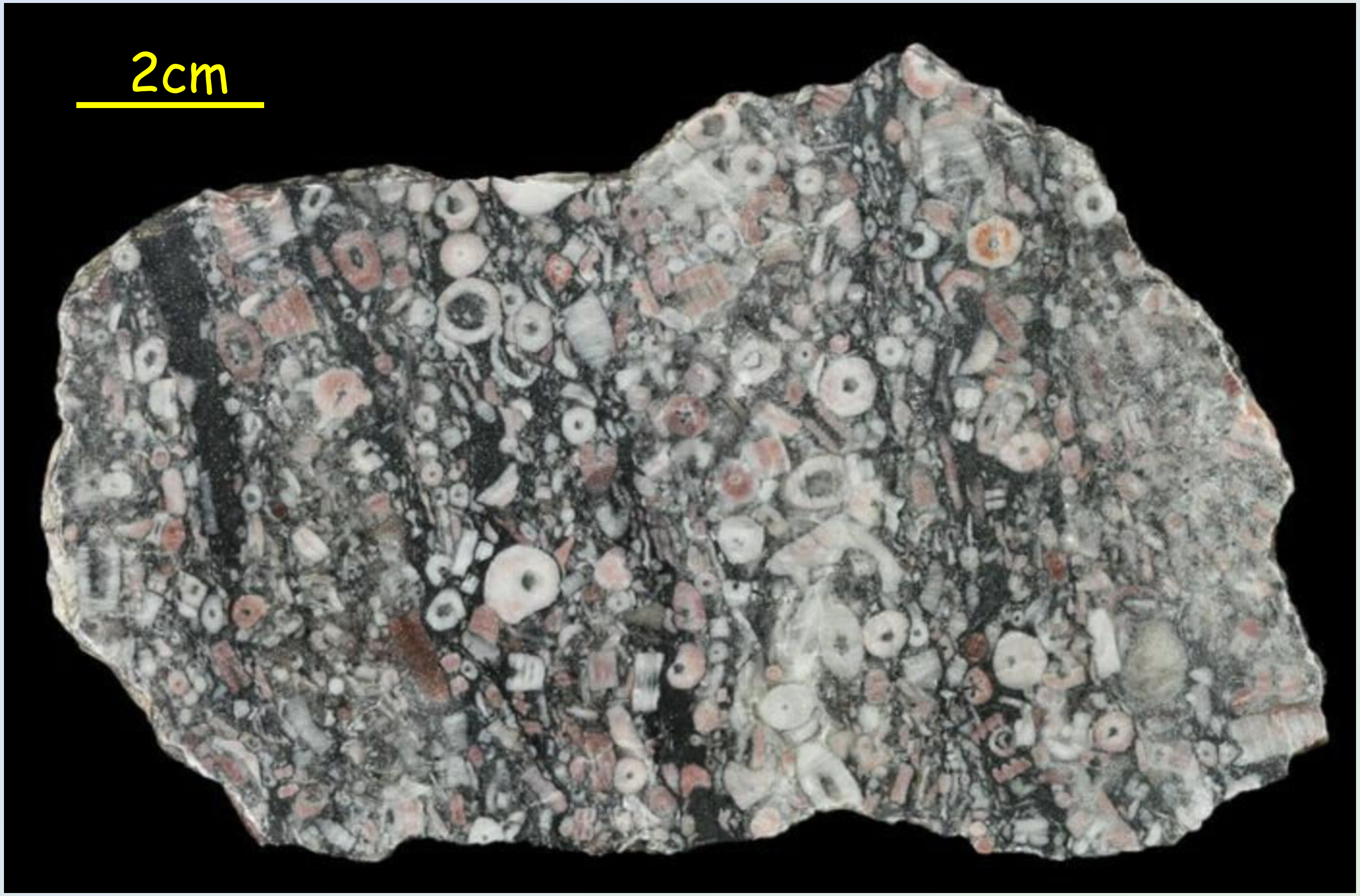
$$Ca^{2+} + 2HCO_3^- \longleftrightarrow CaCO_3 + H_2CO_3$$

- precipitation of calcite and dolomite is controlled by how much CO_2 is dissolved in water

