Chapter 5

Carbonate Sediments

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Carbonate sediments are a part of the carbon cycle (Fig. 1.14). CO_2 in the atmosphere dissolves in water and makes carbonic acid (H_2CO_3) which reacts with Ca^{2+} or Mg^{2+} to precipitate $CaCO_3$ or $MgCO_3$. This process is an important sink for CO_2. The rate of carbonate sedimentation globally is controlled by the supply of cations (mostly Ca^{2+} and Mg^{2+}) into the ocean from rivers. This again is a function of the rate of weathering of Ca-bearing silicate minerals like plagioclase, pyroxene, amphibole and chlorite. Dissolution of basic rock along a spreading ridge may also add to the supply of calcium to the ocean water.

Weathering of limestones will release CO_2 and therefore does not contribute as a sink for CO_2. During contact metamorphism when limestones are heated (to 550–600°C), $CaCO_3$ reacts with SiO_2 to form $CaSiO_3$ (wollastonite) and CO_2. Large amounts of CO_2 formed this way are released through volcanoes. When minerals like wollastonite are uplifted, exposed and weathered, Ca^{2+} is released into rivers and the ocean again. Another part of the CO_2 in the atmosphere is reduced by plants (i.e. algae) and stored as carbon or organic compounds which can generate petroleum. These may also be oxidised to CO_2.

Carbonate sediments are for the most part formed (born) within sedimentary basins even if there may be a clastic supply of carbonate sediments. The sedimentology of carbonates therefore differs in many respects from siliceous sand and mud. Carbonates may precipitate chemically from the seawater, but most of the limestones are composed of calcareous organisms. The properties of limestones are therefore closely linked to their biological origin and the mineralogy of the carbonate skeletons. The primary composition is very important for their alteration during burial (diagenesis) and consequent reservoir properties (porosity and permeability), which to a large extent is controlled by chemical processes. Since both biologically and chemically precipitated carbonate sediments are composed of minerals we will first examine the mineralogy and geochemistry of carbonates. This is important for understanding diagenetic reactions and prediction of reservoir quality.

5.1 Geochemistry of Carbonate Minerals

Carbonate minerals consist of CO_3^{2-} and one or more cations. The most common cations in carbonate minerals together with their mineral names are listed in Table 5.1. The common rock-forming carbonate minerals are either rhombohedral (calcite) or orthorhombic (aragonite) in crystal habit. Where cations with small ionic radii are incorporated into carbonates a trigonal (rhombohedral) crystal lattice is formed, while larger cations result in orthorhombic unit cells.

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Table 5.1 Mineralogy of the most common carbonate minerals

Carbonate sediments formed in normal marine environments consist of three main minerals:

Low-Mg calcite $CaCO_3(<4\%\ MgCO_3)$ (hexagonal)
High-Mg calcite (Ca,Mg) $CO_3(>4\%\ MgCO_3)$ (hexagonal)
Aragonite ($CaCO_3$) (orthorhombic)
Other common carbonate minerals are:
Siderite $FeCO_3$
Magnesite $MgCO_3$
Strontianite $SrCO_3$
Rhodochrosite $MnCO_3$
Smithsonite $ZnCO_3$
Ankerite $Ca(Mg,Fe)(CO_3)_2$
Dolomite $CaMg(CO_3)_2$

Ca^{2+} has an ionic radius close to 1 Å which is intermediate between small and large cations and near the limit of sixfold co-ordination. Thus $CaCO_3$ is dimorphous forming either rhombohedral or orthorhombic structures.

Cations smaller than 1 Å such as Fe^{2+}, Mn^{2+}, Zn^{2+} and Mg^{2+} can be incorporated in the calcite lattice. These metals all have an ionic radius of about 0.6–0.7 Å, and therefore calcite can contain considerable concentrations of these cations. The calcite group of minerals, such as siderite ($FeCO_3$), rhodochrosite ($MnCO_3$), smithsonite ($ZnCO_3$) and magnesite ($MgCO_3$), all have the same crystal structure as calcite.

Two types of calcite are recognised, depending on the magnesium content: low-Mg calcite $(<4\ \text{mol\%}\ MgCO_3)$ and high-Mg calcite $(>4\ \text{mol\%}\ MgCO_3)$. Much of the biologically secreted calcite typically ranges between 11 and 19 mol% $MgCO_3$. Some organisms like coccoliths are however composed of low-Mg calcite (or simply called calcite). Low-Mg calcite is more stable than high-Mg calcite, and fossil fragments originally composed of high-Mg calcite are converted to low-Mg calcite during diagenesis. The alteration of high-Mg calcite to low-Mg calcite takes place by a process of leaching of Mg^{2+} ions, which leaves the microarchitecture of the grain unaffected. The exsolved Mg^{2+} may form microdolomite rhombs that are sometimes seen as inclusions in calcitised high-Mg calcites (quite common in fragments of echinoderms and calcareous red algae).

The orthorhombic lattice has an arrangement of CO_3^{2-} anions where cations larger than 1 Å (such as Sr^{2+}, Ba^{2+} and Pb^{2+}) are preferred. Analogous with this aragonite crystal structure are strontianite ($SrCO_3$), witherite ($BaCO_3$) and cerrusite ($PbCO_3$). Sr in particular is an important trace element in aragonite. Aragonite crystals forming in marine environments today contain 5,000–10,000 ppm Sr. Aragonite is unstable and after some time will be replaced by calcite which still retains relatively high concentrations of strontium. Aragonite may occasionally be preserved, particularly in dense shales, even in Mesozoic rocks.

Iron is only very weakly soluble in the oxidised state, forming hydroxides $Fe(OH)_3$ and oxides (Fe_2O_3), but in the reduced state it occurs as soluble Fe^{2+}. Reduction of iron normally takes place within the microbial sulphate reduction zone where high concentrations of sulphur will cause available Fe^{2+} to be precipitated as sulphides (pyrite, FeS_2), so that very little is available to enter the calcite structure. The principal environment in which Fe^{2+} can enter the calcite lattice to form ferroan calcite is thus in the reducing porewater below the sulphate reduction zone. The ferroan calcite may contain a few thousand ppm of iron.

Dolomite ($CaMg(CO_3)_2$) is a carbonate mineral in which layers of $CaCO_3$ alternate with layers of $MgCO_3$. $Fe^{2+}$is commonly found substituting for Mg^{2+} in dolomite, and a complete series extends to ankerite ($Ca(Fe,Mg)(CO_3)_2$). Dolomite formed early in diagenesis is fine-grained and can often have a magnesium deficit in relation to calcium [e.g. $Ca_{55}Mg_{45}(CO_3)_{100}$]. This is called protodolomite which during burial may be transformed into a regular dolomite.

5.2 Carbonate – CO_2 Systems in the Sea

Even if most carbonate precipitation occurs biologically it is important to understand the chemical constraints on carbonate reactions. Carbon dioxide concentration is the factor which has the greatest influence on pH and the solubility of carbonates in water. CO_2 dissolves in water to form carbonic acid (H_2CO_3), which dissociates into bicarbonate (HCO_3^-) and carbonate ions (CO_3^{2-}).

$$\begin{aligned} CO_2 + H_2O = H_2CO_3 &= H^+ + HCO_3^- \\ &= CO_3^{2-} + 2H^+ \end{aligned}$$

Calcite solubility depends on the solubility product $\left[Ca^{2+}\right] \cdot \left[CO_3^{2-}\right]$. We see that when the water is relatively acid (high H^+ concentrations) the reaction is driven towards the left and the carbonate ions concentration $\left[CO_3^{2-}\right]$ will be low. With high pH (i.e. low H^+ activity), the bicarbonate $\left(HCO_3^-\right)$ concentration will be higher.

Mineral solubility is not strictly a function of the ionic concentration, but of the activity (a) which is influenced by the temperature and other ions present.

The dissociation constants for H_2CO_3 and HCO_3^- are:

$$K_1 = aH^+ \cdot aHCO_3^- / aH_2CO_2^{2-}$$

and

$$K_2 = aH^+ \cdot aCO_3^{2-} / aHCO_3^-$$

This in turn requires that aCO_3^{2-} also must be higher in order to satisfy the dissociation equation. At low pH values the equilibrium will shift to the left, giving more free CO_2 and H_2CO_3 (Fig. 5.1). CO_2 is found in both water and the atmosphere, and is exchanged between them. Statistically, the residence time in the atmosphere is c. 8 years, while it is c. 600–1,000 years in the ocean. The CO_2 in the ocean is partly removed when precipitated as organic matter in the sediments, and partly by precipitation as carbonates.

The solubility of CO_2 in water is greatest at low temperatures and high pressures, decreasing as the temperature rises and pressure decreases. Since it is largely the CO_2 concentration which determines the pH of water, the pH is highest (8.0–8.5) in the warm surface layer at low latitudes, and lowest in polar areas (7.5–8.0).

Photosynthesis also contributes to the consumption of CO_2, increasing the pH of the surface water. pH decreases with water depth, not only because CO_2 is no longer removed by photosynthesis, but also because of the lower temperature and higher pressure.

Whereas photosynthesis involves the removal of CO_2 from the water, respiration adds CO_2.

$$H_2O + CO_2 = CH_2O + O_2$$

CH_2O is a general formula for sugar. During photosynthesis this reaction will go to the right. The reverse reaction is respiration. We see that while photosynthesis raises the pH, respiration will lower it. The water below the photic zone will gain CO_2 from the respiration of zooplankton, and the breakdown (i.e. oxidation) of organic matter which sinks down through the water column will also produce CO_2 and lower the pH. In shallow water, a daily variation in pH has been registered as a result of the fact that photosynthesis takes place only during the day, increasing the pH, while respiration continues at night reducing the pH. Respiration by organisms in the water below the photic zone contributes further to the pH declining downwards through the water column. The recent increase in CO_2 content in the atmosphere (from 280 to 400 ppm) will also influence the ocean water, making it slightly more acidic. Ocean water is, however, strongly buffered and the amount of carbonate that can be precipitated in the oceans is primarily dependent on the supply of cations over geological time, especially Ca^{2+} which is mostly liberated by land weathering of carbonate rocks and calcium silicates such as plagioclase. The pH in modern

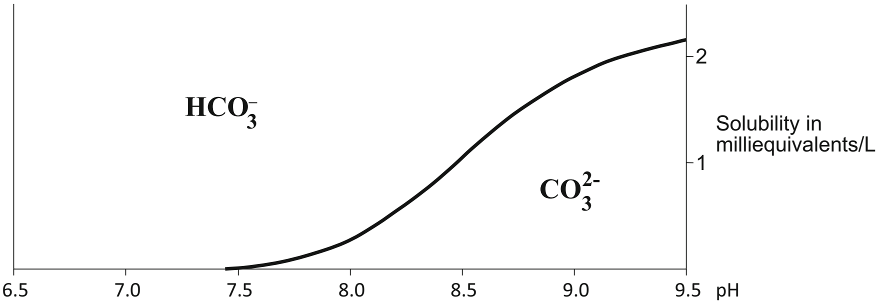


Fig. 5.1 Solubility of carbonate ions in seawater as a function of pH

ocean water varies from 7.9 in zones with upwelling of deep water to about 8.3 in parts of the North Atlantic and the Barents Sea where high productivity removes carbon dioxide from the sea water. Increased CO_2 in the atmosphere and in the ocean, however, shows large local variations due to ocean water circulation, biological activity and reactions with carbonate minerals.

5.3 Skeletal Components

5.3.1 Introduction

The evolution of organisms precipitating carbonate skeletons has played an important role in the accumulation of carbonate sediments and their properties. The skeletal material is widely different in size, with diameters ranging from a few micrometres in coccolithophores to more than a metre in some bivalves and sponges. The range and taxonomic diversity of major groups of skeletal organisms are shown in Fig. 5.2. However, in this text book we have limited the descriptions to those groups which are most commonly encountered in carbonate hydrocarbon reservoirs.

The first condition for obtaining relatively pure carbonate deposits is that there must be very little or no supply of terrigenous sediments such as sand or clay which otherwise would dilute the carbonate content. Many of the carbonate-secreting organisms require clear water because they filter out nutrients from the seawater. The presence of mud will kill organisms like corals, severely reducing carbonate production. This puts an important limitation on the occurrence of carbonate sediments in sedimentary basins.

5.4 Plants

5.4.1 Stromatolites

"Stromatolite" is the term for lamination in carbonate rocks due to the accumulation or precipitation of carbonate ascribed to bacterial growth. Stromatolites have an intermediate status between fossils and sedimentary structures. They consist of cyanobacteria (earlier called blue–green algae) which have a growth form as unsegmented, micron-sized filaments or unicells (coccooids). The filaments occur in rows or strands within a sticky mucilaginous sheath. Only a few forms produce a biochemically precipitated skeleton, usually tubiform. Other cyanobacteria may generate organic films on the sediment surface, which trap and bind lime mud to form irregular laminae.

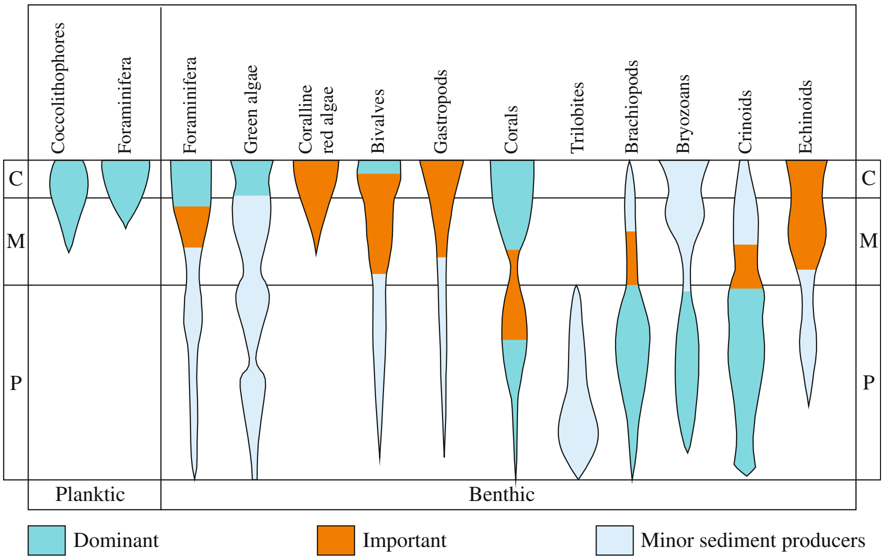


Fig. 5.2 Diversity, abundance and relative importance of various calcareous marine organisms as sediment producers. P = Palaeozoic; M = Mesozoic; C = Cenozoic (modified after Wilkinson 1979)

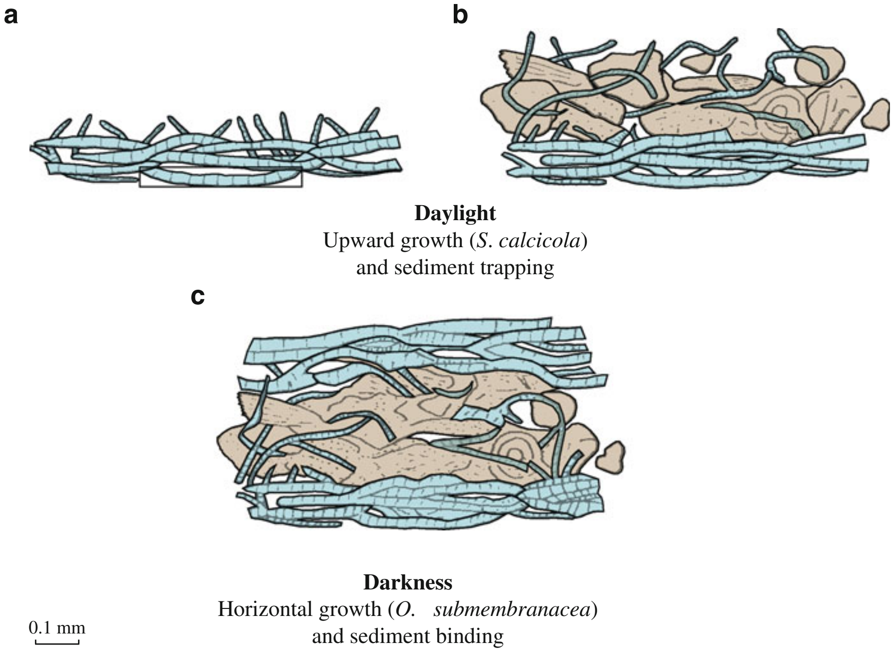


Fig. 5.3 Diagrammatic representation of the day-night accretion in stromatolites. (**a**) and (**b**) During daytime the cyanobacteria trap and bind sediment and proceed to grow up and around the sediment grains. (**c**) A sticky surface that traps and binds the next sediment layer is produced during the night (modified from Gebelein 1969)

Rhythmic variations in bacterial filament growth produce a laminated structure of alternating light, sediment-rich laminae and dark, organic-rich laminae (Fig. 5.3). The end result is either parallel lamination following cyanobacterial (previously algal) mats, more complex bacterial growth structures (stromatolites), or a concentric type of structure (oncoids). However, there are not always cyanobacterial remains to be found, and the only evidence then is the lamination in the rock.

If the laminae are flat-lying they are referred to as *cyanobacterial laminated sediments*, but if they form structures with vertical relief they are called *stromatolites*. The different overall shapes of stromatolites range from:

1. Laterally linked hemispheroids
2. Discrete, vertically stacked hemispheroids
3. Discrete hemispheroids

These main types are shown in Fig. 5.4 and Fig. 5.5, but combinations can occur.

The lamination commonly follows the outline of the structure, or is terminated at the edge of individual heads or stacks. Individual laminae are often thickest at the centre of the structure and thin laterally towards the periphery. Laminae draping over the edge have often accumulated more steeply than the angle of repose because of the sticky surface of the cyanobacteria. Micro-organisms in aquatic environments are usually in a matrix of extracellular polymeric substances, also known as exopolysaccharides, or EPS (also called “biofilm”). The production of EPS is a general property of prokaryotic (bacteria, archaea) and in eukaryotic (algae, fungi) micro-organisms. It is excreted by micro-organisms to keep them aggregated and attached to surfaces.

Cyanobacterial laminae may also form coatings on carbonate grains (e.g. skeletal material), producing structures known as oncoids (Fig. 5.5). These grains become spherical to oval as irregular, sometimes discontinuous, concentric bacterial laminations consisting of cyanobacteria growing around the nucleus. Once again, the layer of sticky bacteria on the surface of the grain will trap microscopic sediment grains, or precipitate aragonite because CO_2 is consumed by photosynthesis. In this way the grains will “grow”. These “growth layers” will not be continuous around the primary grain, as in oolites, because that requires constant movement. Sediment grains coated

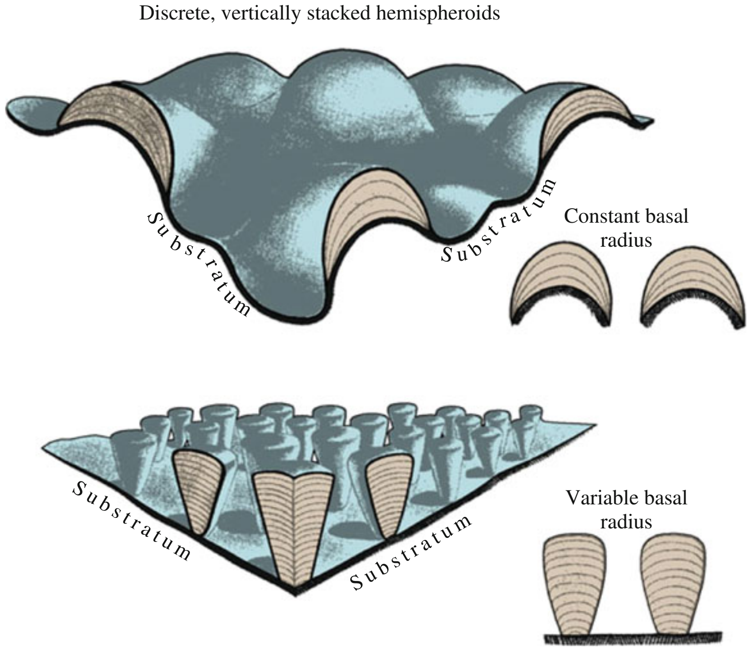


Fig. 5.4 Some of the main types of stromatolites (modified from Logan, Rezak and Ginsburg 1964)

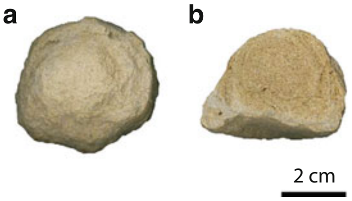


Fig. 5.5 Recent oncoids from the tidal zone. (**a**) Top surface of a hemisphaerical oncoid. (**b**) Vertical section showing the rough lamination. The flat base reflects stationary growth. Ras Muhamad Peninsula, Sinai

in this manner may reach up to 10 cm in diameter. Large oncoids are flattish and often called "bacterial (previously algal) biscuits". A deposit of oncoid sand is called an oncolite.

5.4.1.1 Ecology

Cyanobacteria have inhabited mostly open marine, shallow water and intertidal environments throughout geological time. However, hypersaline and rare freshwater forms have been recorded too.

Stromatolites are most common in upper intertidal to supratidal environments (Fig. 5.6), but have also occasionally been described from subtidal environments. Intertidal to supratidal stromatolites are often associated with fenestral (birdseye) structures, mud cracks and evaporites. The specific growth form may be used for environmental interpretation. Laterally linked hemispheroids often dominate on protected mud flats where wave action is slight. Exposed, intertidal mud flats, where the scouring action of waves and other interacting factors prevent the growth of bacterial mats between stromatolites, are characterised by vertically stacked hemispheroids. Concentrically arranged spheroids (oncoids) may occur in low, intertidal areas that are exposed to waves, and in agitated water below the low-tide mark. Oncoids are generally formed in shallow subtidal environments of low to moderate turbulence.

5.4.1.2 Geological Range

Cyanobacteria range from the early Precambrian to Recent. Stromatolites were very important in the Precambrian, but gradually decreased during the Phanerozoic due to the evolution of grazing organisms, in particular gastropods. Today, stromatolites are mostly present in stressed environments where high evaporation and therefore enhanced salinity limit grazing species.

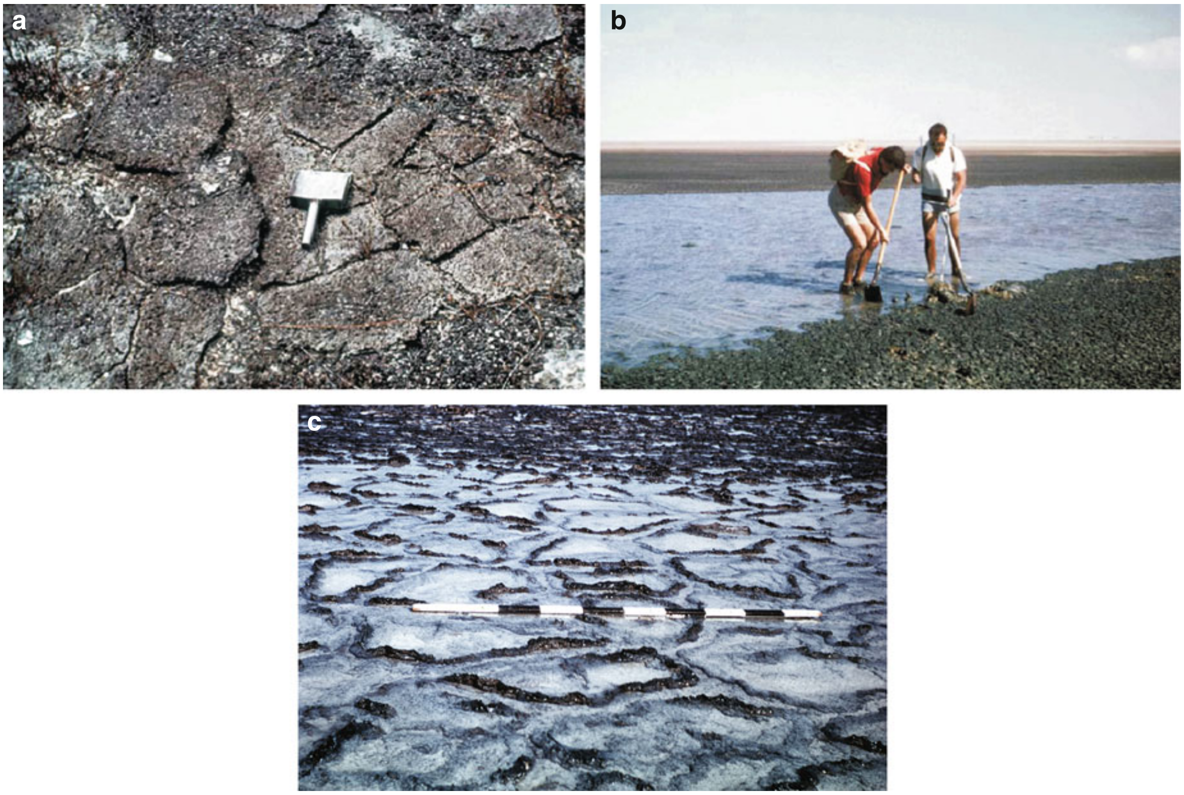


Fig. 5.6 (**a**) Supratidal crust composed mainly of fine-grained dolomite. Bahamas (Photo G.M. Friedman). (**b**) Supratidal environment (sabkha), Abu Dhabi. Photo D. Kinsmann. (**c**) Cyanobacterial mat with gypsum from supratidal environment (sabkha), Abu Dhabi (Photo D. Kinsmann)

5.4.1.3 Significance for Petroleum Geology

Some unicellular cyanobacteria synthesise oil and their remains may accumulate to form sapropelic deposits. These deposits may be important source rocks for oil. Oncolites may possess primary interparticle pores, but high porosity is not as common as in oolites because of poor sorting in less turbulent water. Oncolites also form thinner and less persistent beds than oolites and have relatively low reservoir and source rock potential.

5.4.2 Calcareous Algae

Calcareous algae form a diverse group of plants that inhabit most shallow marine, clear water environments. They prefer normal marine salinity although some forms may be euryhaline. Most calcareous algae are sessile, although a few, such as the coccolithophores, are planktonic. Most important are red algae and green algae, but one species of brown algae (*Palina*) also secretes a calcareous skeleton, which consists of aragonite.

A wide range of growth forms exists, and the most important are:

- **Encrusting calcareous algae**
  These are usually red algae and form smooth or uneven crusts, nodular shapes and rigid branching forms (Fig. 5.7). They vary in size from a few millimetres to many centimetres.
- **Calcareous algae with erect growth morphology**
  Usually segmented, branching algae which may become several centimetres high (Fig. 5.8). Each segment is normally less than a few millimetres, often cylindrical with circular or oval cross-section. Since the segments generally come apart when the alga dies, it is very difficult to reconstruct the original plant body (thallus) of fossil species.

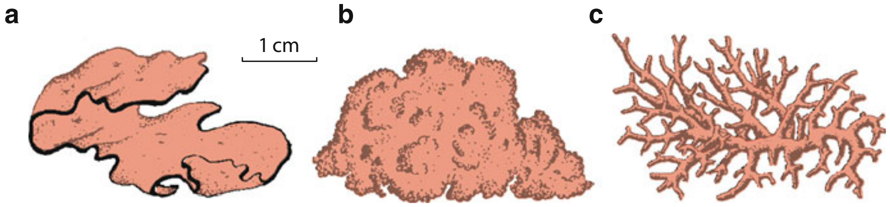


Fig. 5.7 Encrusting calcareous algae comprise many different growth forms including smooth and uneven crusts, nodular shapes and rigid, branching forms. (**a**) Irregular crust. (**b**) Nodule. (**c**) Rigid branching form (modified from Wray 1977)

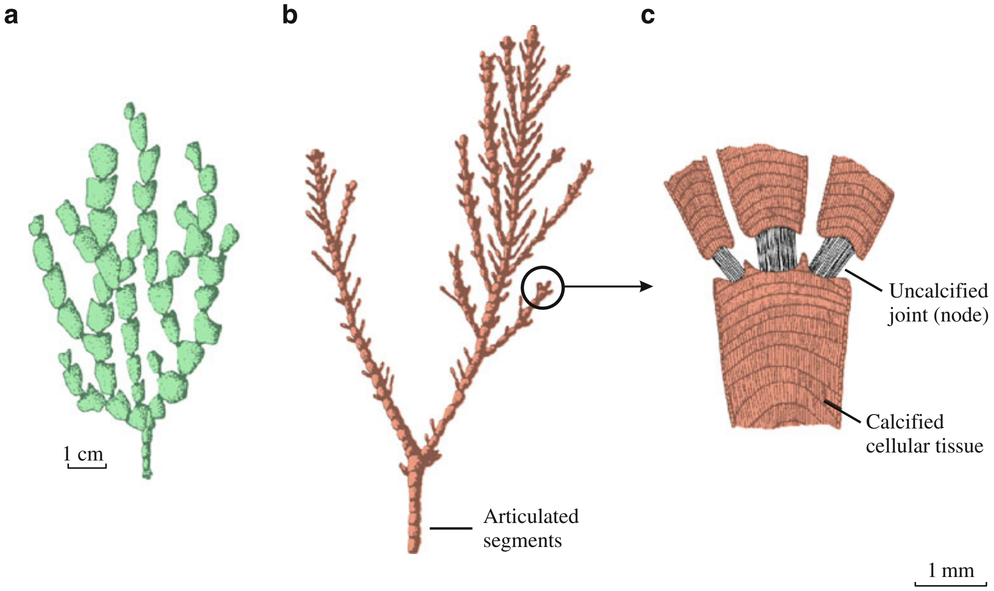


Fig. 5.8 (**a**) Segmentary growth form of the green alga *Halimeda* sp. Each segment is wide and flat with a roughly triangular cross section. The segments are separated by joints. Since there is no calcification near the joints, the algae have some flexibility. (**b**) Typical growth form of articulated coralline algae (*Corallina* sp.). (**c**) Internal structure of calcareous segments as seen in longitudinal section. Between each joint there is a poorly calcified region, giving the plant some flexibility (modified from Wray 1977)

5.4.2.1 Ecology

Red algae are almost exclusively marine and prefer shallow (<25 m) subtidal environments where the light is strong. They may, however, range down to a depth of approximately 250 m. Some of the growth forms can withstand fairly strong agitation and are common on shallow, rocky substrates associated with reef and near-reef environments on platform margins. Red algae are generally less tolerant of salinity variations than green algae and cyanobacteria.

During photosynthesis, algae consume CO_2 and produce oxygen. The absorption of sunlight by water is not, however, equally rapid for the various constituent wavelengths, the red portion of the spectrum (longwave light) being more rapidly absorbed than the blue (shortwave). Red algae can also use blue shortwave light, enabling them to live at greater depths than, for example, green algae, which are dependent on long-wave red light (Fig. 5.9). Areas with carbonate sedimentation normally have little clastic material in suspension, and the water is therefore very clear. The absorption of light drops off exponentially with depth and below about 50 m there is very little light left.

Most recent green algae grow in shallow marine, tropical waters of normal salinity, but some tolerate hypersaline or brackish water. Recent green algae are abundant in depths of 5–10 m, but may range down to 100 m and also extend into lagoons and mangrove

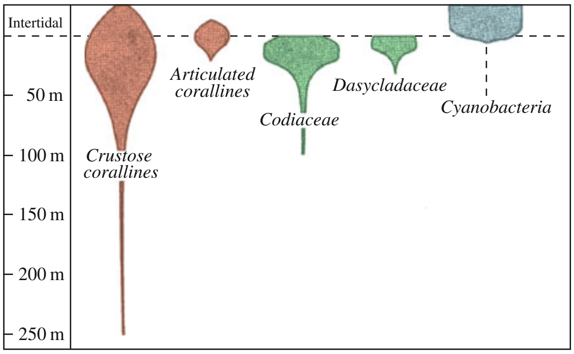


Fig. 5.9 Generalised depth distribution of the major groups of Recent marine calcareous algae. The red algae have been drawn in *red*, the green algae in *green* and the cyanobacteria in *blue* (modified from Wray 1977)

swamps. Some species can grow on firm substrates, but most grow in sand or mud. They generally prefer environments with only moderate wave energy. The calcareous green algae are major producers of small aragonite crystals which form lime mud. The presence of green algae therefore ensures that lime mud is deposited in the lagoons.

5.4.2.2 Mineralogy

The skeletal material in living algae is either calcite or aragonite, never mixtures of these two minerals in the same species. The extent of calcification is highly variable and may be only partial in some groups while other groups have a pervasive calcification of the whole plant body. Recent calcareous algae consist usually of small crystals (<4 μm) of precipitated calcite (e.g. coccolithophores produces low-Mg calcite and *Lithophyllum* produces high-Mg calcite) or aragonite (e.g. *Peyssonnelia*). The same is assumed to apply to pre-Quaternary species too. The preservation of the plant bodies depends on the extent of calcification, with the most calcified parts selectively preserved in the fossil record.

Modern red algae deposit either aragonite or high-Mg calcite with a Mg content up to about 30 mol% $MgCO_3$. The skeletal elements in green algae consist only of aragonite. This primary difference in their skeletal composition is an important preservation factor. The solubility of skeletal aragonite in pure water is about twice that of low-Mg calcite, whereas the solubility of skeletal high-Mg calcite is up to 10 times that of low-Mg calcite. Hence, the fine-grained aragonite skeleton of the green algae is replaced by sparry calcite, whereas coralline red algae with a primary calcitic composition of varying magnesium content show different degrees of alteration (often partial dissolution).

5.4.2.3 Geological Range

Calcareous green algae first appeared in the Cambrian, which led to the production of large amounts of lime mud. These algae are still an important factor in modern shallow-water carbonate sedimentation. Red calcareous algae also evolved in the Cambrian. In Recent marine environments they are commonly encountered both in cold and warm water deposits within the photic zone, although most of them live in fairly shallow water (<25 m).

5.4.2.4 Significance for Petroleum Geology

Red algae, particularly those with erect growth forms, may form primary framework porosity in reefs. The algae are susceptible to neomorphic replacement and develop secondary porosity when exposed to extensive freshwater dissolution.

Red algae are common associates of many oil and gas producing reefs, notably stromatoporoid and coral reefs. This includes the Middle Silurian pinnacle reefs (stromatoporoid-coralgal reefs) in the Michigan Basin of southeastern Michigan, USA, the Upper Palaeocene Intisar "D" Field (coralgal reef) in Libya, the Miocene coralgal reefs in the Salwati Basin of Irian Jaya, Indonesia and the Miocene Central Luconia Fields of offshore Sarawak, Malaysia.

Calcareous green algae may form important source rocks for oil.

The biota of Late Palaeozoic warm-water carbonates is often characterised by a photozoan tropical to subtropical assemblage of phylloid algae and *Palaeoaplysina* (if the latter is indeed a alga?). In the Paradox Basin of USA some hydrocarbon reservoirs of phylloid algal mounds are overlain by grainstones. These mounds may have been formed by aggradational growth of phylloid algae and/or as wave- or tide-generated current-emplaced mounds. Meteoric water may have invaded and dissolved algal plates of probable aragonite, increasing the porosity and permeability.

Large *Palaeoaplysina*–phylloid algal build-up complexes started as separate mounds and developed into stacked build-ups with a height of tens to hundreds of metres. The build-ups can be situated close together forming elongated ridges separated by canals or ring-shaped to polygonal structures surrounding a lagoon (Figs. 5.10 and 5.11). Many of the build-ups and their associated lateral facies form reservoir rocks for oil and gas in the Timan-Pechora Basin of northern Russia and in the pre-Caspian basin of Kazakhstan. They are also currently of interest to the petroleum industry in the Norwegian Barents Sea, Arctic Canada and Greenland.

5.4.3 *Coccolithophores*

Coccolithophores are an example of free-floating algae with carbonate shells. They are single-celled, microscopic (5–20 μm) plants belonging to the golden-brown algae. A coccolithophore is generally spheroidal or ovoidal and is covered with an external calcareous skeleton (coccosphere) (Fig. 5.12). The coccosphere is composed of a variable number of small (a few μm), commonly round to oval, calcareous plates (coccoliths). The coccoliths are made of tiny, platy low-Mg calcite crystals (0.25–1 μm) with a flattened rhombic form, and are stacked in an imbricate fashion that produces a spiral pattern. The coccolithophores usually disaggregate after death and accumulate as individual coccoliths, sometimes forming extensive chalk deposits.

5.4.3.1 Ecology

Coccolithophores are most common in the photic zone of open seas, although they may also range into nearshore lagoons. They swim freely in the surface waters (commonly the upper 100 m) of the ocean, occurring in greatest abundance in temperate zones.

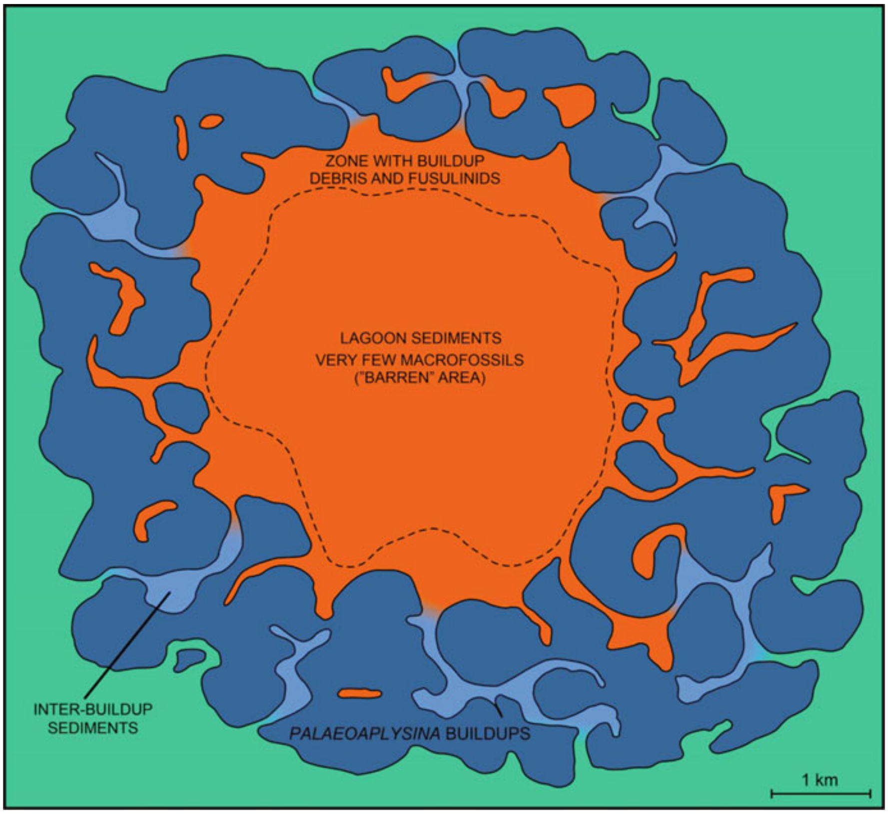


Fig. 5.10 A lagoon surrounded by a ring-shaped to polygonal *Palaeoaplysina* build-up complex. As a dry climate results in evaporation and the build-up complex restricts the exchange of water, hypersaline conditions develop in the lagoon. The salinity increases toward the middle of the lagoon, while the biodiversity decreases. Although low in number of species, the adapted species have little competition from other groups and the organic production can be very high. Hypersaline setting is also favorable in preserving organic matter, and therefore hypersaline sediments might be potential source rocks for hydrocarbons. Modified from Hanken and Nielsen (2013)

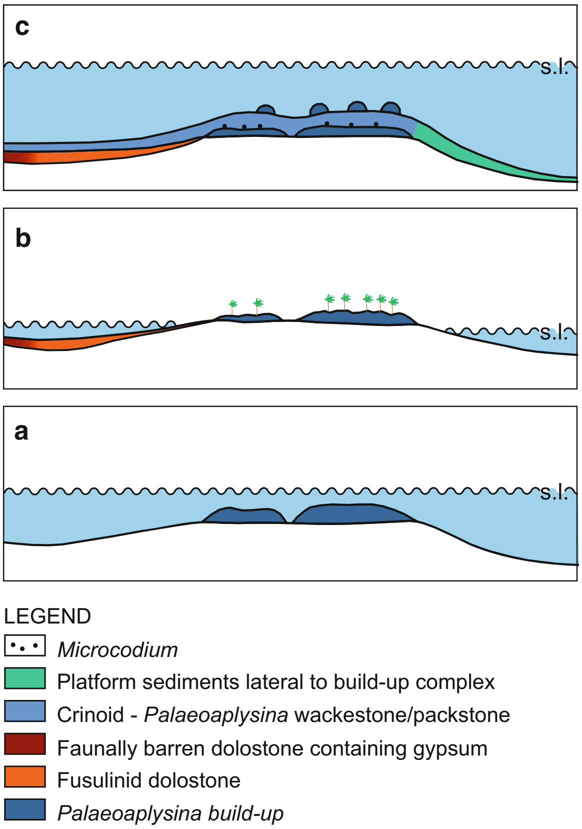


Fig. 5.11 (**a**) *Palaeoaplysina* build-ups initiate their growth on palaeo-highs. (**b**) Subaerial exposure of the *Palaeoaplysina* build-up complex and the development of vegetation on top of build-ups. Hypersaline conditions in the lagoon result in precipitation of evaporites such as gypsum. (**c**) During transgression, deposition of marine sediments characterised by normal marine fauna and flora extends across the lagoon and build-up complexes. On the highs, the *Palaeoaplysina* build-ups initiate their growth as small disconnected structures which may develop into larger complexes. Based on observations from Svalbard. Modified from Hanken and Nielsen (2013)

Fig. 5.12 (**a**) Skeletal structure of coccospheres and coccoliths. In this example the spheroidal coccosphere is composed of many round calcareous plates (coccoliths) which consist of tiny, platy calcite crystals stacked in an imbricate pattern. Modified from Hjuler (2001). (**b**) SEM picture of Lìge chalk consisting of a mixture of coccoliths and loose platy calcite crystals. (**c**) SEM picture of Upper Cretaceous coccoliths in the Ekofisk field, North Sea. Petroleum occurs between the small plate-like coccoliths. The limestone has 32% porosity and 1 mD permeability (from Bjørlykke 1989)

Coccolithophores are abundant (commonly as many as half a million individuals per litre of water) in the photic zone of modern oceans. Coccoliths are important constituents of some fairly deep basinal and distal shelf sediments.