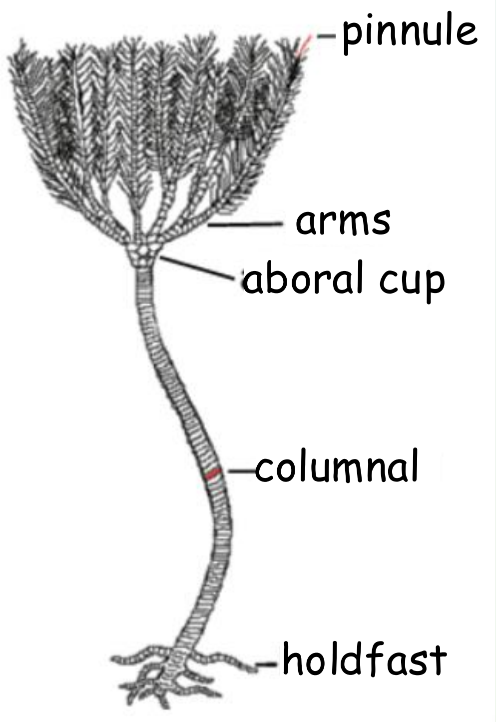
Carbonate sand

- Most carbonate rocks are composed of $CaCO_3$, sand and mud
- whole and broken skeletons (broken up by waves and currents) of invertebrates and calcareous algae may produce carbonate sand
- the type of texture and mineralogy depend on organisms available age of rock and environment of formation
- Crinoidal thickets during the Palaeozoic produced abundant grains that compose limestone
- great patches of shallow-marine, calcareous algae produce grains that accumulate as carbonate sediment

Crinoidal limestone



Crinoidal limestone slab, China



Crinoid

Organic precipitation of carbonates

- Carbonates are common in seawater and freshwaters and marine organisms use $CaCO_3$ to produce shells and other skeletal parts
- most marine carbonates are produced by micro-organisms with carbonate tests (nanoplankton) like forminifera and coccolithophores
- reefs are constructed of carbonate rocks by reef building organisms e.g. corals, bryozoans and stromatolites
- carbonate precipitation occurs preferentially in warm water, therefore reefs occur in tropical and sub-tropical areas nowadays

Carbonate depositional environments

- Most modern and probably most ancient carbonates are predominantly shallow water (<10-20m)
- organisms that produce carbonates are either photosynthetic or require presence of photosynthetic organisms that require light from the Sun
- most carbonate deposition also requires warm waters → enhance abundance of carbonate secreting organisms
- warm water decreases the solubility of calcite
- carbonate rocks can form in deep ocean basins if the conditions are right

Principal carbonate depositional environments

Carbonate platforms and shelves

- Warm shallow seas attached to continents are ideal places for carbonate deposition
- other shelves surround oceanic islands after volcanism ceases and island erodes → atolls
- carbonate platforms are buildups of carbonate rocks in deeper parts of the ocean, reef-building organisms build framework

Tidal flats

- areas that flood during high tides and are exposed during low tides
- carbonate sands carried by tides → cemented by carbonate secreting organisms forming algal mats and stromatolites

Principal carbonate depositional environments

Deep ocean

- Carbonate deposition can only occur in the shallower parts of the deep ocean
- at depths between 3000 and 5000m, dissolution of carbonate is very high and seawater is so undersaturated with respect to $CaCO_3$ → carbonate cannot accumulate
- this depth is called the Carbonate Compensation Depth (CCD)
- main type of carbonate deposition consists of accumulation of planktonic foraminifera → carbonate ooze
- carbonate ooze undergoes diagenetic recrystallisation on burial forms micritic limestone

Principal carbonate depositional environments

Non-marine lakes

- Carbonate deposition can occur in non-marine lakes as a result of evaporation
- and, as a result of organisms present that remove CO_2 from water causing it to be oversaturated with respect to calcite

Hot springs

- when hot water saturated with $CaCO_3$ reaches the surface in hot springs → water evaporates → precipitation of travertine limestone e.g. Mammoth Falls, Yellowstone

Modern carbonate deposits

Calcareous sediments are widely distributed in the modern world.

In general, there are five groups of carbonate deposits:

(1) Shallow-water marine

(2) Deep-water marine

(3) Carbonates of evaporitic basins

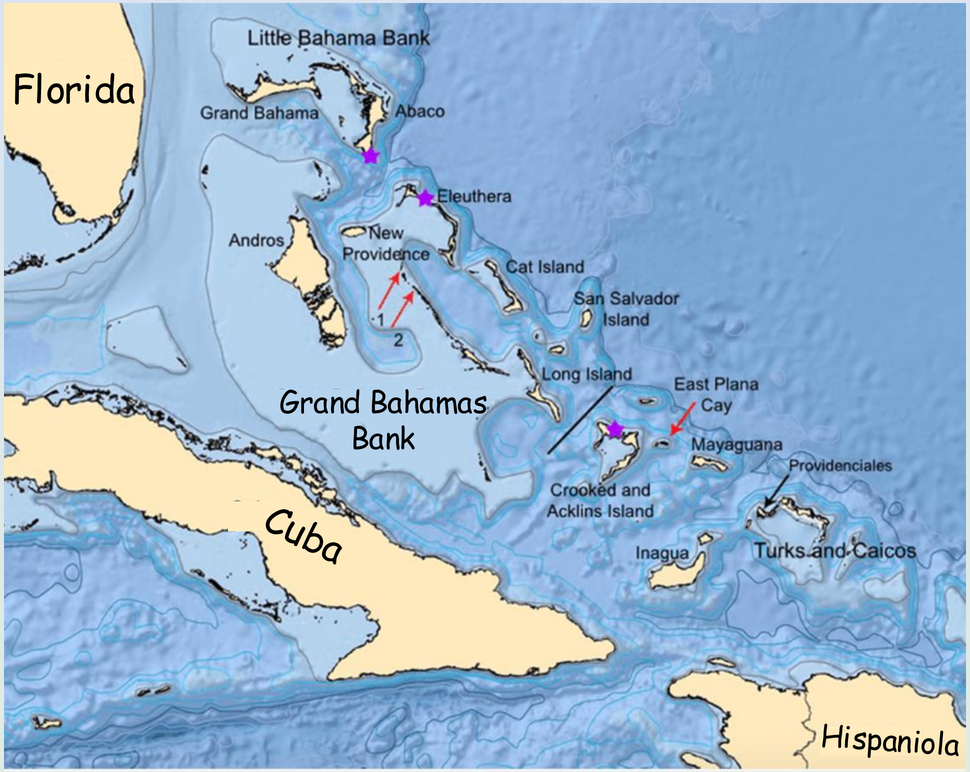
(4) Carbonates of freshwater lakes and springs