Deep-sea drilling has shown that coccolithophores were very much more widespread during the Cretaceous and Lower Tertiary than they are today. The colder climate which began in the Miocene shifted the northern limits for coccolithophore sedimentation southwards. Many pelagic species have very specific temperature requirements and their occurrence provides an important contribution to the palaeoecology of marine sediments of various ages.

5.4.3.2 Mineralogy

The plates of the coccolithophores consist of low-Mg calcite which makes them fairly stable during diagenesis.

5.4.3.3 Geological Range

Coccolithophores range from the Triassic to Recent, but were not common before the Jurassic. They were particularly abundant in the Cretaceous and Lower Tertiary, forming thick, extensive chalks. They comprise approximately 25% of present-day calcareous oozes and up to 90% of some Cretaceous and Tertiary chalks.

5.4.3.4 Significance for the Petroleum Industry

Chalks made up of coccoliths may be extremely porous. The porosity is in the form of primary interparticle micropores and may be as high as 40–50%, even in deeply buried chalks. Although their porosity may be high, permeability is generally low (less than a few mD) because of small pore-throat diameters (generally <1 μm). Hydrocarbon-filled interparticle pores in chalks are therefore productive only in combination with some other pore type, preferably fracture pores, which increases the permeability. Fractured chalks of Maastrichtian (late Cretaceous) to Danian (early Tertiary) age form major hydrocarbon reservoirs in the Central Graben of the North Sea (Ekofisk and associated fields). These are in fact the world's only major oilfield in such rocks, but the low permeability of this fine-grained lithology creates some production problems.

5.4.4 *Calcispheres*

Calcispheres are of uncertain biological affinity, but many consider them to be algae because there is a great similarity between non-ornamented fossil calcispheres and reproductive cysts of some living green algae (dasycladacean algae). They are generally 40–200 μm in diameter and are composed of a thin (commonly 3–30 μm), well-defined calcite wall, enclosing a single spherical chamber (Fig. 5.13). The wall may be singly layered or have several concentric layers distinguishable by the alternation of uniform micritic texture with a fabric showing radial elements. The wall has radial pores, but there is no aperture. The outer surface may bear spines. The chamber is normally filled with cement or sediment.

5.4.4.1 Ecology

Many fossil calcispheres seem to owe their origin to dasycladacean algae, and as such, they provide a useful palaeo-environmental indicator. Devonian and Permian calcispheres are most common in shallow subtidal environments, especially in restricted or back-reef environments. In the Cretaceous, calcispheres are especially important in pelagic deposits such as Chalk sediments in the North Sea.

5.4.4.2 Geological Range

Calcispheres are widely known from Upper Palaeozoic limestones, especially Devonian and Carboniferous, but also occur in older and younger strata.

Calcispheres have no particular significance for petroleum geology. However, they may be an important component improving the overall potential of a source rock.

5.4.5 *Distribution of Algae in Modern and Older Carbonate Sediments*

If one places a profile extending from a basin centre to a coast with reef development (Fig. 5.14), we see the following distribution of algae:

A. The sedimentation basinward consists largely of planktonic algae (coccolithophores), planktonic foraminifera and some other calcareous organisms.
B. In the reef facies we find mainly red algae which build strong, solid structures of carbonate, which in conjunction with the corals can resist waves which

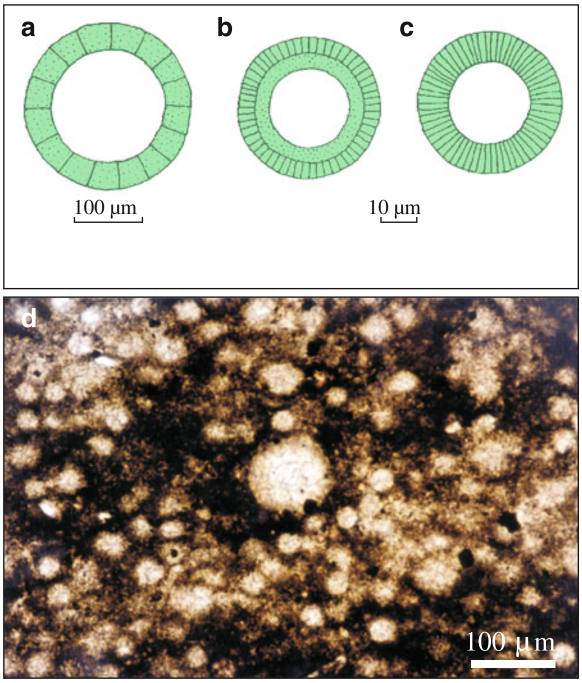


Fig. 5.13 Sections of calcispheres. In most cases, the calcitic wall consists of only one layer (**a, c**), but multilayered walls are also known (**b**). (**d**) Micrograph of the abundant calcispheres, partially replaced by euhedral pyrite as viewed in transmitted light, Ravnefjeld Formation (Upper Permian), East Greenland. See Nielsen and Hanken (2002). **a, b** and **c** are modified from Scoffin (1987)

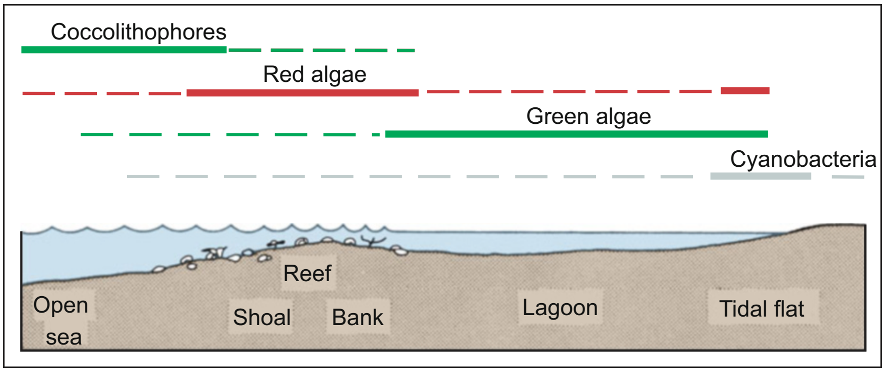


Fig. 5.14 Generalised distribution of recent skeletal and non-skeletal algae across a sediment basin in a low-latitude region (modified from Wray 1977)

break against the reef. In the lagoons landward of the reef we find green algae. These have bush-shaped skeletons and can only grow where the wave energy is moderate. They are major producers of small aragonite crystals which form lime mud. The green algae therefore ensure that lime mud is deposited in the lagoon.

C. In protected parts of lagoons and in the tidal zone, the sea bed is often covered with cyanobacteria which lie like a gelatinous carpet over the sediments. These algae consist of a network of threads which hold the sediment in place and protect it against moderate currents and wave erosion. However, they may be eaten by grazing animals, e.g. snails. In high-energy nearshore environments we find red algae.

The age range and taxonomic diversity of the major calcareous algal groups are shown in Fig. 5.15.

5.5 Invertebrate Skeletal Fossils

5.5.1 *Foraminifera*

Foraminifera (or forams for short) are a very important group of single-celled animals that secrete chambered, calcareous or sometimes agglutinated tests. Agglutinated tests are made up of foreign particles like mineral grains and/or shell fragments such as coccoliths, small foraminifera and sponge spicules (Fig. 5.16a–c). These particles are attached by calcitic or ferruginous cement to a layer of tectin (an organic compound composed of protein and polysaccharides).

Most foraminifera have an outer carbonate shell with one or more openings (apertures). A few species have only one chamber, but most foraminifera add new chambers as they grow. The individual chambers are arranged in a specific pattern (Fig. 5.16d–e), either in a single row (uniserial) or in two or three alternating rows (biserial and triserial). The shell may also be spirally coiled, either flat (planospiral) or as in a cone (helicoidal). The partitions (septa) between the individual chambers are the former front wall, and the former aperture is then often retained as an opening (foramen) between the chambers (Fig. 5.17).

5.5.1.1 Ecology

Virtually all foraminifera are marine, but a few live in brackish or fresh water. Although they occur at all depths down to the abyssal zone and at all latitudes, they have their greatest abundance and diversity in shallow, tropical, open marine waters. Some foraminifera live in symbiosis with algae living in their protoplasm, and these species are of course limited to the photic zone. Most foraminifera are benthic (living on the sea bed; both vagrant and sessile forms are known), but some are planktonic (freely drifting).

Many species require very specific ecological conditions. Some have left- or right-curved tests, depending on the temperature. Benthic forms are sensitive to current conditions, temperature, salinity, supply of nutrients etc. Foraminifera thus are useful as indicators of palaeoecological conditions. The amount

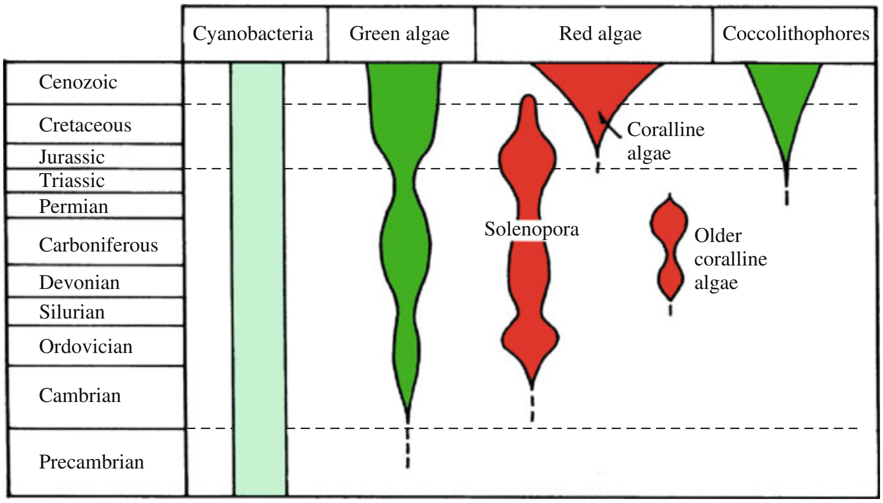


Fig. 5.15 Distribution of the important algal groups through geological time. Cyanobacteria have existed since early Precambrian times, and the oldest stromatolites known are up to about 3.5 billion (3.5×10^9) years old. Both green and red calcareous algae first appeared in the Cambrian. The evolution of calcareous green algae led to the production of large amounts of lime mud without chemical precipitation. The Solenoporaceae family (red algae), which was widely distributed in the Palaeozoic, died out during the Cretaceous. Coralline algae appeared in the Jurassic, and still exist. The evolution of the planktonic algae, mainly coccolithophores from the Triassic to present, has been a vital factor in global carbonate sedimentation (modified from Ginsburg et al. 1971)

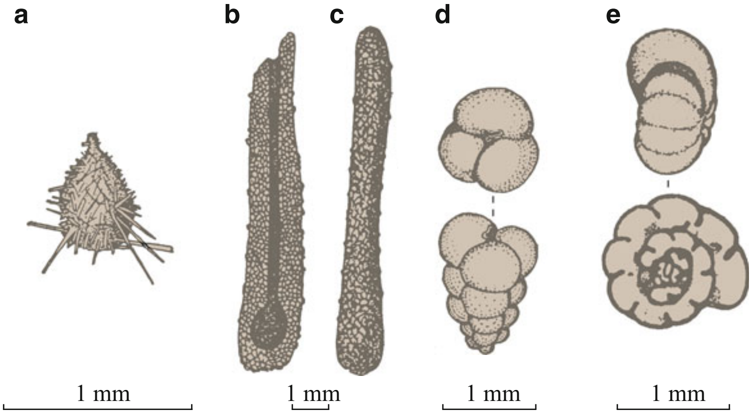


Fig. 5.16 Examples of variations in shape, size, arrangement of chambers and mineral composition in foraminifera. (**a–c**) Agglutinated forms. (**d–e**) Foraminifera with carbonate shells. (**a**) *Reophax* sp., agglutinated with sponge spicules. (**b**) (longitudinal section) and (**c**) (external view) *Hyperamina* sp., agglutinated with fine-grained detrital material. (**d**) *Verneuiliana* sp., triserial shell. (**e**) *Lenticulina* sp., planospiral shell. Lowermost is a median horizontal section showing the individual chambers (modified from Shrock and Twenhofel 1953)

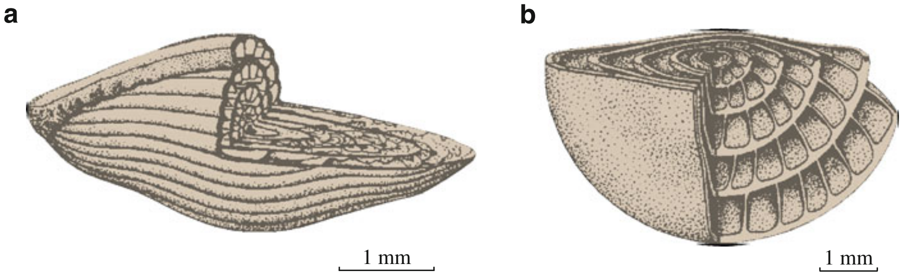


Fig. 5.17 Partially sectioned fusulinid (**a**) and nummulitid (**b**), showing the internal arrangement of chambers. The fusulinids are important index fossils for the Upper Carboniferous/Lower Permian while nummulitids have been widely used for correlation of Miocene marine deposits (modified from Rasmussen 1969)

of planktonic foraminifera relative to benthic ones declines in shallower water, and so can be used in reconstructions of palaeobathymetry.

However, only a small percentage of the foraminiferal tests are preserved in the geological record because they are generally fragile and easily broken by the action of scavangers and burrowing organisms. The calcareous tests also dissolve as they sink through the deeper and colder waters and will not be preserved if they are deposited below the carbonate compensation depth (CCD).

5.5.1.2 Mineralogy

Benthic foraminifera may have tests of precipitated calcium carbonate, usually calcite, or of small sand grains cemented together (agglutinated shell). Some foraminifera have aragonite tests. The calcite tests vary from high-Mg to low-Mg calcite, so that their solubility in seawater varies greatly. Benthic foraminifera with high-Mg calcite are found especially in warm-water environments, where they are less soluble.

5.5.1.3 Geological Range

Foraminifera range from the Cambrian to Recent. Most of the Lower and Middle Palaeozoic forms had an agglutinated test whereas calcareous forms were most common in late Palaeozoic and later times. Planktonic foraminifera did not appear until the Mesozoic but are important constituents of Cretaceous and younger deep-sea deposits. The large-sized, lens-shaped nummulitid foraminifera (up to about 15 cm) are widely distributed in Early Tertiary carbonate ramp and platform deposits. They are particularly useful as an index fossil in Cenozoic marine deposits of the Mediterranean Sea region. Foraminifera provide the basis for much of the stratigraphic subdivision of the Upper Palaeozoic, Mesozoic and Cenozoic.

5.5.1.4 Significance for the Petroleum Industry

Foraminifera commonly have a low reservoir potential due to their small particle size and stable primary mineralogy or neomorphic replacement. Some primary intragranular porosity may be of local significance, but generally connectivity is poor, giving low permeability.

Important hydrocarbon reservoirs along the North African coastline (Tunisia and Libya) and those in the South China Seas are largely composed of nummulitid foraminifera. The high amount of intra-skeletal porosity and the low density of *Nummulites* tests and clasts make them easily transportable by bottom and wave currents. Apparently their hydrodynamic behaviour controlled their distribution and the predominance of them in reservoir facies mainly found as banks or bars of grainstones and packstones.

5.5.2 *Sponges*

Sponges may vary considerably in size, commonly from a few centimetres to more than a metre in diameter. Their external morphology is also highly variable, but plate-shaped, globular, vase- or bowl-shaped forms are common. In its simplest form, the body is sac-shaped with a large internal cavity which opens upwards, the closed end being attached to the substrate. The wall is perforated by numerous small pores leading to the central cavity.

The skeleton is internal and may be spongin (an iodine-bearing protein which is rarely preserved in the geological record), siliceous or calcareous. Some sponges may incorporate foreign particles like sand grains in their skeleton. However, the skeleton typically consists of soft tissue supported by a complex network of spicules (Fig. 5.18). The soft tissue decays

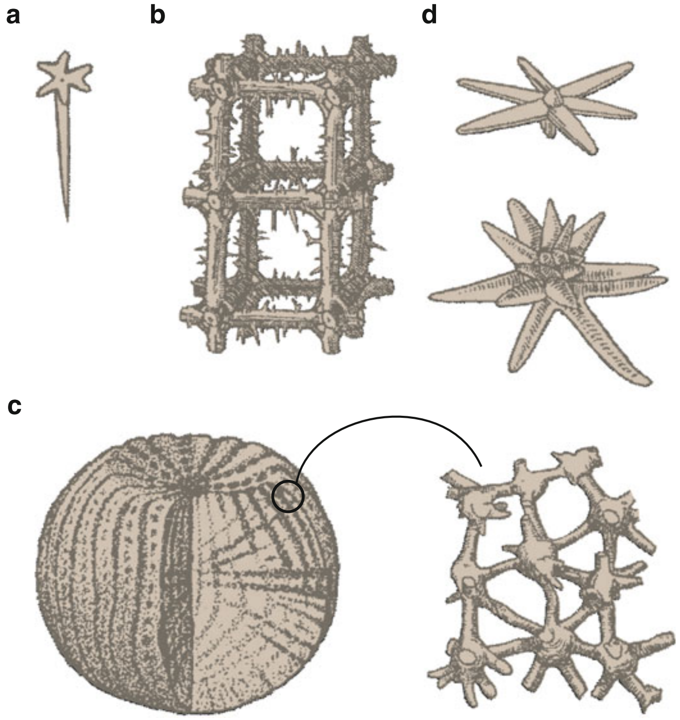


Fig. 5.18 Examples of different forms of sponge spicules. (**a**) Monaxon spicule. (**b**) Part of a sponge with triaxon spicules. (**c**) Part of a sponge skeleton built up of tetraxon spicules. (**d**) Various kinds of tetraxon spicules (modified from Rasmussen 1969)

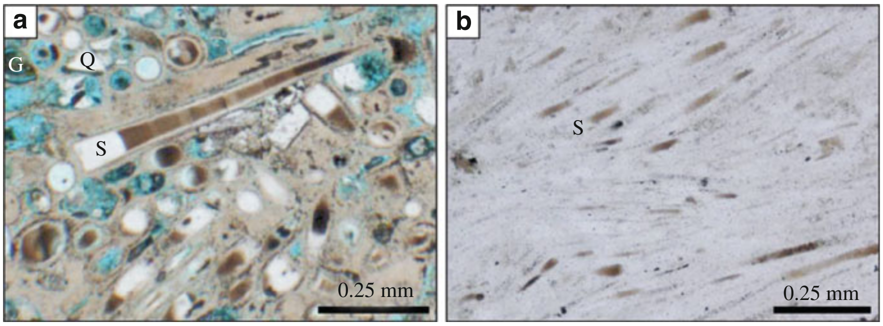


Fig. 5.19 (**a**) Photomicrograph of porous spiculite consisting of spicules from hyalospongiea (siliceous sponges). Note spicule in longitudinal cross-section (S), quartz (Q) and glauconite grains (G). Pores have been impregnated with blue epoxy. (**b**) Well cemented spiculite with very low porosity. Kapp Starostin Formation (Upper Permian), Svalbard. Thin sections as seen in plane polarised light. (Photographs courtesy of Sten-Andreas Grundvåg)

on death and spicule-bearing forms are therefore seldom preserved intact. The spicules may occur in two different sizes within a single individual. The large spicules (megascleres) vary from 0.1 to 1 mm and constitute the skeleton proper. The small spicules (microscleres) vary from 0.01 to 0.1 mm and are found isolated in the sponges, especially around the pores. The megascleres may occur as isolated spicules, be in close contact with each other, or be firmly intergrown to form a skeleton.

5.5.2.1 Ecology

Nearly all sponges are marine although a few freshwater forms are known. Sponges live mostly in relatively clear water, from the littoral zone down to abyssal depths. Siliceous sponges are generally found in deep water, whereas calcareous forms are more common in shallow-water environments. Most sponges lived attached to the bottom.

Many sponges are important boring organisms which help to break down calcareous rocks and carbonate skeletons produced by larger organisms into finer-grained material. The holes are 0.2–1 mm in diameter, forming thin holes up to 0.5 cm long.

5.5.2.2 Mineralogy

The main division of the sponges is based on the chemical composition of the spicules and the symmetry of the skeletal elements. Calcispongiea (calcareous sponges) have spicules of calcite or aragonite. These spicules are characterised by having a monocrystalline microstructure where each individual spicule extinguishes as a single entity in polarised light. Hyalospongiea (siliceous sponges) have spicules of amorphous silica (opal A, $SiO_2{\cdot}nH_2O$), Fig. 5.19. However, opaline silica is relatively unstable and siliceous sponges are commonly replaced by calcite. Demospongiea have spicules which are made exclusively of either spongin or amorphous silica, or of both silica and spongin.

Sponge spicules are locally very abundant, especially in cherts and silicified limestones. Siliceous sponge spicules have often been invoked as the source of silica in such deposits.

5.5.2.3 Geological Range

Sponges range from the Cambrian (Precambrian?) to Recent. They are minor sediment contributors in modern settings but have been prolific in the past. Siliceous forms were common in the Lower Palaeozoic; calcareous forms first appeared in the late Devonian. Sponges are major constituents of some Upper Carboniferous, Permian, Triassic and Jurassic build-ups.

Sponges have extremely high primary porosity due to their network of internal canals. However, this porosity is rarely preserved during burial. Occasionally, high primary porosity is preserved in hollow spicules, but permeability is generally extremely low and most of the porosity is ineffective.

Secondary porosity may form by dissolution of siliceous and aragonitic spicules, but rarely constitutes a significant part of a reservoir.

5.5.3 Stromatoporoids

The systematic position of stromatoporoids has been much debated, but they are now regarded as belonging to the demosponges. They form colonies of variable

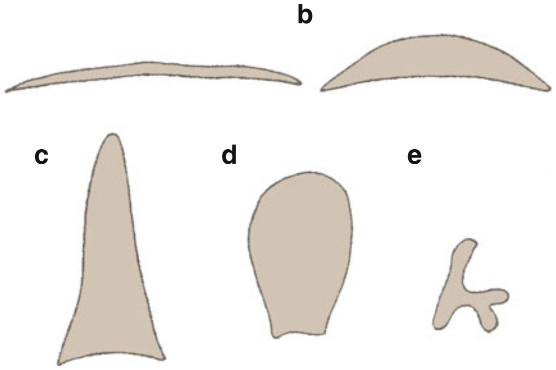


Fig. 5.20 Examples of growth forms in stromatoporoids. (**a**) Laminar. (**b**) Low dome-shaped. (**c**) High dome-shaped. (**d**) Hemispherical. (**e**) Branched (modified from Kershaw and Riding 1978)

size and shape. They are commonly from a few centimetres to about a metre in diameter and their shape may be tabular, hemispherical, cylindrical or branched (Fig. 5.20). The skeleton tends to split into concentric layers each a few centimetres thick, and therefore stromatoporoids often occur as larger or smaller fragments if they have been exposed to mechanical abrasion prior to their final deposition.

5.5.3.1 Ecology

Stromatoporoids are sessile, open-marine, colonial organisms. Since the growth form is to a certain degree dependent on the environment, some forms can be used in palaeoecological analysis relating the growth rate vs. sedimentation rate. Stromatoporoids were important constituents of Ordovician to Devonian reefs along with tabulate corals, colonial rugose corals and calcareous algae. These species mostly lived in agitated, shallow, warm seas, while Jurassic and Cretaceous forms were more adapted to life in muddy environments.

5.5.3.2 Mineralogy

The stromatoporoids had a very porous skeleton (coenosta) forming a laminar structure transected by fine vertical pillars. However, the primary structures readily underwent diagenetic modifications and therefore were commonly lost during diagenesis, leaving only a reticulate pattern of anastomosing elements. This often renders primary microstructures difficult to differentiate from secondary modifications. The neomorphic fabric indicates that the original composition of the stromatoporoid coenostae was aragonitic.

5.5.3.3 Geological Range

Stromatoporoids range from the Cambrian to Oligocene, but were most important during the Silurian and Devonian.

5.5.3.4 Significance for Reservoir Quality

Stromatoporoid reefs and associated reef detritus may form important hydrocarbon reservoirs in Silurian and Devonian rocks, e.g. Middle Silurian pinnacle reefs in the Michigan Basin of southeastern Michigan, USA and Middle to Upper Devonian reefs in Alberta, Canada. Although stromatoporoids may form high primary framework porosity, this porosity is commonly obliterated by synsedimentary infilling and cementation of the pores. Secondary porosity is generally more important and may be related to dolomitisation or freshwater dissolution. Stromatoporoid reefs were topographically higher than adjacent sediments and were therefore more prone to be subaerially exposed and dissolved.

5.5.4 Corals

Most corals are colonial, although solitary forms are also common. Colonial corals may be from a few centimetres to several metres in diameter, but are commonly less than 0.5 m. The external form of the colonies may be extremely variable, but can generally be described as crustose, hemispherical, irregular or shrub-like branched (Fig. 5.21). The colonies grow in size by repeated budding from the side or top of the individual corallites. The newly formed corallites may abut against one another like the cells in a beehive,

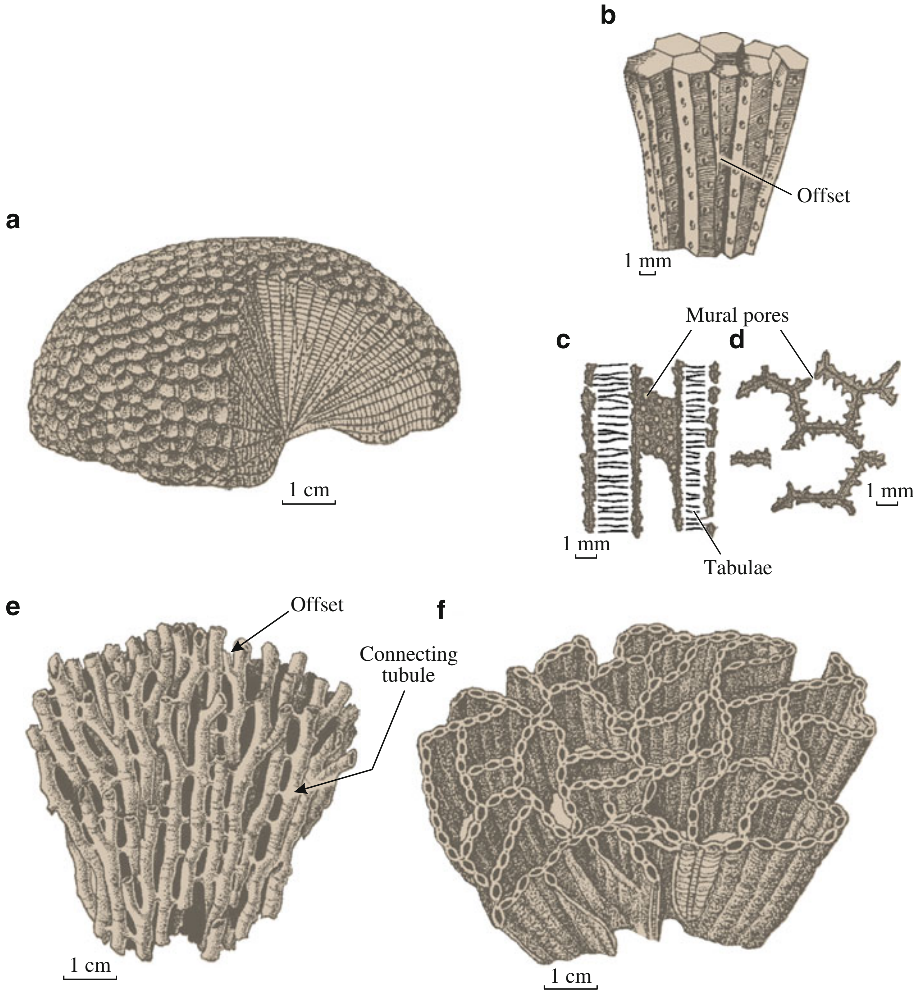


Fig. 5.21 Examples of different growth forms in colonial tabulate corals. (**a**) *Favosites* sp. Massive growth form with polygonal (generally hexagonal) corallites. Part of the *right side* has been removed to expose the corallites in longitudinal section. (**b**) Enlarged section of corallites viewed in longitudinal section. Note the vegetative reproduction in that one of the corallites is dividing into two, giving rise to an offset. (**c**) Enlarged longitudinal section through three corallites where tabulae are clearly visible. Mural pores are seen where the plane of the section passes slightly obliquely through the corallite wall. (**d**) Enlarged transverse section showing mural pores and septal spines. (**e**) *Syringopora* sp. Open growth form with round corallites linked by short, horizontal, connecting tubules. (**f**) *Halysites* sp. Cylindrical corallites which form palisade-like, dendritic rows in an irregular, reticulate pattern with large open spaces (modified from Moore 1956, Rasmussen 1969)

thus forming compact colonies with polygonal, generally hexagonal corallites (Fig. 5.21). However, some species form more open colonies so that the individual corallites are free-standing and rounded in cross-section.

Solitary corals may be curved or erect, and their fundamental shape appears to be a reversed cone. Depending on the apical angle of the cone and other characteristics, such as the growth form of the mature region and the occurrence of sharp angulations or flattened areas, several main types of growth forms can be recognised (Fig. 5.22).

Individual corallites are usually divided by radially arranged vertical elements (septa), horizontal partitions (tabulae) and small partitions in the lower periphery of the corallite (dissepiments). The presence or absence of these structures is a basis for classifying corals into four major groups: rugosa (horn corals), tabulata, scleractinia (hexacorals) and alcyonaria (octacorals).

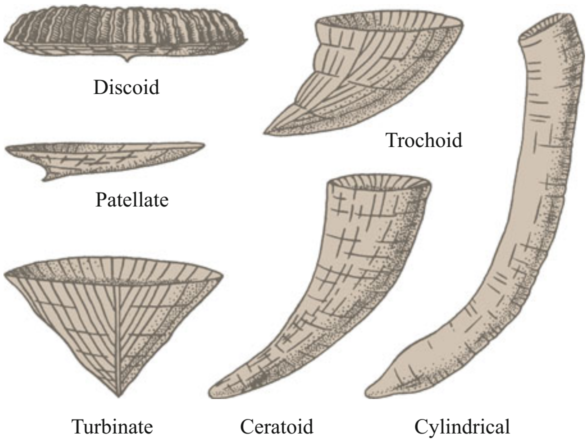


Fig. 5.22 Examples of different growth forms in solitary rugose corals (modified from Moore 1965)

Rugose corals: Rugose corals consist of both solitary and colonial growth forms. All rugose corals have both tabulae and septa. The septa are arranged in a radial pattern and generally have a marked bilateral symmetry. Both the form, size and number of septa vary up through the corallite (Fig. 5.23). During growth, the deepest part of the horn (calice), may be cut off by transverse partitions (tabulae) or contracted by small, curved partitions (dissepiments).

Many rugose corals are colonial. There are two main types: fasciculate where the corallites are cylindrical and isolated from each other, and massive where the corallites are closely packed and polygonal in cross-section.

Tabulate corals: All tabulate corals are colonial and individual corallites may be connected by small pores through a common wall, porous tissue or tube-like canals (Fig. 5.21c, d). Most tabulate corals have horizontal tabulae. Septa, as seen in rugose and scleractinian corals, are absent, but some species have small septal spines.

Scleractinia (hexacorals): Scleractinian corals consist of both solitary and colonial growth forms. They have an aragonitic skeleton in which septa form a sixfold radial symmetry, and tabulae may form horizontal partitions.

Alcyonaria (octacorals): A fourth group of corals is the alcyonaria. All alcyonarian corals are colonial. Most have an endoskeleton consisting of spicules of sclerites. In its simplest form, the sclerite is a rod with more or less acute ends. More complex forms have irregularly sculptured rods with spines and protuberances. Sclerites may be locally relatively common in Recent sediments, but since they are often difficult to recognise in pre-Quaternary deposits, the fossil record of alcyonarians is sparse.

5.5.4.1 Ecology

Corals are bottom-dwelling, sessile, marine organisms which are most common in shallow, well-oxygenated, tropical to subtropical waters of normal marine salinity. However, some forms live in deep water below the photic zone and/or in cold waters. Their growth forms are useful environmental indicators.

Scleractinian corals have been major reef builders since the Triassic and tabulate corals were important constituents of Silurian and Permian build-ups. Some recent scleractinian corals (hermatypic corals) corals live in symbiosis with single-celled algae (dinoflagellates or zooxanthella). They do best in very shallow areas (1–20 m deep, but some species might be found down to 90 m) and in warm water (18–29°C, but they flourish best between 25 and 29°C). Most Mesozoic and Cenozoic reef corals are hermatypic, and are therefore restricted to shallow warm water. Most of these corals are euryhaline and do not tolerate turbid water.

The other main type of scleractinian corals (ahermatypic corals) do not live in symbiosis with algae, and often occur below the photic zone. They are most abundant down to 500 m, but have been found at water depths as great as 6,000 m. They can live in water with temperatures as low as 0°C. Ahermatypic corals can form reef-like structures at depths of several hundred metres. *Lophelia* reefs or biostromes are found, for example, in deep water settings off the Norwegian coast.

Rugose and tabulate corals were important components of Ordovician and Silurian reef structures.

5.5.4.2 Mineralogy

All scleractinaian corals are aragonitic and pre-Holocene specimens are therefore normally preserved as moulds or have been more or less cemented with calcite spar. Rugose and tabulate corals have usually retained their primary microstructure, which indicates that the skeleton consisted of calcite. Recent octacorals have sclerites consisting of calcite or

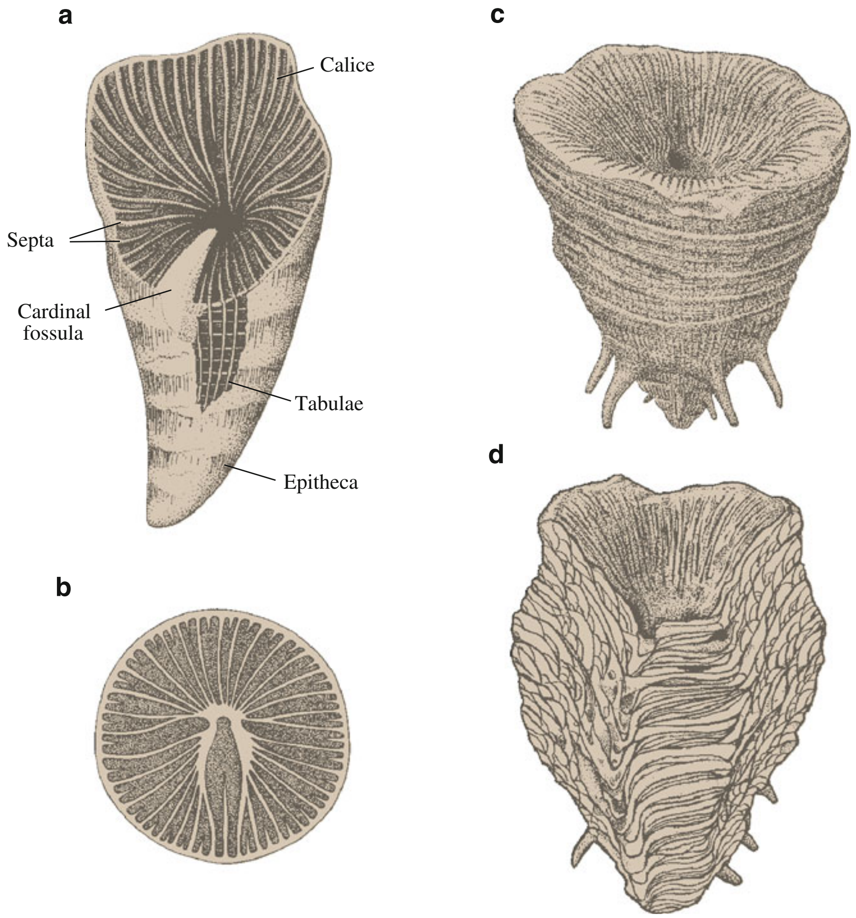


Fig. 5.23 (**a**) The rugose coral *Zaphrentites* with part of the epitheca removed, showing septa and tabulae. (**b**) Transverse section showing the tabulae. (**c**) *Ketophyllum*. Solitary rugose coral with tentacle-like appendages producing tabular holdfasts. (**d**) Longitudinal section through *Ketophyllum* showing tabulae in the middle part and dissepiments along the periphery (modified from Clarkson 1979)

aragonite, and it is believed that pre-Quaternary species also had the same mineralogical variations.

5.5.4.3 Geological Range

Rugose corals range from the Middle Ordovician to the Upper Permian. They were not common until the Silurian, after which their numbers gradually increased to a peak in the Lower Carboniferous. Their numbers and diversity then declined until they finally became extinct by the end of the Permian.