(5) Aeolian carbonates

Shallow marine carbonates

- The largest occurrences of modern shallow marine carbonates are located in the Florida-Bahamas region
- the Great Bahamas bank of the east coast of Florida is a barely submerged plateau 700km long and 300Km wide
- most of it is covered by waters less than 10m deep
- deposits are largely calcareous sands, both skeletal and oolitic with a lesser volume of carbonate muds and reef rock
- sands cover large areas of the banks and in places are in motion forming sub-aqueous sand dunes

Shallow marine banks Bahamas region



Map of Bahamas Region

Satellite image of Bahamas region

Shallow marine carbonates

- Muds are confined to very shallow waters or tidal flats on lee-side of Andros Island. Carbonate deposits of the Florida platform are similar and consist of reef carbonates, back reef sands and lagoonal muds
- sands are partly skeletal and partly oolitic
- other areas of shallow-water carbonates deposits include the coasts of Queensland and Western Australia
- the Shark Bay area of WA is in part hypersaline and famous for its stromatolites

Deep-sea carbonates

- Present day deep-marine carbonates belong to two classes:
  (1) turbidite or basinal deposits (shelf sediments)
  (2) pelagic deep-sea deposits
- turbidite deposits although less extensive are more common in the ancient rock record (probably because no pelagic sediments could form prior to evolution of carbonate-secreting plankton)
- pelagic deep-sea carbonates (the most common in the modern world), are poorly represented in the ancient record
- carbonates form in deep basins and are derived from reefs and banks → transported to deep-water environments by turbidity flows

Pelagic deep-sea carbonates

- The most widespread pelagic deep-sea carbonates are pteropod and Globigerina oozes
- the average depth of these deposits is 3000 and 2000m respectively
- carbonate content of oozes ranges from 30 to over 90%
- deposits are most abundant in lower latitudes
- distribution correlates with salinity of surface waters → most abundant where surface salinity is highest

Lysocline and carbonate compensation depth (CCD)

- The lysocline and carbonate compensation depth (CCD) are the two phenomena that affect stability of $CaCO_3$ in the deep ocean
- lysocline → depth at which rate of dissolution of calcite increases dramatically (up to 90%)
- water above lysocline is super saturated in calcite structures but as depth and pressure increase and temperature decreases, solubility of calcite increases
- below lysocline → CCD where rate of supply of $CaCO_3$ equals rate of dissolution → no more $CaCO_3$ deposited

Carbonate compensation depth

- Carbonate compensation depth (CCD)