Tabulate corals occur in rocks of Cambrian (Middle Ordovician?) to Permian (and possibly Triassic to Eocene?) age. Scleractinian corals range from the Middle Triassic to Recent, and alcyonarian corals range from the Precambrian to Recent. Scleractinian corals are the dominant coral group today.

5.5.4.4 Significance for Reservoir Quality

Corals may form high primary framework porosity in reefs. Scleractinian corals have an unstable primary mineralogy (aragonite) so may develop high secondary mouldic porosity during dissolution. Corals, in particular scleractinian corals, therefore have relatively high reservoir potential.

5.5.5 *Bryozoa*

Bryozoans form colonies which are usually 0.5–2 cm in diameter, but colonies up to about 60 cm are known. They live permanently fixed to a substrate, which may be a stone, shell (living or dead), algae or other objects. The colonies have a wide range of external

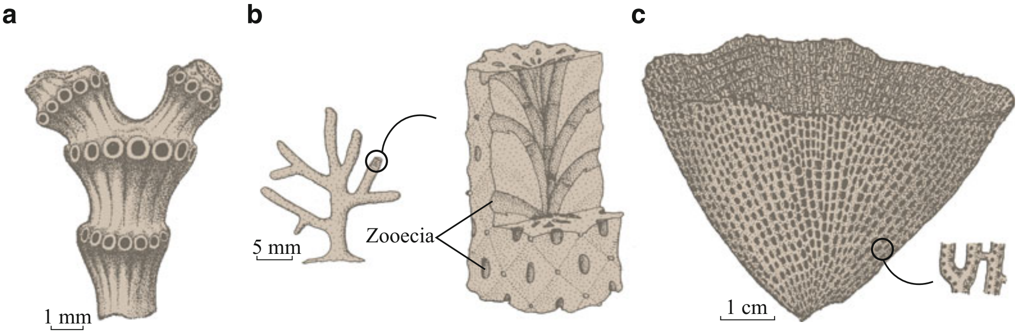


Fig. 5.24 Examples of different growth forms in bryozoa. (**a**) Cyclostomata. *Spiropora* sp. with a dendroid growth form with mouths on separate polypides. (**b**) Trepostomata. Colony and enlarged section showing part of the interior. (**c**) Cryptostomata. *Fenestrellina* sp. with a cornet-shaped colony. All the zooecia are placed on the radial, longitudinal branches, with their mouths inside the cornet. (modified from Rasmussen 1969)

morphologies, including encrusted (flat, hemispherical or irregular), branched (hollow or massive, flattened or circular), and lacy network (Fig. 5.24). Individual colonies may consist of tens to hundreds of circular or polygonal tubes or boxes (zooecia) which contain the individual organisms.

5.5.5.1 Ecology

Bryozoans are widespread, colonial, sessile, suspension feeding organisms which have a limited tolerance for strong wave action, soft sediment surfaces and desiccation. They prefer normal marine salinity but can tolerate short-term salinity variations. Most bryozoans are marine, occurring in shallow to abyssal depths (most common down to 200 m water depth), although a few Recent forms live in freshwater. In spite of their broad environmental distribution, bryozoans are generally most abundant in shallow to moderately deep, marine settings.

5.5.5.2 Mineralogy

There are five orders of bryozoans with a fossil record. In the Cyclostomata, Trepostomata and Cryptostomata, the skeleton is composed of calcite with less than 8 mol% $MgCO_3$. Bryozoans belonging to the Ctenostomata are poorly mineralised with more than 50% organic matter. The most primitive members of the Ctenostomata and Cheilostomata possess a skeleton of calcite only, whereas the more specialised cheilostomes have a secondary thickening of aragonite. However, in general, most Palaeozoic bryozoans had a calcitic skeleton, while many Recent forms are composed of aragonite or mixed aragonite and calcite.

5.5.5.3 Geological Range

Bryozoans range from the Ordovician to Recent. They are relatively rare in modern environments, but were especially important as framebuilders or sediment binders in many Ordovician to Permian build-ups.

5.5.5.4 Significance for Reservoir Quality

Bryozoans may have relatively high primary porosity in the form of interparticle, intragranular and framework porosity, although this porosity is not always preserved during burial. Intragranular pores are usually poorly interconnected giving low permeabilities, and are therefore generally of minor importance in petroleum reservoirs. Framework and interparticle pores are usually better interconnected and may be important in some bryozoan build-ups, e.g. in the Middle Carboniferous of Central Spitsbergen, occasionally forming good petroleum reservoirs.

Bryozoans generally have a low potential for secondary porosity formation due to a stable primary mineralogy. However, bryozoan-rich sediments may still be highly porous when they form build-ups. Bryozoan build-ups formed topographical highs during deposition and were therefore prone to be subaerially exposed during sea level fluctuations. In a humid climate, these build-ups may be pervasively dissolved with the formation of secondary, non-fabric selective porosity. The Lower Permian bryozoan-*Tubiphytes*

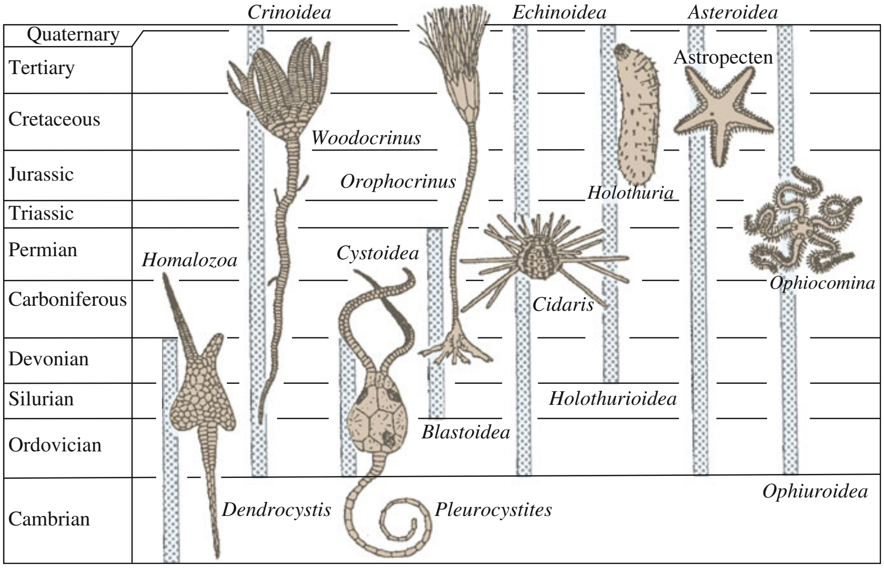


Fig. 5.25 Time range and classification of echinoderms with representative genera illustrated (modified from Ziegler 1983)

build-ups in the Midland Basin of West Texas, USA, are examples of this.

5.5.6 *Echinoderms*

The phylum Echinodermata comprises several classes, of which crinoidea and echinoidea are most common in the fossil record (Fig. 5.25). Modern representatives include the sea urchins (echinoids), starfish and brittle stars (stelleroids), and sea lilies and feather stars (crinoids). However, only crinoidea and echinoidea are dealt with in this book because these groups are most commonly encountered in the field. One of the characteristic features of the echinoderms is that, almost without exception, various degrees of endoskeleton calcification are found in the body wall. A single individual may be composed of a very large number of plates (often several hundred, or even thousands). On death, the individual plates, ossicles and spines disarticulate, unless the organism is quickly buried and thus avoids physical destruction of the skeleton. These plates are fairly sturdy and are often found whole in limey deposits.

Because of their microporous texture, echinoderm plates have a low density and may be readily transported into virtually all kinds of environments after death, though a high concentration of plates or the presence of articulated specimens normally indicates deposition within the area they inhabited.

5.5.6.1 Crinoids

The length of crinoids varies greatly, from a decimetre up to several metres (even 25 m). Their general structure is shown in Fig. 5.26. In the upper part is a cup (calyx), which consists of 10–15 plates in two or three rows. Five (or a multiple of five) arms (brachia) extend from the calyx and may have small branches (pinnulae). The mouth is centrally located in the top of the calyx, and the anus is often situated on an outgrowth from the calyx (anal conus). The calyx is situated on a flexible stem consisting of various types of small segments (columnal plates or stem plates). These columnals consist of variously shaped and sized plates, generally arranged in a single series (Fig. 5.27b). Each plate has a central round, or less commonly pentapetoloid, perforation, which together form an axial canal (Fig. 5.27a). The surface separating the stem segments often has a regular radial pattern of fine chambers and furrows. The stem may have thin lateral branches (cirri) which serve to fasten the crinoid to nearby objects (Fig. 5.27c). Lowermost, the stem may form a root-like, branched system that serves as a holdfast to objects, or forms an anchor in loose sediments. When the crinoid dies, the column is

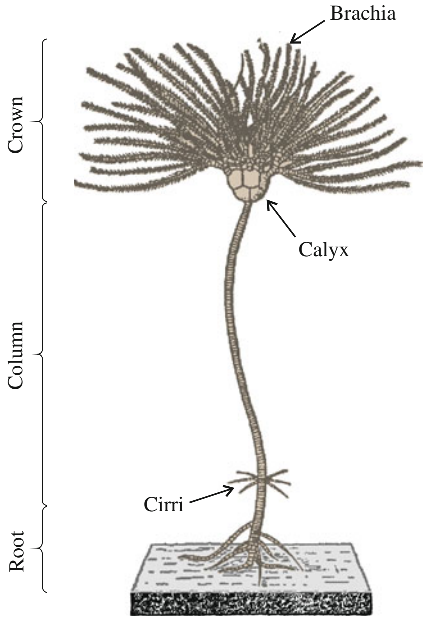


Fig. 5.26 Features of the general crinoid morphology showing a complete crinoid skeleton in living position (modified from Shrock and Twenhofel 1953)

quite likely to fall apart to a greater or lesser extent. Some fossil crinoids have the entire stem and root system preserved, but fragmental stems and single columnal plates are much more typical. The skeleton in Recent echinoderms is exceedingly porous (ca. 50%) with a reticulate pore structure (Fig. 5.27d). The pore diameter is about 25 μm.

5.5.6.2 Echinoids (Sea Urchins)

Echinoids have a hemispherical, disc- or heart-shaped endoskeleton consisting of interlocking plates. The outer surface is covered by spines situated on the interambulacral plates which alternate with the spine-free, mostly smaller, ambulacral plates (Fig. 5.28).

5.5.6.3 Ecology

All echinoderms are marine, preferring normal marine salinity and ranging from shallow water to abyssal depths. Crinoids inhabited shallow marine environments during the Palaeozoic, sometimes forming small bioherms or beds dominated by crinoid

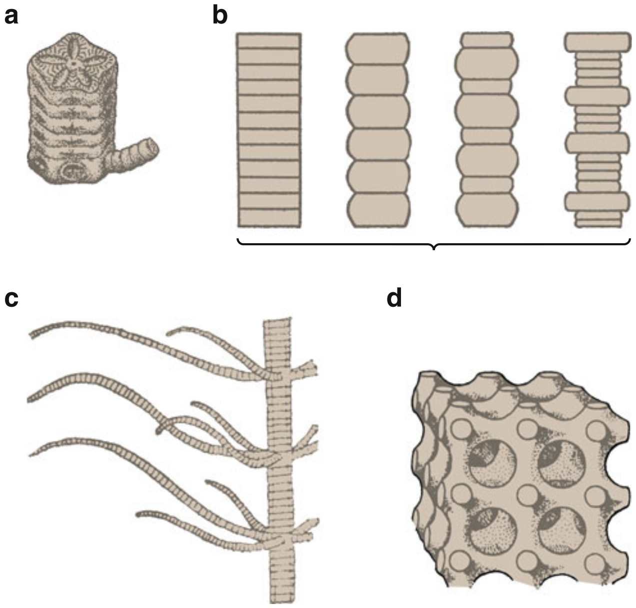


Fig. 5.27 (**a**) Part of crinoid columnal showing the general morphology with radial grooves for connective tissues on the top plate. Note the round lumen in the centre of the plates. (**b**) Schematic drawing of columnals viewed from the side showing examples of the great variation in stem morphology. (**c**) Part of the cirrate column of *Comastrochinus* sp. (**d**) Enlarged section of an echinoderm showing the network of large openings which transects the structure (modified from Shrock and Twenhofel 1953, Rasmussen 1969)

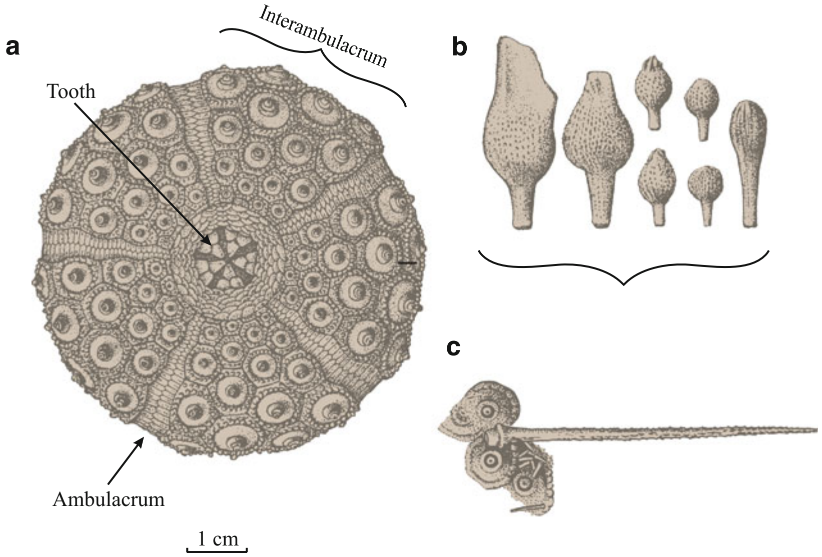


Fig. 5.28 (**a**) Adoral surface of the regular *Archaeocidaris* sp. with terminology. (**b**) Part of the surface showing ambulacra and interambulacra with tubercles. (**c**) Interambulacra with spines preserved. (**d**) Examples of different growth forms of spines from regular echinoids. (**e**) Part of *Archaeocidaris* sp. showing a few ambulacral plates with spines preserved. (modified from Rasmussen 1969, Clarkson 1979)

debris, but since then they have been most common in relatively deep waters (>100 m). In contrast, other echinoderms have commonly inhabited shallow marine environments throughout their geological time range.

Most echinoderms are benthonic and a few are pelagic. Echinoids are usually vagrant, whereas crinoids are generally sessile.

5.5.6.4 Mineralogy

The skeleton is composed of high-Mg calcite (5–15 mol% $MgCO_3$). Each plate, spine or sclerite has a single-crystal microstructure behaving optically as a single calcite crystal when viewed under the polarising microscope. However, the optically uniform crystals are really a mosaic of submicroscopic crystals whose *c*-axes are aligned almost perfectly parallel.

5.5.6.5 Geological Range

Echinoderms range from the Lower Cambrian to Recent, but were not common before the Ordovician. Their greatest abundance was during the Carboniferous. Crinoids appeared for the first time in Lower Ordovician sediments, but did not become abundant before the Silurian. They remained numerous in the Devonian and Carboniferous, sometimes forming small bioherms or beds dominated by crinoid debris. Their abundance declined in the Permian, but revived in the Mesozoic, although they never equalled their Palaeozoic peak. Crinoids remain prolific today.

Echinoids appeared for the first time in the Upper Ordovician, but are most common in Mesozoic and Cenozoic sediments. They remain a vital part of the invertebrate marine realm and are probably as abundant now as at any time in the past.

5.5.6.6 Significance for Reservoir Quality

Echinoderms are commonly overgrown by syntaxial calcite cement which completely obliterates both intragranular and intergranular porosity in echinoderm-rich rocks. This, along with the common neomorphic replacement of the echinoderm skeleton, gives these rocks low reservoir potential. Dolomitised crinoidal sediments may occasionally be oil producing, as for example in the Silurian crinoid-rich skeletal build-ups in the northeastern Anadarko Basin of Oklahoma, USA (Morgan 1985).

5.5.7 Post-mortem Destruction

As shown in the preceding review, carbonate grains differ widely in size with diameters ranging from a few micrometres in coccolithophores to more than a metre in some bivalves and sponges. Apart from grain type, grain size is also dependent on mechanical abrasion and bio-erosion prior to final burial. These physical and biological processes can be described as:

- **Mechanical destruction**. The rate of abrasion is highly dependent on the transport mechanism and energy available in the environment for particle movement. Shell fragments and other skeletal particles are rapidly crushed and ground down to become structurally unrecognisable in a high-energy environment such as a surf zone, while in low-energy environments the integrity of the original material may remain more or less intact. Mechanical destruction of skeletal material has characteristic rates of destruction, depending on shell thickness, microstructure and possible prior bio-erosion. A primary factor is the surface area to weight relationship (Fig. 5.29). These differences in abrasion rate may sometimes give rise to a fossil assemblage that deviates markedly from the original composition (Fig. 5.30). In general, in any given abrasive environment, skeletal material with a small surface area per unit weight is generally more durable than those with a large surface area per unit weight.
- **Biological destruction**. As soon as any organism dies, its skeletal material begins a process of deterioration due to the activity of a great variety of organisms. In particular many species of sponges, worms, bivalves, fungi and algae have the ability to sculpt or penetrate hard calcareous substrates e.g. skeletal material lying exposed on the sea bottom. Skeletal material has a low hardness (e.g. low-Mg calcite has a hardness of 3 and aragonite 3.5–4 on Moh's scale of hardness) and is easily dissolved in weak acids which render these substrates attractive for bioeroding organisms. The density and diversity of bioeroding organisms may therefore be high on carbonate material which has been exposed on the sea bottom for a year or more. Bioerosion is a self-destructive process, and the sculpture that is produced can only be preserved if covered by sediment, which suffocates the endolithic community. Bioerosion increases the vulnerability of skeletal material to mechanical destruction, with the result that a significant part of carbonate deposits may consist of a combination of bio-eroded and mechanically fragmented material (Fig. 5.31).

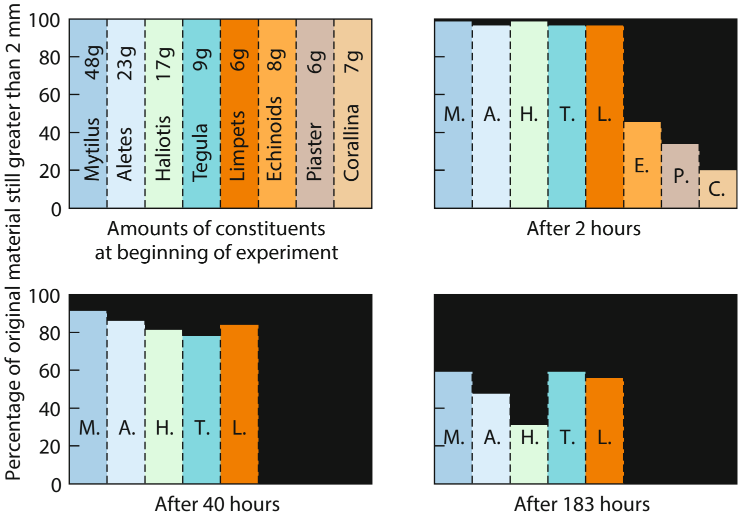


Fig. 5.29 Experimental abrasion of skeletal material. Starting sample (*upper left*) contained fresh specimens of the bivalve *Mytilus* sp., the gastropods *Aletes* sp., *Haliotis* sp. and *Tegula* sp., various species of limpets and enchinoids, the starfish *Pisaster* sp. and the calcareous algae *Corallina* sp. The series of diagrams shows selective destruction of the assemblage by tumbling (modified after Chave 1964)

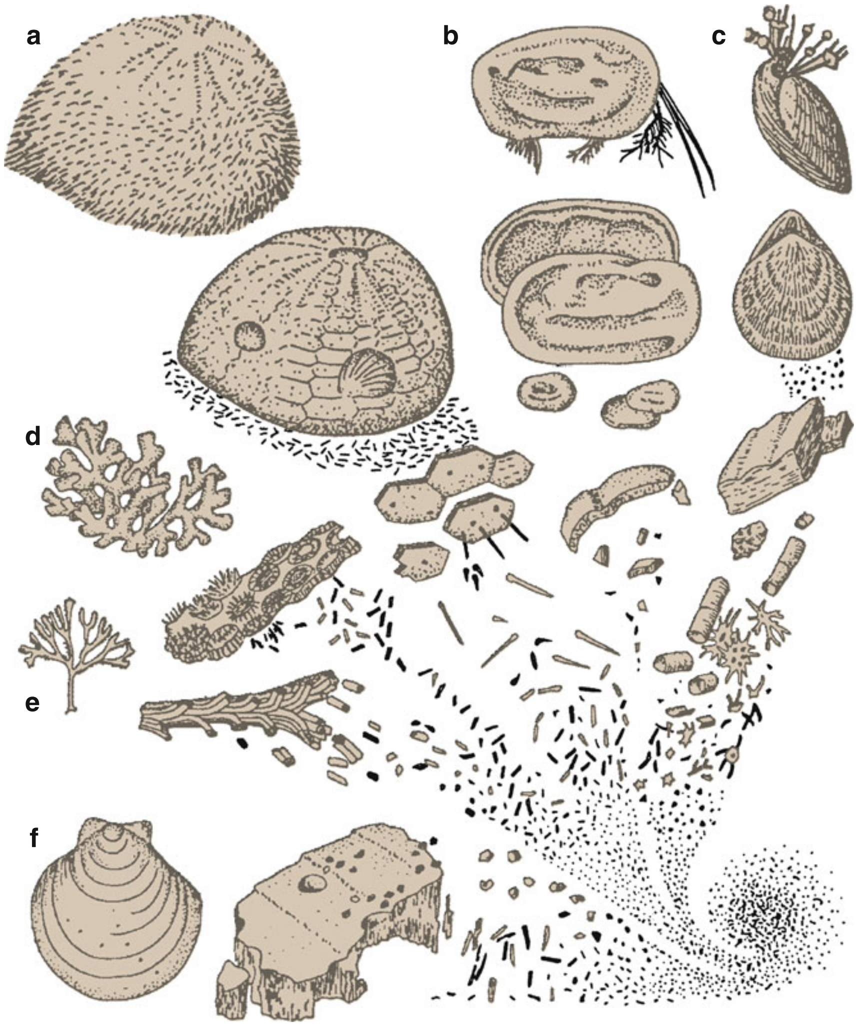


Fig. 5.30 Examples of breakdown of various skeletal components by mechanical abrasion. Echinoderms, coccoliths and many bryozoans are particularly fragile. (**a**) Echinoid; (**b**) ostracod; (**c**) brachiopod; (**d**) calcareous red algae; (**e**) bryozoan; (**f**) bivalve. Not to scale (modified from Bromley 1980)

5.5.8 Micritisation

This process, which was first described by Bathurst (1975), is due to the fact that exposed skeletal fragments within the photic zone may serve as suitable substrates for various green algae, cyanobacteria and fungi. These organisms destroy the surface by boring a fraction of a millimetre into the fragment by secreting acids which dissolve tubular boreholes in which the filaments reside. The diameter of each hole varies somewhat, but usually it is around 5–7 μm (maximally 15 μm).

When the bioeroding organisms die, each hole gets filled with tiny crystals (micrite) of aragonite or high-Mg calcite. Which crystal type is precipitated depends on the primary mineralogical composition of the shell. Usually the precipitate is aragonite if the shell is aragonite, and likewise for fragments of high-Mg calcite. However, some bacteria can secrete aragonite, and therefore aragonite-fills in empty boreholes may have been produced by bacteria which lived on the algae. In pre-Quaternary sediments low-Mg calcite has usually replaced both high-Mg calcite and aragonite micrites. Repeated borings followed by precipitation and

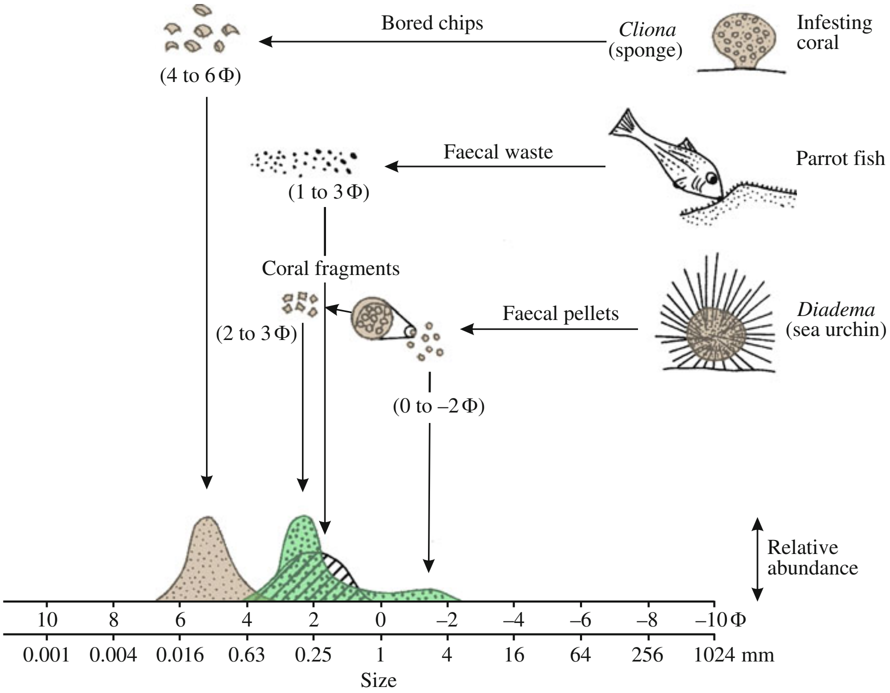


Fig. 5.31 Diagram of the dominant size fractions of grains produced by biological destruction of massive corals by endolitic sponges, parrot fish and sea urchins. The endolitic sponges infest calcareous substrates to create a sheltered site for habitation. Both the parrot fish and sea urchins are important grazers that break down the surface of calcareous substrates in search of epilithic and endolithic plants for food (modified from Scoffin 1987)

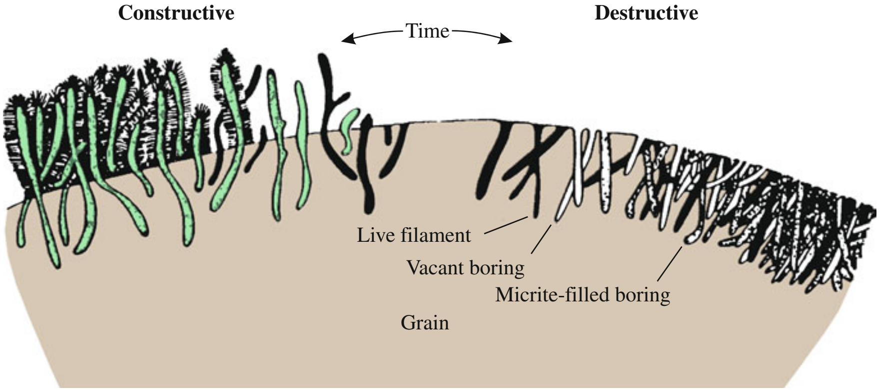


Fig. 5.32 Micritisation of a calcareous grain. The process is related to the activities of microboring algae, cyanobacteria and fungi. A micritic envelope is developed if the micritisation is confined to the outer surface. If the grain is completely micritised, a peloid or cryptocrystalline grain may be the end result. Not to scale (modified from Kobluk 1977)

infilling of the empty cavities cause the fragments to be replaced by a dark micritic coating (Fig. 5.32). The micritised coating is highly stable and is commonly preserved in both Quaternary and pre-Quaternary sediments. Where aragonite fossils have been micritised, the coating (now consisting of low-Mg calcite) often clearly indicates the original shape of the fossil (Fig. 5.33).

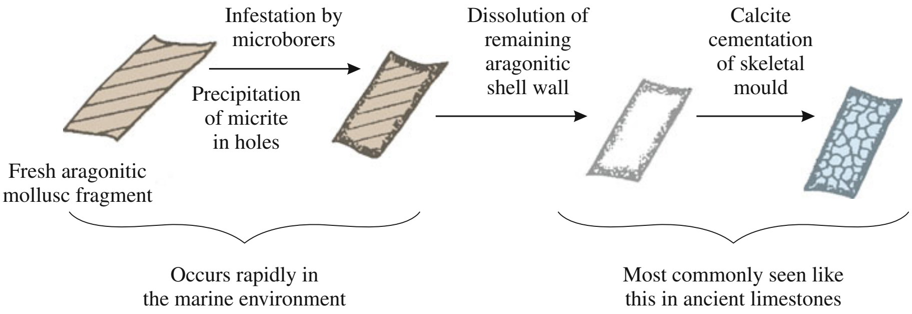


Fig. 5.33 Diagram showing the formation and preservation of a micritic envelope. Skeletal fragments of aragonite may be dissolved and replaced by calcite by one of two processes. *Left*: much of the original structure, such as organic inclusions, may be preserved (albeit not perfectly) through gradual solution of the skeletal material and immediate precipitation of calcite along a thin solution film. *Right*: complete solution of the skeletal fragment. During later diagenetic stage(s), the mould may be partly or completely cemented by calcite (modified from Bjørlykke 1989)

5.5.9 Microcrystalline Lime Mud (Micrite)

Lime mud deposited in areas with carbonate sedimentation has a grain size of about 1–4 μm. This precludes effective study under an ordinary microscope, only with an electron microscope can each individual grain really be seen.

Carbonate mud (micrite) was previously assumed to be chemically precipitated carbonate, as opposed to fossils or fossil fragments of clearly organic origin. However, a very large amount of modern lime mud, for example from the Bahamas, has been found to consist of aragonite needles from the breakdown of calcareous green algae, particularly *Halimeda*, *Rhipocephalus* and *Penicillus*. This was confirmed partly by studies of the shape of aragonite needles (by electron microscope) and partly through isotope studies of the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios in the aragonite mud. The isotope values for the aragonite mud correspond well with the values in needles formed by various types of algae.

In shallow marine areas near the equator, like the Bahamas, the seawater is often saturated with respect to aragonite. Nevertheless it has not been possible to prove conclusively that any purely chemical precipitation of aragonite takes place in these areas. Sudden whitings of the seawater that are often observed in these areas, has been interpreted as spontaneous crystallisation of aragonite, but the phenomenon can also be interpreted as a disturbance of the lime mud from the bottom, for example by shoals of fish which are present in large numbers where there is whiting of the seawater.

In areas where strong evaporation and high salinity approach evaporite conditions, such as in the Dead Sea and the Persian Gulf, this kind of chemical precipitation does occur, but only when the salinity is very high, about every fifth year. A sudden proliferation of diatoms could also consume so much CO_2 that the pH rises and causes aragonite to be precipitated.

Microcrystalline lime mud may also be formed by mechanical abrasion. Fossils which lie exposed to wave and current activity will be abraded mechanically, and a fine-grained lime mud formed. However, this process will not produce the well-crystallised aragonite needles of which modern lime muds are found largely to consist. We may therefore conclude that mechanical abrasion of fossils or carbonate fragments is not the main source of lime mud.

Through diagenetic processes, the microcrystalline mud will dissolve and be replaced by microsparite, but this is clearly distinguishable from other sparites, not least by its brownish colour due to incorporated organic matter (Fig. 5.34).

5.6 Non-skeletal Grains

Carbonate grains can be classified as skeletal or non-skeletal. Non-skeletal components are defined as grains which do not appear to have been precipitated as skeletal material. However, this neither proves that they could not once have been skeletal, nor that they have an inorganic origin, it only signifies that in their present state no skeletal origin can be ascertained.

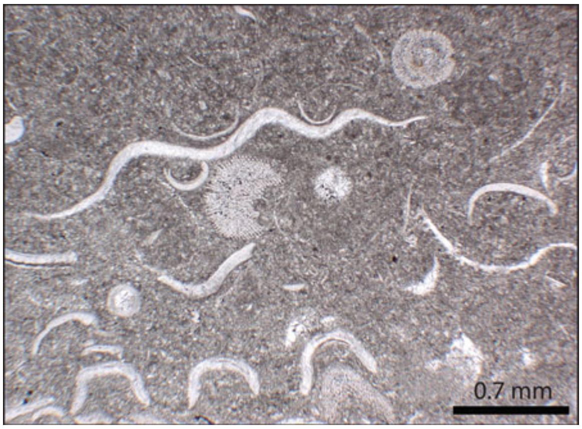


Fig. 5.34 The original microcrystalline mud (micrite) has been replaced by microsparite which consists of a mosaic of small brownish crystals. The skeletal remains are dominated by trilobite and ostracod fragments. Thin section seen in plane polarised light. Silurian, Gotland

5.6.1 Intraclasts

Intraclasts are erosional fragments of essentially penecontemporaneous carbonate sediment. They are of intrabasinal origin, i.e. were eroded from the sea bottom or adjacent tidal flats and deposited within the area of original deposition. Early cementing, e.g. in the beach zone, or freshwater cementation due to regressions, may result in cemented sediments which are later broken up. We may also find early cementation in a marine environment, forming seafloor hard grounds. If these are then eroded by tidal channels, for example, the resulting intraclasts may accumulate as characteristic intraformational conglomerates. Intraclasts can also consist of semi-consolidated pieces of stromatolites.

Intraclasts may be of any size or shape. They are quite common in shallow water limestone facies and are good indicators of early cementation and erosion.

5.6.2 Lithoclasts

Lithoclasts, which encompass both intraclasts and extraclasts (or extrabasinal clasts), are produced by the erosion of exposed older or synsedimentary lithified or partially lithified sediment. On carbonate platforms, lithoclasts are normally derived from erosion of the landward margin, where exposed, cemented limestones are broken up by physical, chemical and/or biological processes. Lithoclasts may be of any size or shape, but have generally become well rounded during transport. Because carbonates are vulnerable to weathering and are mechanically weak, the content of extrabasinal carbonate clasts declines with increasing transport distance, particularly in humid climates.

5.6.3 Faecal Pellets

Faecal pellets are organic excrements generally produced by mud-eating grazing animals such as crustaceans, worms and molluscs. They are generally round, oval or rod-like in shape and commonly consist of carbonate mud. Most faecal pellets are 0.1–0.6 mm in length and 0.1–0.4 mm in diameter, but can be up to 2 mm long. Animals which eat mud deposit vast quantities of carbonate mud pellets in carbonate environments, and clay and silt pellets where fine-grained siliciclastic material forms the seafloor. Faecal pellets have a characteristic dark brownish colour imparted by their organic content.

Faecal pellets are produced in all environments, often in well-sorted large quantities forming pelsparite/pelloidal grainstone (Fig. 5.35). Their preservation within a sediment generally requires intragranular lithification, a process occurring in shallow waters which are supersaturated with respect to calcium carbonate. The presence of a low-energy environment is also important to prevent physical destruction. This implies that faecal pellets are most

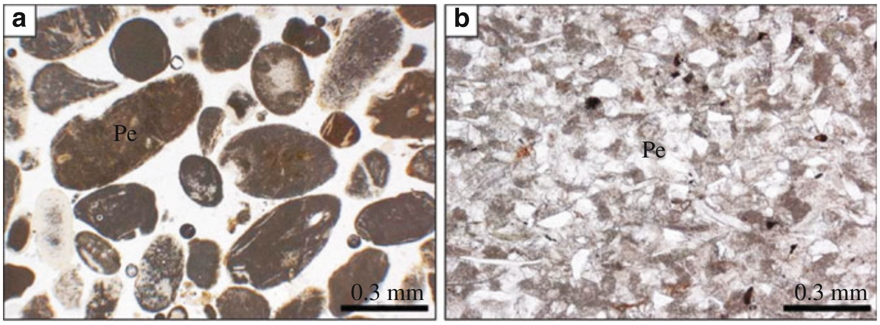


Fig. 5.35 (**a**) Rounded rod-shaped pellets (Pe). Upper Cretaceous, France. (**b**) Dark pellets (Pe) in a sandy matrix. Silurian, Oslo Region, Norway. Thin sections as seen in plane polarised light

commonly encountered in low-energy, muddy depositional environments in the platform interior.

5.6.4 Peloids

The term peloid is used for a polygenetic group of spherical, ellipsoidal or angular grains with diffuse margins but no internal structure. The grains consist of fine-grained carbonate irrespective of size or origin. Because of the diverse origin of the particles, the term peloid is purely descriptive and does not denote origin. Various origins are possible: faecal pellets, micritised grains, intraclasts, a type of abiogenic precipitate, and a microbially mediated precipitate. Most peloids, however, are formed by extensive micritisation of preexisting carbonate grains which is related to the activities of microboring algae and fungi within the photic zone. Thus, peloids generally indicate shallow, non-agitated waters.

5.6.5 Ooids

Ooids are round grains of carbonate formed through chemical or biological precipitation by the rolling action of waves and/or tidal currents in shallow water. Sediments consisting of ooids are called oolites. Ooids are by definition less than 2 mm, but most are 0.3–1.0 mm in diameter (Fig. 5.36a,b). They have a concentric structure with layers of carbonate around a

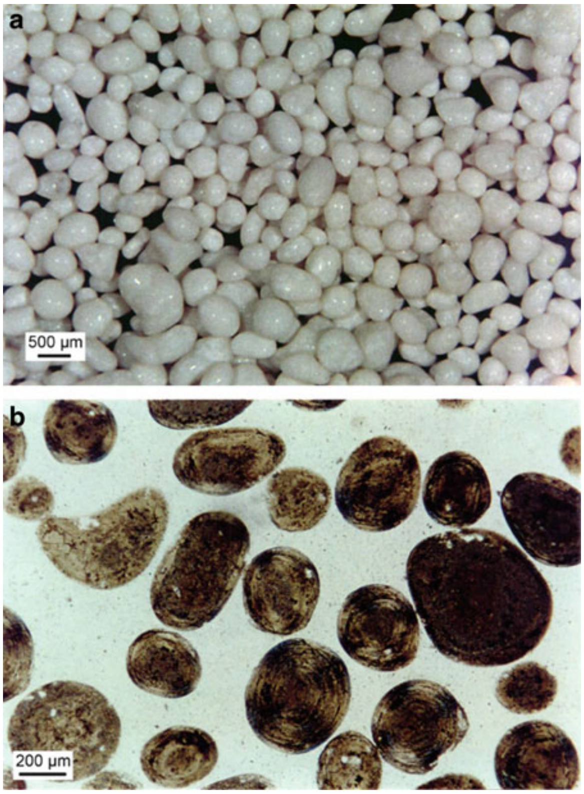


Fig. 5.36 (**a**) Recent ooids from Bahamas. They are well sorted with grain size mostly between 0.5 and 1 mm. (**b**) Ooids are composed of a nucleus overlain by successive concentric coatings of aragonite. Thin section, plane polarised light. Recent, Bahamas. (Photograph courtesy of Arve Lønøy)

core which may consist of small clastic grains or a carbonate fragment. Similar concentric structures larger than 2 mm are called pisolites, and these are usually precipitated by algae.

Modern ooids consist of aragonite with a concentric tangential structure composed of small aragonite crystals (<3 μm) with their *c*-axis parallel to the lamination.

We find ooids only in very warm marine environments and in some saline lakes. The water must be close to saturation with carbonate. Agitation from waves or tidal currents is necessary to roll the ooids around to so that precipitation is even and forms concentric layers. Some studies indicate a thin organic membrane of bacteria on ooids which helps to precipitate aragonite, and which also may trap small aragonite particles in the sediment or suspended in the bottom water. If direct chemical precipitation was involved we would expect the needles to orientate themselves radially on the surface of the ooid, whereas snowball-type growth through the accumulation of small aragonite needles would give the observed concentric layers.