  - $CaCO_3$ formation → limited by water depth

  - below CCD supply of $CaCO_3$ = dissolution rate

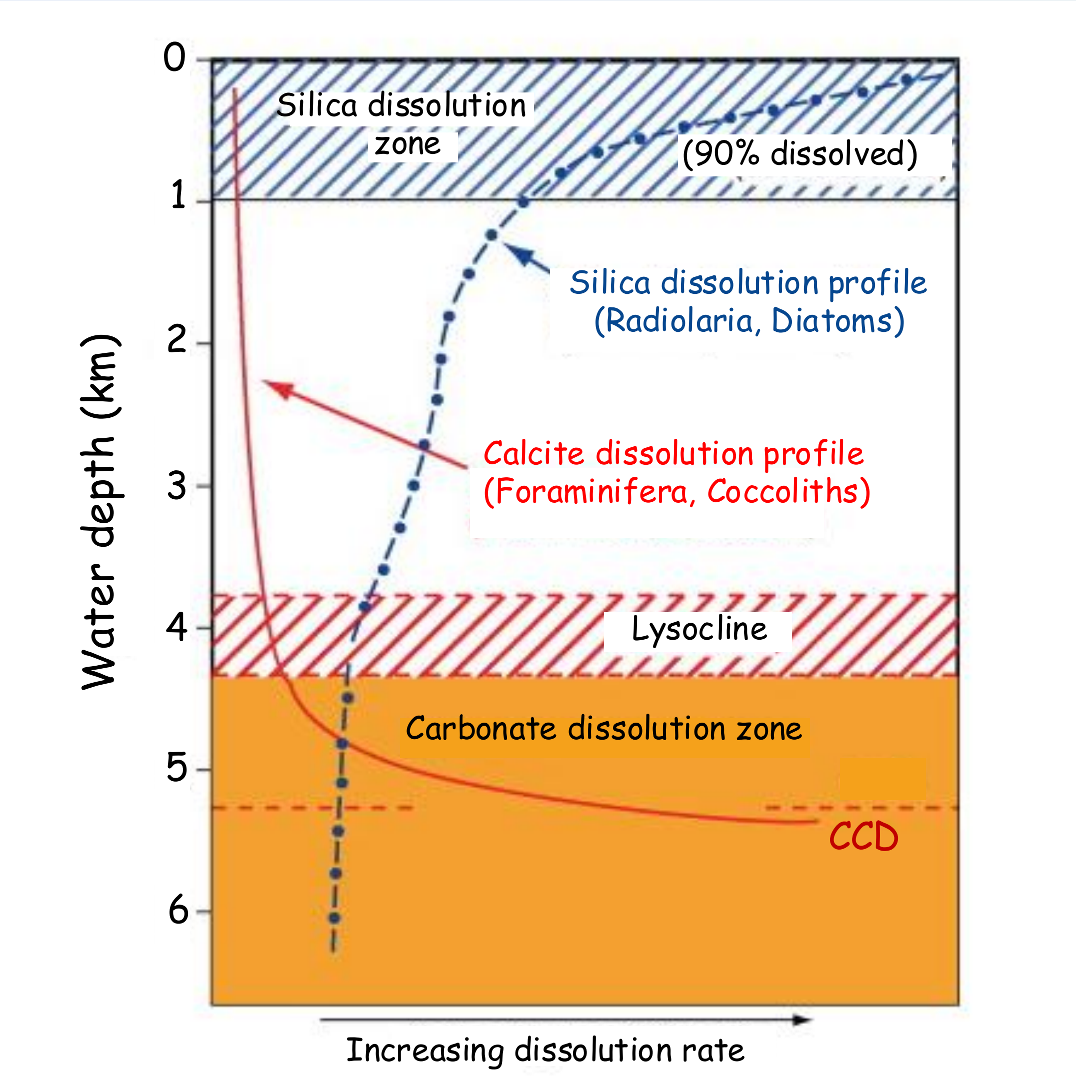
  - different depths in different oceans → 6km in Atlantic, 4.5km in Pacific

  - deeper at equator than at poles

- Mid-ocean ridge <5km deep → calcareous ooze accumulates along ridge. Also on flanks of seamounts above CCD

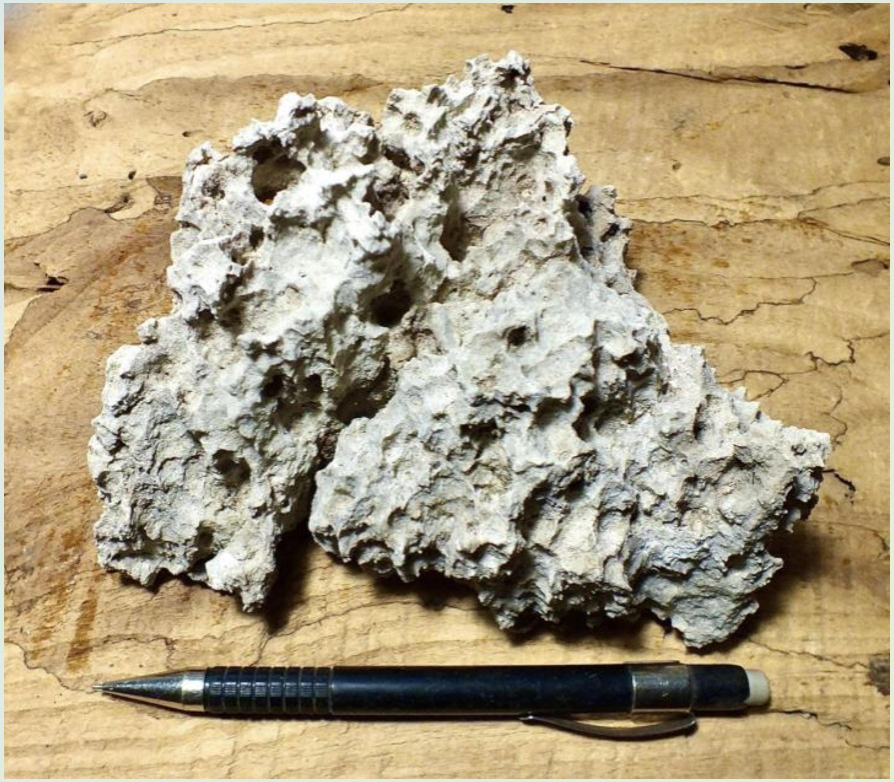
- away from ridge, where water depth increases > 5km depth → no calcareous ooze accumulates

Carbonate Compensation Depth (CCD)