Because ooids require warm water and frequent wave agitation, they are only formed in very shallow water, normally 2–7 m deep (Fig. 5.37). During storms, however, they may be carried out into greater depths and deposited there. Ooids are typical of the Bahamas, of many areas around the Indian Ocean and on islands in the Pacific Ocean. On the east side of the Atlantic Ocean – along the coast of Africa – the water is too cold to permit sufficient carbonate saturation. Ooids are therefore an important indicator of depositional environment and climate.

Fig. 5.37 Aerial photograph of ooid sand bar prograding over carbonate mud. The mud is covered with blue–green algae (cyanobacteria) which is cohesive and protects the sediments from erosion to certain extent

5.6.5.1 Mineralogy

Ooids from earlier geological periods with warm climates (greenhouse) have a radial structure and may have been composed of primary Mg-calcite. During cold periods in the Earth's history (icehouse conditions), as now in the Quaternary and during the Permo-Carboniferous glaciation, ooids are initially composed of aragonite (Fig. 5.38).

5.6.5.2 Significance for Reservoir Quality

Ooids may form extensive bank-margin or shoreline sand bodies which can be cemented together to form a sedimentary rock called an oolite. These deposits may have excellent reservoir qualities because of a combination of secondary mouldic porosity related to the dissolution of ooids and/or primary intergranular porosity (Fig. 5.39). Permeability may vary depending on the degree of cementation or dissolution, but is generally high.

Examples of petroleum production from secondary mouldic pores include the Upper Silurian oolite shoals of the northeastern Anadarko Basin, Oklahoma, USA, the Lower Permian oolite shoals of the Midland Basin, West Texas, USA, the Upper Jurassic oolites of the Smackover Formation of the Gulf of Mexico coastal plain, USA and the Lower Cretaceous oolite shoals of offshore Angola. Petroleum production from primary intergranular pores is exemplified by Lower Carboniferous oolite shoals in the St. Genevieve Formation, Illinois Basin, USA.

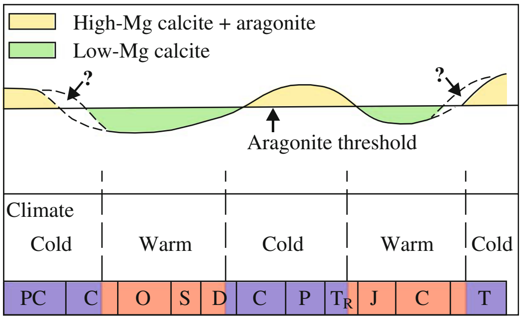


Fig. 5.38 A comparison between the mineralogy of ooids and climate. During warm climate conditions ooids consist of low-Mg calcite while during cold periods they consist of high-Mg calcite or aragonite (modified from Sandberg 1983)

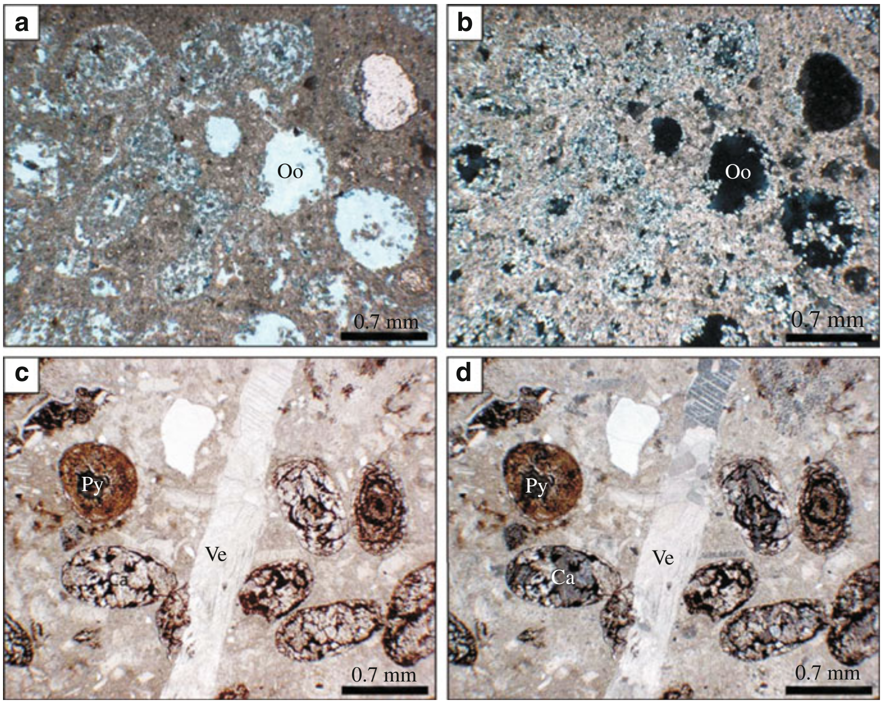


Fig. 5.39 (**a**) and (**b**) Oomoulds (Oo) formed by dissolution of ooids as viewed in transmitted light and plane polarised light respectively. The matrix consists of dolomite. Roker, England. (**c**) and (**d**) Calcite vein (Ve) cross-cutting partially cemented oomoulds infilled with calcite cement (Ca) and pyrobitumen (Py), viewed in transmitted light and plane polarised light respectively. Upper Ordovician, Oslo Region, Norway

5.7 Carbonate Environments

5.7.1 Introduction

Most carbonate deposits are due to the production of skeletal material rather than being precipitated chemically. The composition of the sediments is therefore largely a function of the type of organisms which produced them. Biological precipitation removes $CaCO_3$ from seawater at a sufficient rate that the seawater does not become supersaturated with respect to calcite, except locally. Shallow seawater may be supersaturated with respect to calcite and in the tropics also with respect to aragonite and high-Mg calcite. It is mostly in evaporite basins that chemical precipitation is dominant but even there it is often assisted by algae. However, a very large fraction of the carbonate precipitated by organisms is dissolved in the water column or soon after deposition at the sea bottom and will therefore not be incorporated in the geological record. The total biological production of carbonate is approximately equal to the total amount of carbonate which becomes dissolved in the oceans plus the supply of Ca^{2+} released by weathering on land and transported to the ocean by rivers.

Accumulations of carbonate deposits require:

- A supply of nutrients to feed the carbonate-precipitating organisms.
- Clear water with a low content of suspended clastic material.

The effect of suspended fine-grained clastic material is to dilute the carbonate content, but it may also retards the growth of filter feeding organisms like corals. These sessile organisms require a through-flow of water to obtain enough planktonic organisms for nutrition, and too much suspended clastic material tends to clog up their filtering system.

Carbonates accumulate along coastlines with little clastic supply from rivers. This is often the case when the adjacent land has a dry climate with little runoff. Carbonates also accumulate on submarine highs and carbonate platforms which are surrounded by deeper water that traps the clastic sediments. The Bahamas platform is a good example of such a setting. Reefs commonly grow at the edge of deep waters where they are exposed to light, high wave energies and a steady supply of nutrients through upwelling.

During periods of global transgressions (highstand) more carbonate is deposited on the continental shelves leaving less carbonate to be deposited in deep-water environments. In the stratigraphic record an abundance of carbonate rocks is seen from the Ordovician to Devonian periods and from the Cretaceous. This is not because more carbonate sediments were precipitated during these periods, but because more of what was precipitated was preserved on the cratons.

During transgressions there is little supply of clastic material that could dilute the carbonate precipitated. These carbonate deposits therefore generally contain little clastic material. However, during sea level lowstand more of the carbonate becomes mixed with clastic sediments to produce carbonate deposits with a fairly high terrigenous content.

5.7.2 *Major Controls on Carbonate Sedimentation*

Temperature and salinity are the main factors affecting shallow marine carbonate-secreting organisms. On this basis it is possible to distinguish between three principal skeletal grain associations; chlorozoan, foramol and chloralgal associations (Lees and Buller 1972) (Fig. 5.40). We may also distinguish between warm-water carbonate - photozoan, and colder water carbonates - heterozoan (James 1997).

5.7.2.1 Chlorozoan Association

The chlorozoan association is found in warm shallow seas at low latitudes as in the Bahamas and the Persian Gulf. Such warm-water carbonates are mostly derived from algae, or from benthic organisms living in symbiosis with algae. Warm-water carbonates are formed in areas with clear water and little clastic supply. The reef-building corals in warm areas (hermatypic corals) live in symbiosis with algae and can only grow in shallow water with abundant sunlight. These corals are very vulnerable to cold (and very warm) waters and tolerate only a quite narrow salinity range. Therefore the chlorozoan association does not exist where the minimum surface temperature falls below 15°C and the salinity ranges lies outside 32–40‰.

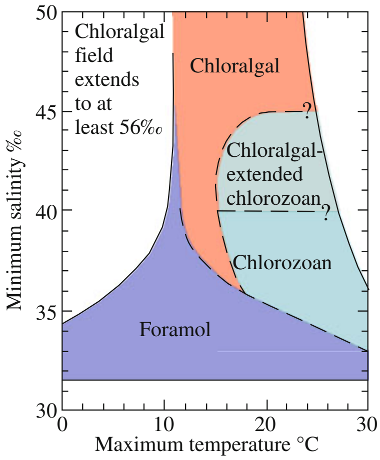


Fig. 5.40 Relationships between salinity-temperature annual ranges and occurrences of skeletal grain associations in modern shelf carbonate environments (modified from Lees 1975)

It is important to remember that the distribution of warm-water carbonate facies is not only governed by latitude, but also depends to a large extent on ocean circulation patterns. On the western side of the Atlantic Ocean, warm-water carbonate facies with reefs and oolites are found up to about 30°N from the Equator, while on the eastern side, off West Africa, the ocean is generally too cold, even close to the Equator. This pattern is due to the east-west equatorial winds producing upwelling on the eastern side of the ocean, and accumulation of warm surface water on the western side.

5.7.2.2 Foramol Association

Where the seawater temperature range is 0°C up to about 15°C, the sediments are dominated by benthic foraminifera and molluscs, together with a somewhat minor contribution from echinoderms, barnacles, bryozoans, calcareous red algae and ostracods. This association is referred to as foramol or heterozoan (James and Clarke 1977). The foramol association thus comprises temperate and cold water carbonates currently being deposited e.g. the North Sea and the Spitsbergen Bank northwest of Bear Island in the Barents Sea. The Spitsbergen Bank is 30–100 m deep and surrounded by deeper channels so receives little clastic matter (Bjørlykke et al. 1978). The area lies on a cold oceanic front where cold currents from the north and east mix with the warmer water of the Atlantic Ocean. This results in powerful currents down to 80–100 m and high productivity of molluscs, benthic foraminifera, bryozoans and barnacles. The seafloor sediments are characterised by a Holocene 80–90% pure carbonate sand deposited across the top of Pleistocene moraines (Bjørlykke et al. 1978). Similar carbonate deposits are encountered on other banks off North America, for example Grand Bank, and along the coasts of western Scotland and Norway.

The biological precipitation of carbonate is not dependent on the water being warm or saturated with calcium carbonate. On the contrary, we often find the highest productivity in cold areas because the water there is richer in nutrients, particularly in areas of upwelling. Cold seawater is undersaturated with respect to carbonate minerals so that the skeletal material begins to dissolve as soon the organisms die. Net accumulation of skeletal material on the sea bottom is possible because carbonate deposition merely requires that the biological production rate of carbonate skeletons exceeds the rate of dissolution. Skeletal material with a primary aragonite or high-Mg calcite composition will dissolve faster than that composed of low-Mg calcite, because of the lower pH due to increased CO_2 in the cold water.

In the interpretation of ancient limestones we should not always assume that we can use the well-known warm water carbonate models, but also consider the possibility that we are dealing with cold water carbonate sediments at higher latitude.

5.7.3 Modern Environments of Carbonate Sedimentation

5.7.3.1 Reefs

From a sedimentological point of view a reef may be defined as a laterally restricted body of carbonate rock whose composition and relationship with the surrounding sediments suggest that the bulk of its biota were bound together as a framework during deposition, maintaining and developing a positive topographic structure on the sea bottom. Modern reef structures are dominated by hermatypic corals and calcareous red algae (Fig. 5.41), but the biotic composition of the reef structures through the Phanerozoic has been fairly variable (Fig. 5.42). Generally, all these different reef types show similar facies patterns to modern coralgal reefs. Recent reef formation, and the shape of the reef complexes, is essentially a function of the ecological environments of the reef-building organisms:

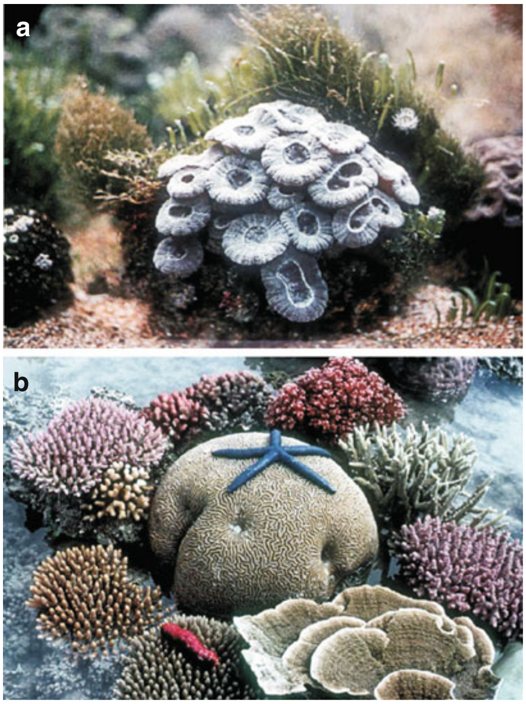


Fig. 5.41 Corals from the modern Great Barrier Reef. Mainly brain corals and stag corals

1. Reef-building corals require warm surface water and their distribution today is therefore limited to the lower latitudes. However, palaeogeographical reconstructions must take into account that surface water temperature is not a simple function of latitude. This is illustrated by the coasts of West Africa and along the western side of the American continent. Where there is upwelling of cold water the surface layers are in most cases too cold for reefs to form, even near the equator. Off the coast of East Africa and in the Caribbean, on the other hand, the water is warm because of prevailing onshore winds, and coral reefs are abundant.
2. The hermatypic corals which build reefs live in symbiosis with algae and require sunlight. The reefs are therefore sensitive to changes in sea level since reef organisms tolerate neither exposure nor “drowning” below the photic zone. The Holocene transgression about 10,000 years ago raised sea level about 100 m in a few thousand years, but most reefs managed to grow quickly enough to keep pace with the rising sea level.

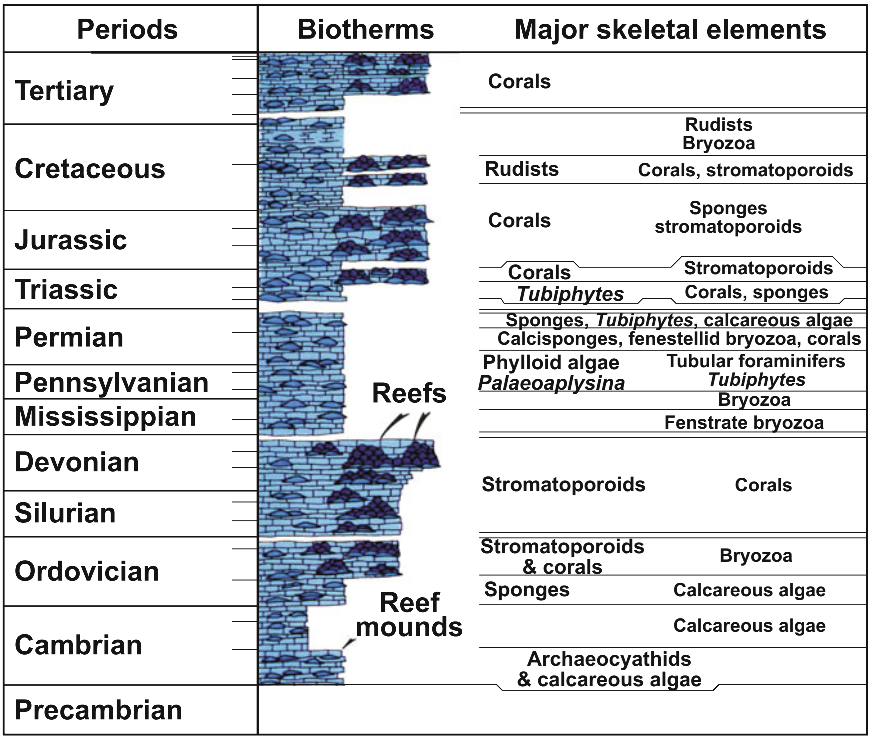


Fig. 5.42 Simplified stratigraphic column showing how the dominating biota in reefs and reef mounds has changed through the Phanerozoic. Gaps indicate times when there appear to be no reefs or reef mounds (modified from James 1983)

3. If sea level rises faster than the coral reef can grow, the reef may drop below the photic zone and "drown", but this is very rare because they can gain height rapidly.
4. Reefs provide a favourable ecological environment for animals which are not part of the reef structure itself, but which live on other organisms.
5. Many organisms in coral reefs live by filtering water to trap planktonic organisms and organic material. If the water contains too much siliciclastic mud, the clay minerals can choke the filtering organs so that the organisms die. Corals are particularly sensitive to the clay content in the water and can only live in clear water. The addition of clay, for example from a delta, will kill a coral reef. Pollution will have the same effect.
6. Clear sea water, however, is usually very poor in nutrients, so the organisms in a reef are dependent on good water circulation to obtain enough food. Consequently, reefs tend to grow on the edge of ocean basins, or as structures projecting high up from deeper waters. In this way, high water temperature is combined with low mud content and good water circulation.
7. The reef facies is built up as a wave-breaking structure, with powerful networks of corals which are braced by an encrustation of coralline algae. Red algae are massive and strong and have an important function in supporting the reef structure so that it can withstand the strong waves. However, parts of the most exposed parts of the reef structures can be mechanically destroyed by wave action during heavy storms. In this way reef fragments of various sizes may fall down the fore-reef slope, be transported up onto the reef flat or be deposited in gaps and cavities in the reef framework. This mechanical destruction is aided by the boring and grazing action of different bioeroding organisms. The bio-erosion can be so extensive that many of the primary structures of fossil reefs are destroyed. Boring mussels are particularly effective, excavating elongated cavities about 1 cm in diameter in corals, algae etc. Boring sponges, worms and algae are also important reef-damaging organisms, typically

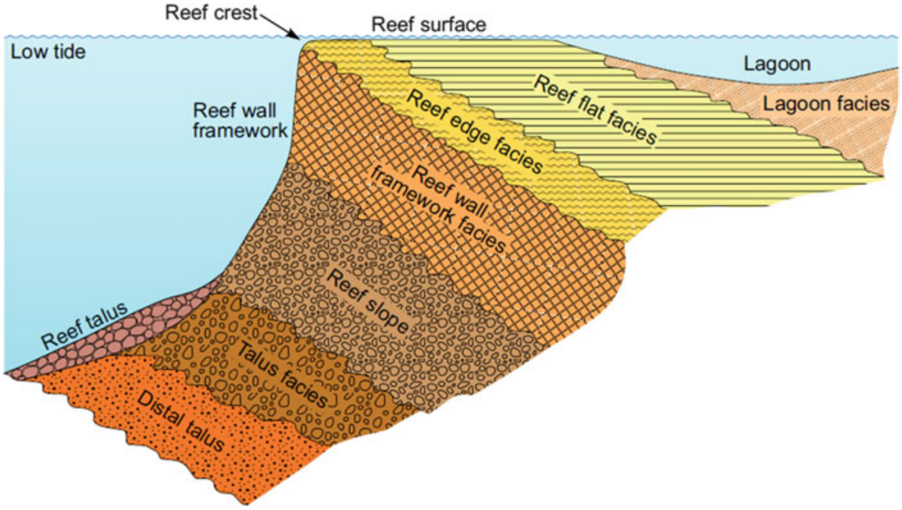


Fig. 5.43 Section through a reef which is developing out into a basin. Note the distribution of various reef facies and their diachronous nature (modified from Bjørlykke 1979)

forming minutely thin but densely spaced holes which destroy the skeletal material. Coral reefs provide a very favourable environment for a variety of fish, and the cavities in the structure offer protection against predators, but some species of fish also live by literally eating the reef. They take small bites, and obtain nutrients from the surface. In this manner they contribute to the bioerosion of the reef and the deposition of lime sediment on the sea bed.