Carbonates of evaporitic basins

- Minor accumulations of $CaCO_3$ are associated with arid climates, forming caliche that is widespread
- caliche is a natural cement of $CaCO_3$ that bonds other materials e.g. sand, gravel, silt, clay
- capillary action draws lime-bearing waters to the surface through evaporation, lime-rich calcite is formed



caliche

Carbonates of freshwater lakes and springs

- In some freshwater lakes, friable carbonates are forming
- these carbonates are marls and also underlie some freshwater and swamp peats recording an earlier lacustrine stage
- carbonate deposits are also forming today by evaporation of some springs and river waters
- tufa is a spongy porous material that forms superficial deposits about some springs and seeps. It is rarely extensive
- travertine is a dense banded deposit especially common in limestone caves and around hot springs

Tufa

Tufa deposit, Soda Dam, New Mexico

Travertine

- Travertines are carbonate rocks produced by inorganic precipitation from hot springs and fresh water
- hot springs are derived from deep waters released by geothermal systems and may contain large amounts of CO_2 (may be released from cooling igneous intrusions)
- when these waters reach the atmosphere they rapidly evaporate causing precipitation of carbonate from water
- travertine deposits encrust the surrounding rocks and soil and may produce molds of fossils

Travertine

Travertine limestone terraces, Pamukkale, Turkey

Aeolian carbonates

- Aeolian dunes composed of $CaCO_3$ are widespread today along tropical and sub-tropical shorelines
- coastal aeolianites consist of carbonate of shallow marine biogenetic origin that are self-cementing
- conditions favourable for formation are:
  - warm climates
  - onshore winds
  - low onshore topography
  - low onshore rainfall

Aeolian carbonate dunes, Sorrento, Vic.

Grains in carbonate rocks

- The grains that are present in carbonate rocks are called allochemical particles or allochems
- they are grains commonly precipitated by organisms formed elsewhere and become included in carbonate sediment
- because calcite and aragonite are soft and soluble in water they do not travel very far
- the degree of rounding and sorting of grains may not reflect energy of transport but may be biologically determined
- some organisms produce particles that already have a rounded shape

Grains in carbonate rocks

The following grain types are found in carbonate rocks:

(1) Whole or broken fossils

(2) Ooids - spherical, sand-sized carbonate particles

(3) Peloids – spherical aggregates of microcrystalline $CaCO_3$

(4) Limeclasts- fragments of earlier formed limestone

Ooids (ooliths)

- Ooids → sand-sized grains <2mm in diameter, consisting of one or more concentric layers of calcite or aragonite around a core grain of quartz or carbonate
- thickness of concentric layers may vary from 50% of the ooid particle to a superficial coating
- concentric shells usually a few microns thick likely form from direct precipitation of $CaCO_3$ on ooid
- limestone composed of ooids is called oolite or oolitic limestone
- ooids form in high energy environments by wave or current action e.g. Bahamas Platform

Ooids

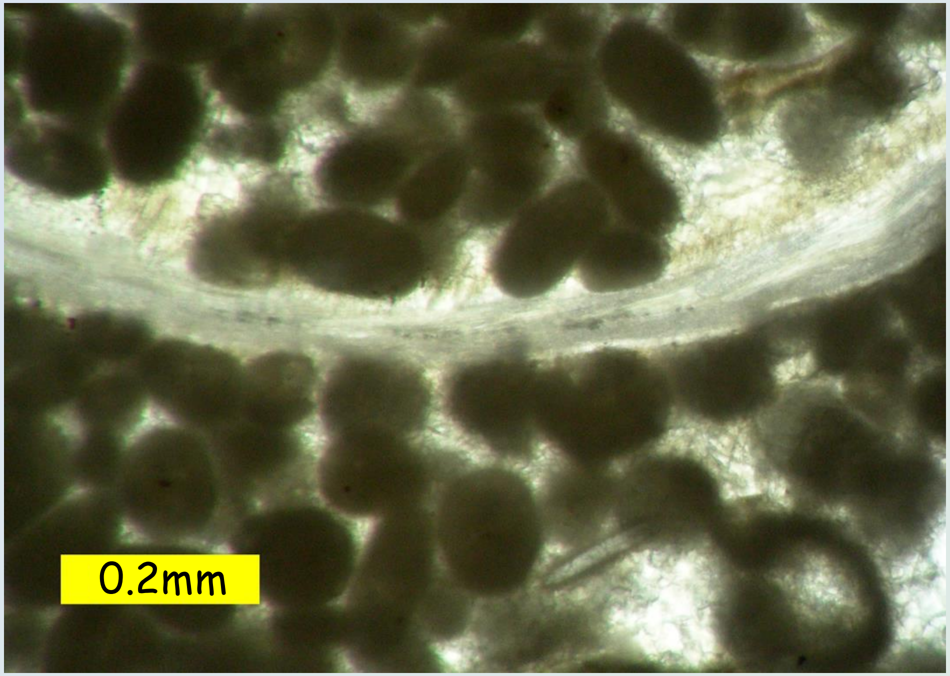
Ooids, Bahamas

Photomicrograph ooids in thin section PPL

Peloids

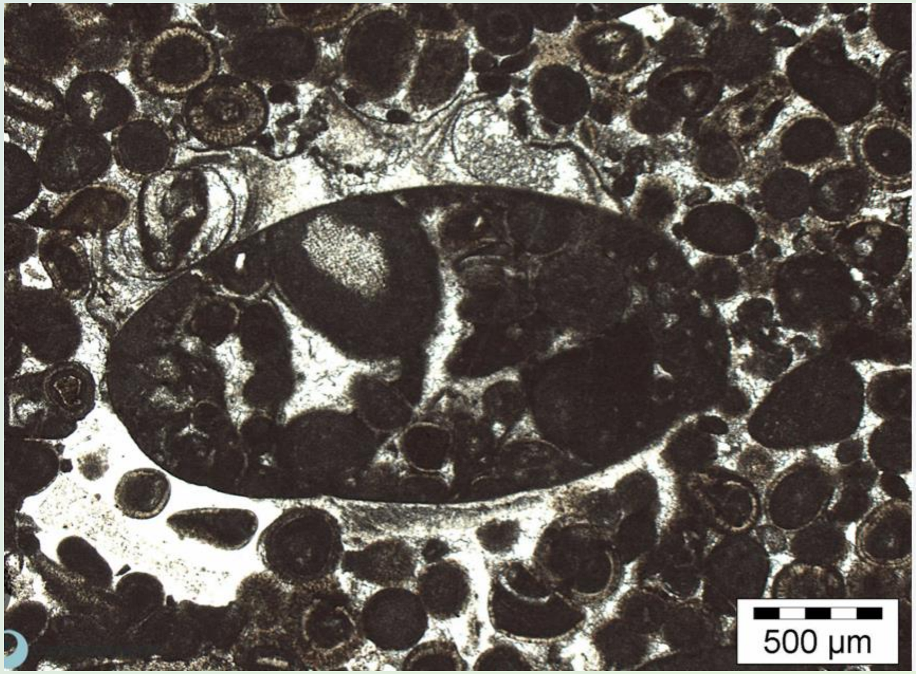
- Peloids → structureless grains of microcrystalline carbonate likely produced by a number of processes
- the two primary types of peloids are pellets and intraclasts
- many are thought to be fecal pellets produced by marine organisms
- others may form by boring algae or other micro-organisms through breakdown of mollusk shells
- intraclasts originate close to where they develop while extroclasts come from carbonate depositional areas

Peloids



Photomicrograph. Peloid pellets and a brachiopod shell in limestone. PPL

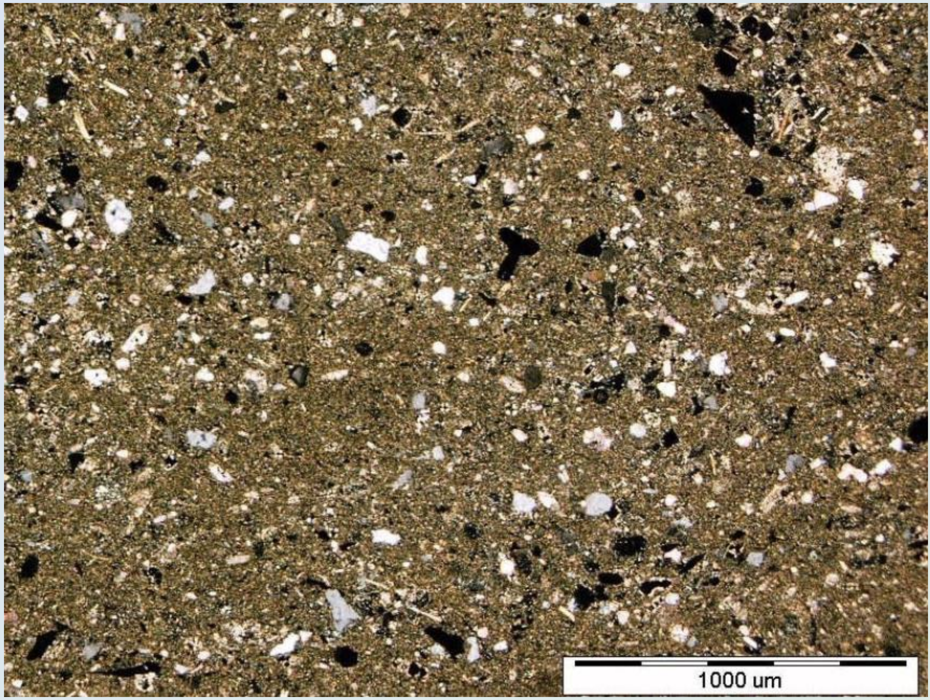
Intraclast in oolitic limestone



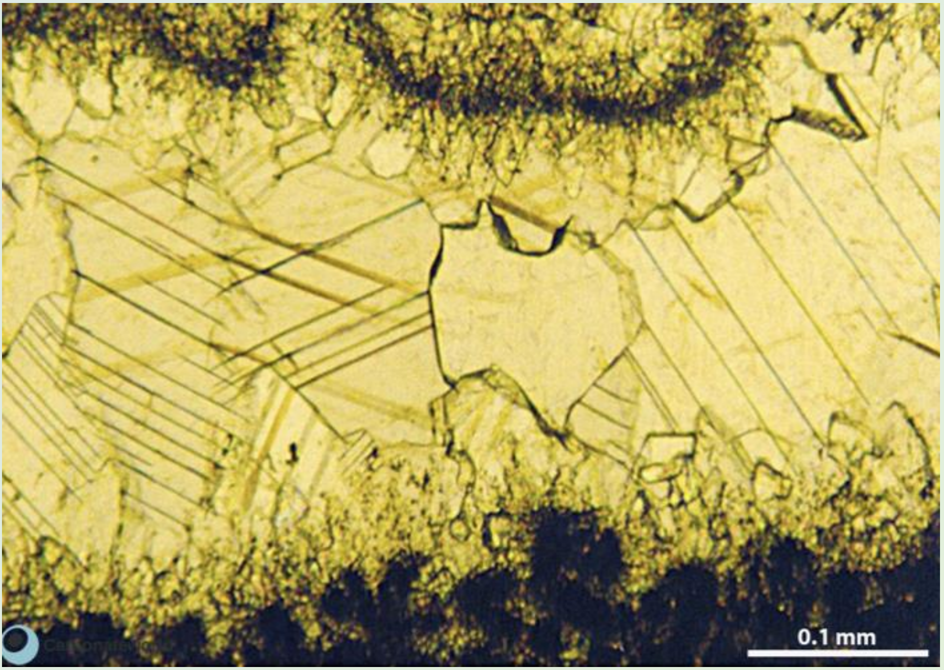
Matrix

- Grains of most limestones are embedded in a matrix of carbonate mud
- mud consisting of individual crystals <5μm across is called micrite
- micrite is typically the largest fraction of ancient carbonate rocks
- in fresh carbonate mud, micrite is mostly small aragonite needles that precipitate directly from seawater
- limestones often contain larger crystals of calcite 0.02 to 0.1mm across, described as calcite spar or sparite that are distinguished from other carbonate grains by their shape

Matrix



Photomicrograph. Micrite PPL



Photomicrograph. Sparite PPL

Structures - laminations

- Since most limestones are formed by clastic processes – many of the same structures as clastic rocks are present
- laminations → most common type produced by organisms forming mats by trapping and binding microcrystalline carbonate
- this leads to the formation of laminated layers consisting of layers of organic tissue interbedded with mud
- another type of lamination occurs as bulbous structures called stromatolites
- these are produced in a similar fashion by blue-green algae (cyanobacteria)

Structures - laminations

Algal limestone, Yass, NSW

Stromatolite laminations

Structures - stylolites

- Stylolites are irregular surfaces resulting from pressure solution of large amounts of carbonate
- in cross-section, they appear like sutures with stylolites composed of insoluble residue
- studies indicate that stylolites represent anywhere from 25% to as much as 90% of missing rock dissolved away

Stylolite in dolomite

Limestone

- Limestone forms from biological and non-biological processes
- fossils are common, biological processes such as accumulation of marine corals and shells most important in last 540myr
- limestones often contain various amounts of silica in form of chert or siliceous skeletal fragments e.g. sponge spicules, diatoms, radiolarians
- limestone commonly white or grey in colour, when rich in organic material can be almost black
- limestones show little variability in composition but great diversity in texture

Limestone

Jurassic limestone outcrop, Malaga, Spain

Folk classification of limestone textures

- The Folk classification scheme divides carbonates into two groups:

  Allochemical rocks → contains grains derived externally

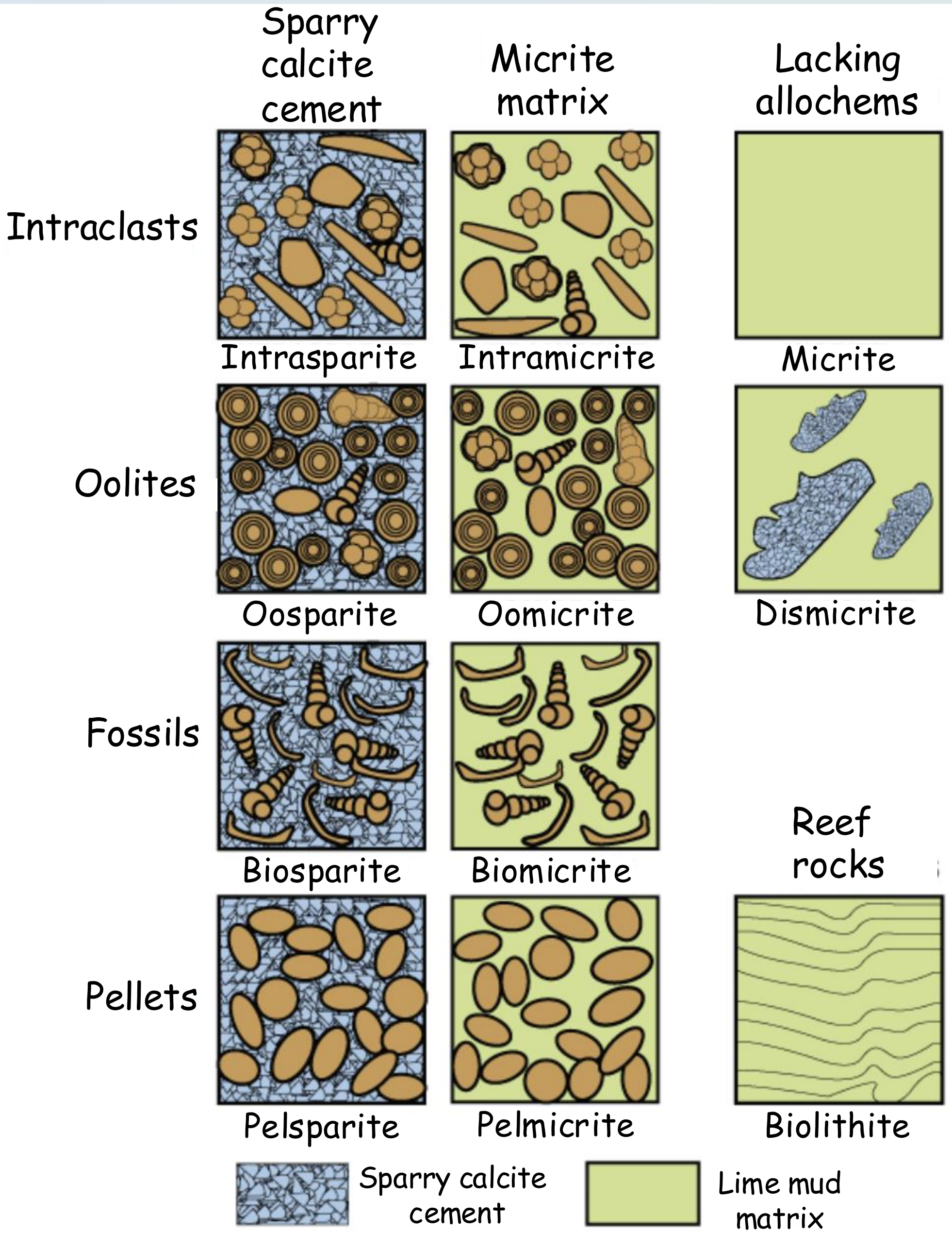
  Orthochemical rocks → carbonate crystallises in-situ

- allochemical rocks have grains that may consist of fossil material, ooids, peloids or intraclasts

- these grains are embedded in a matrix consisting of microcrystalline carbonate (micrite) or larger visible crystals of calcite called sparite

- sparite → clear granular carbonate formed through recrystallisation of micrite or, crystallization in pore spaces during diagenesis

Folk classification of limestone textures



	Sparry calcite cement	Micrite matrix	Lacking allochems
Intraclasts	Intrasparite	Intramicrite	Micrite
Oolites	Oosparite	Oomicrite	Dismicrite
Fossils	Biosparite	Biomicrite	
Pellets	Pelsparite	Pelmicrite	Reef rocks Biolithite

▨ Sparry calcite cement

🟩 Lime mud matrix

C.G.St.C. Kendall, 2005 (after Folk 1959)

Dolostones

- Dolostones are carbonate rocks composed almost entirely of dolomite $CaMg(CO_3)_2$
- although no dolomite rocks are being directly precipitated in modern times, they have formed through geological times
- most dolostones appear to result from diagenetic conversion of calcite to dolomite after primary deposition of original $CaCO_3$ minerals
- Two mechanisms of dolomitisation of limestone are proposed based on field and laboratory studies:
  - (1) Evaporative reflux – evaporation of seawater → Mg brine
  - (2) Mixing of seawater and meteoric water in limestone

Dolostone

Dolostone, Flinders Ranges, South Aust.

Identification of carbonates

- Limestone easy to identify → effervesces when 10% diluted HCl dripped onto its surface
- dolostone does not effervesce when dripped with 10% diluted HCl or when diluted HCl is dripped onto powdered dolomite
- dolostone will fizz with a less dilute HCl solution (around 30%)
- cleavage and crystal faces of dolomite show slight but noticeable curvature

Karst and caves

- Karst environments occur anywhere there are outcrops of carbonate rocks exposed at the surface
- rainwater that falls on carbonates contains atmospheric CO_2 that progressively dissolves carbonate rocks
- infiltration of acidic waters into fractured carbonate rocks progressively enlarges fractures enhancing infiltration of acidic waters to depth and ultimately leading to forming cave systems
- once water reaches caves, carbonate precipitation can occur producing cave formations e.g. flowstone, stalactites, stalagmites

Karst landscape Guilin, China