A reef grows by virtue of the ability of its reef-building organisms to keep pace with the biological and mechanical processes which are continually breaking it down. Reefs will grow fastest on the outside, where wave energy and nutrient supply are greatest. In the case of barrier reefs, lagoons form on the landward side and contain a mixture of carbonate sand and fragments which have been transported from the reef facies during storms, together with skeletal material derived from organisms living in the lagoon (Fig. 5.43). The lagoons are usually only 2–6 m deep and protected from the highest waves by the reefs (Fig. 5.44) and contain a rich flora of calcareous green algae such as *Halimeda* and *Penicillus*. These are low, bush-like forms which cannot withstand high energy waves and require the protected environment of the lagoon. However, they secrete small (c. 1 μm) needle-like crystals of aragonite. When the algae die, the aragonite needles are released and form carbonate ooze. Green algae are therefore considered to be the most important source of carbonate ooze on the Bahama Bank; chemical precipitation is of minor importance. Other characteristic elements in the lagoon fauna are bivalves, gastropods, echinoderms and annelids. Of particular sedimentological importance are crabs and shrimps (*Callianassa*) which dig tunnels and churn up the sediments, destroying the primary structures. Their tube-like trace fossils (e.g. *Ophiomorpha*) are typical of shallow marine sediments. The stability of the bottom sediments in the lagoons is enhanced by the presence of plants, e.g. *Thallassia* grass which covers much of the sea bottom on the Bahama Bank.

Fig. 5.44 Aerial photograph showing reef facing the deep ocean and the protected lagoon, Bahamas. (Photo G.M. Friedman)

5.7.3.2 Reef and Carbonate Platforms Surrounded by Deep Oceans

Volcanic sea mounts reaching up to sea level are ideal places for carbonate sedimentation since all the clastic sediment will be trapped in the surrounding deeper water (Fig. 5.45). Smaller sea mounts may host circular atolls while larger areas of volcanic rocks may form platforms. Carbonate production may then keep pace with the seafloor subsidence over long periods of geological time. Even during the Pleistocene most of the carbonate platforms have been able to survive sea level changes of more than 100 m without drowning. Nearly all the carbonate production occurs in the photic zone (<100 m) and most of it occurs within the upper 20 m.

Also the Maldive Islands in South Asia are carbonate platforms. They have grown to form a submarine mountain 3 km above the surrounding seafloor and its growth has kept pace with the subsidence and changes in sea level.

The Bahamas Bank is one of the best researched areas of modern carbonate banks in the world and covers a very large area, about 700 km N–S and 200–300 km wide (Fig. 5.46). The greater part of this area is less than 10 m deep. There is deep water on the west side towards the Mexican Gulf, so there is no clastic sediment supply from land in that direction. Sediments on the Bank are almost pure carbonate, and the carbonate-producing organisms are often not subjected to pollution from clay minerals produced by weathering. Most of the small amounts of clastic sediments deposited on Bahamas are aeolian dust blown all the way from the Sahara region in Africa.

Carbonate platforms like the Bahamas represent the more or less continuous build-up of carbonate on the seafloor from Jurassic, Cretaceous and Tertiary times right up to the present. As the seabed has subsided, carbonate sedimentation has built up the area so that it has remained in the photic zone. This has led to it being surrounded by deeper areas of sea which have acted as traps for clastic sediments from neighbouring continents. East of Andros Island the edge of the carbonate platform gives way to a very steep submarine slope (20–30° in many places). At the Tongue of the Ocean it slopes down to 2,500 m, and east of the little Bahamas Bank that lies to the north, it descends to 4,500 m in the Atlantic Ocean. Throughout its existence, the eastern side of the Bank has been reinforced by reef structures which are solid carbonate rock capable of forming steep submarine slopes without submarine slides. Diving with submersibles has, however, revealed great blocks of limestone at the foot of the slope. The stresses in the rock in a steep slope such as this may have contributed to fracturing, releasing the blocks from the rock wall. Near the base of the slopes there are very high differential stresses due to the high vertical stress from the overlying carbonate rocks compared to the water pressure in the horizontal

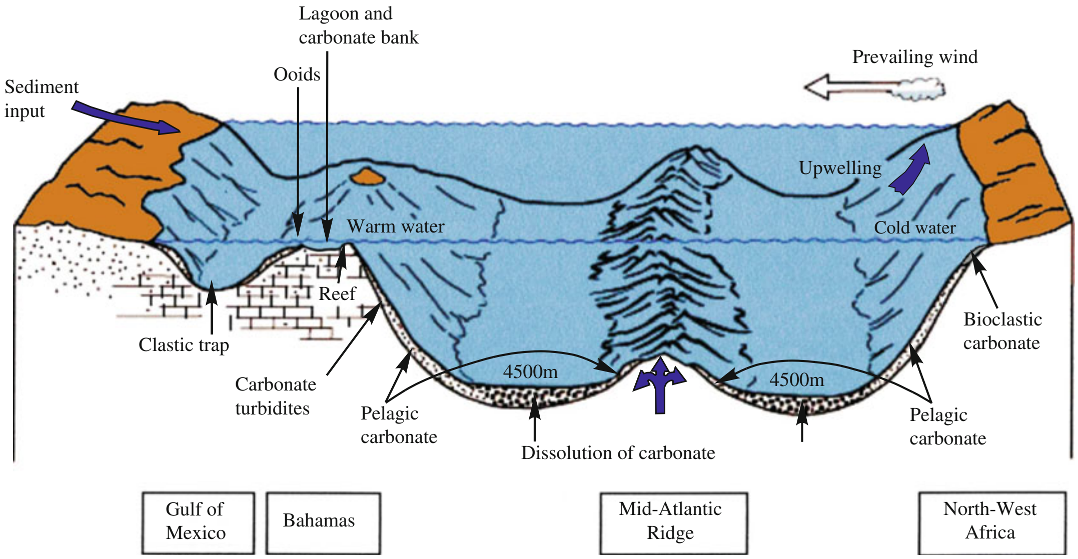


Fig. 5.45 Distribution of carbonate sediments across the Atlantic Ocean (modified from Bjørlykke 1989)

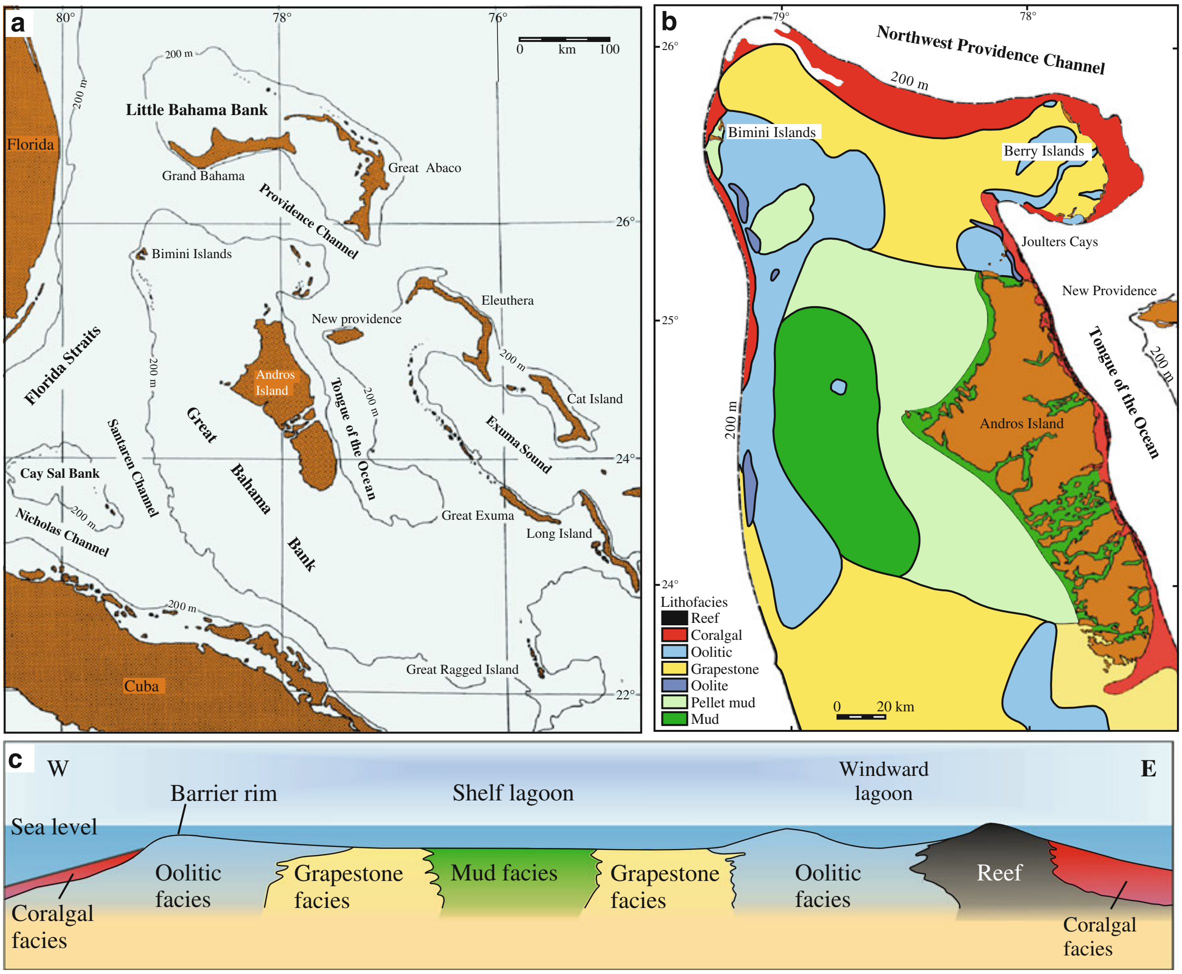


Fig. 5.46 (**a**) Map of the Bahamas Platform with surrounding areas. Note the deep ocean basin on the landward side. (**b**) Part of the Bahamas platform showing the distribution of recent carbonate sediments. (**c**) Simplified E–W section across the Bahamas platform. Note that the coral and oolite facies, which require high energy, are distributed along the edge of the basin, where wave power is greatest. Reef facies, which require the highest wave energy, only develop on the east side against the prevailing winds (modified from Bathurst 1975)

direction. This may cause fracturing and the release of carbonate slabs from these submarine slopes. A 2 km thick carbonate sequence represents a load (stress) of about 40–50 MPa assuming an average density of 2.0–2.5 g/cm. In the water column at the same depth the water load is only 20 MPa and the differential stress is then about 25 MPa.

When the Bahamas Bank, and other carbonate banks in the world, was exposed by the >100 m sea level drop during the glacial periods, it became lithified by percolating meteoric water which dissolved the aragonite and precipitated it as calcite cement. The loose carbonate sediments deposited over the last 10–12,000 years are not more than 3–4 m thick and rest unconformably on well-cemented, Pleistocene carbonate rocks.

Sedimentation on the Bahamas Bank reflects the climatic and bathymetric conditions. The temperature of the surface water varies from about 20–22°C in winter to 30–32°C in summer. Because of the limited exchange between water overlying the Bahamas platform and the surrounding ocean, the water in the interior of the Bank, particularly in summer, has a higher salinity than normal – up to 40‰. In winter the salinity is reduced by increased water circulation with the surrounding ocean, by rainwater and by runoff from Andros Island. Since the prevailing winds are from the east, where we also have deep water, wave energy is strongest on the east side of the platform. We therefore find reef facies along the east side of the platform, but not along the west side. However, corals and algae (coralalgal facies) are also present on the west side of the bank, but they do not form proper reef structures there.

Oolite banks form in shallow areas with constant wave agitation and strong tidal currents. In water deeper than the normal wave base, we find large bedforms of oolites and other carbonate sand which are only mobilised by major hurricanes. Dunes or sandwaves with a wavelength of about 50–100 m, mapped from aerial photograph surveys, show no sign of having moved in 20–30 years. Extensive areas of seabed where the wave energy is less than on the oolite banks are covered with algal mats. The algal threads forming this mat help to protect the sediments from erosion, inhibiting bed transport and current ripple development. They also contribute, through photosynthesis, to the creation of a chemical environment with low CO_2 concentrations which may cause local precipitation of carbonate within the mat.

In the middle areas, sedimentation of carbonate mud facies prevails. This is because wave energy is reduced along the edge of the Bank, and the whole of the shallow area within is a low-energy environment. Tidal currents are also reduced in the shallow water because most of the tidal energy is dissipated in overcoming the friction against the bottom and the tidal range drops from about 0.7–0.8 m along the edge to practically zero in the centre. The most important sediment transport mechanism is probably hurricanes. These can mobilise normally stable sediments, forming large dunes or sandwaves. Large oolite banks may migrate along the edge of the platform, and storms also inflict some erosion of the reefs. Towards the centre of the platform wind stress can cause changes in sea level of up to 3 m, and create great turbulence which brings large quantities of mud and sand into suspension. Some of this material will be transported off the platform and down the submarine slopes.

The areas west of Andros Island, which are the shallowest and best-protected against storms from the east, consist mainly of lime mud (Fig. 5.47). Over wide areas the carbonate mud is dominated by pellets. They form small grains (0.1 mm) consisting of clay and silt particles so that the “recycled” lime mud now behaves like fine sand when transported by currents. The faecal pellets consist of mud which has passed through the alimentary canal of marine organisms such as gastropods, bivalves and annelids. Crustacea, such as the shrimp *Callianassa*, are also important pellet producers.

Fig. 5.47 Arial view of supratidal environments with tidal channels. Bahamas. The tidal range is reduced in the inner part of the platform

5.7.3.3 Carbonate Platforms and Reef Environments Along the Coast; the Persian Gulf

Attached carbonate platforms can only form if there is little sediment supply from land. In dry areas, in particular, there will be very little runoff from land which could add clastic sediments. The drainage pattern also plays a major role. During transgressive periods a shallow sea will invade the low-lying land, raising the base level of the rivers. In this way the clastic sediment supply is trapped in the lower valley reaches and much of the shelf will have clear water dominated by carbonate sedimentation.

The Persian Gulf (Fig. 5.48) provides an important present day model of a carbonate-producing environment which is fundamentally different from the Bahamas Bank. Whereas the Bahamas Bank is surrounded by deeper water, and therefore represents a pure carbonate environment, the Persian Gulf lies in a fold zone between the alpine mountain chain of Iran to the north and the stable Arabian shield to the south and southwest. The Gulf is at the most only 80–90 m deep, and a delta is being built out into the

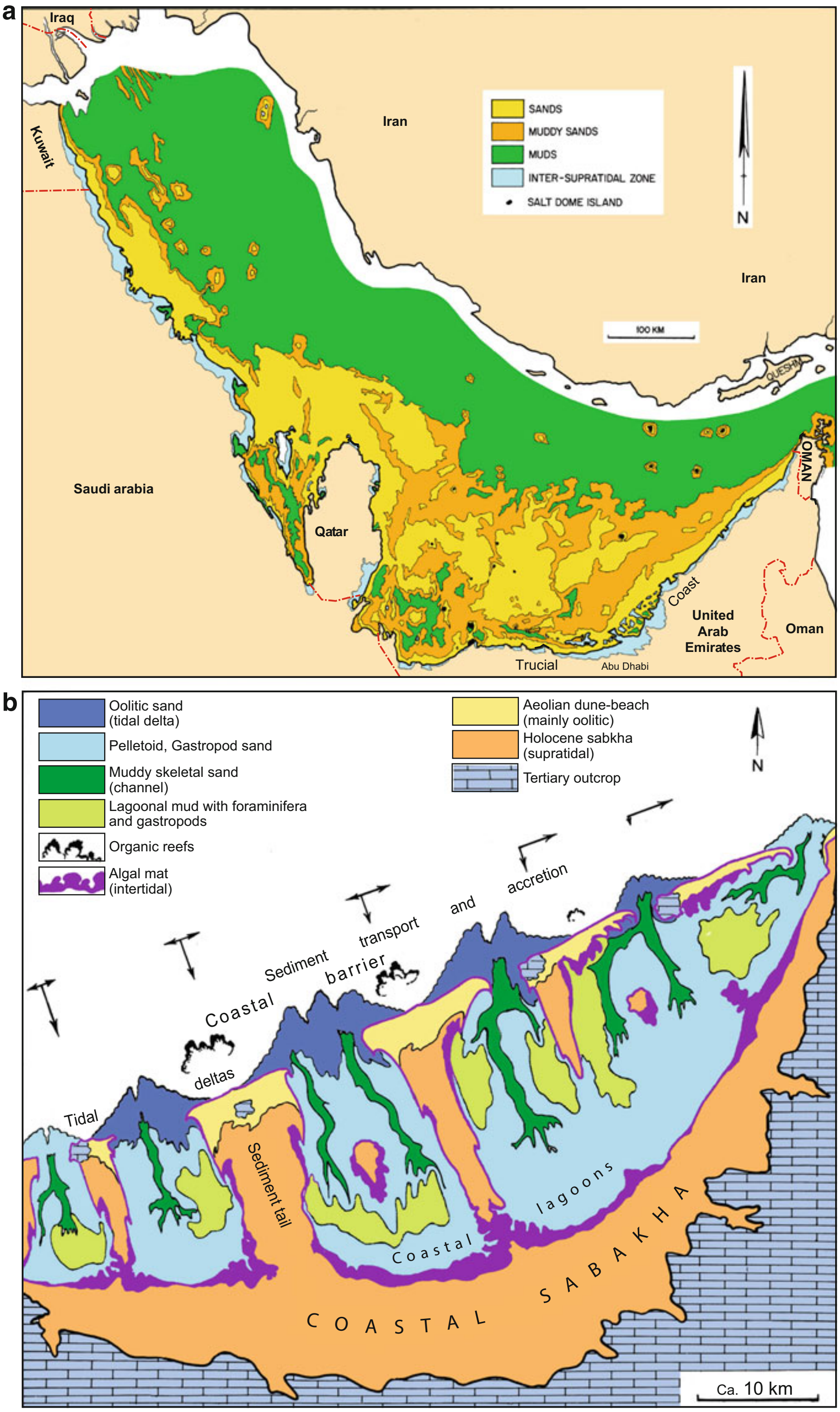


Fig. 5.48 (**a**) The Persian Gulf showing the facies distribution of Recent bottom sediments. (**b**) Map of the carbonate facies in the Abu Dhabi area (modified from Wagner and van der Togt 1973, Purser and Evans 1973)

northwestern end by the Euphrates and Tigris. Clastic siliceous sediments are also being added from the north, from the mountains in Iran with abundant limestones and dolomites. Much of the sediment therefore consists of impure carbonates (marl). Only on the south (Trucial Coast) side are there purer carbonate sediments, because there is very little runoff from the deserts on the Arabian shield. Here too, though, there is some supply of clastic material, particularly through aeolian transport from the desert. Sedimentation has been proceeding in a marine basin/embayment in this area since Mesozoic times.

The sea temperature in the Persian Gulf varies from 20°C in winter to 34°C in summer, and in the shallow areas it can be even hotter. The salinity in the open water is around 39–42‰, and may be higher due to evaporation in the lagoons. The tidal range varies from 0.5 to 2 m. The innermost supratidal area consists of a 10–15 km broad marginal belt covered by cyanobacteria and salt deposits. This belt is called *sabkha* in Arabic, and the word has become a geological term.

Because of the high temperature and salinity few organisms can live on the sabkha, which is dominated by algal mats (stromatolites) that form a crust of precipitated carbonate and gypsum. The stromatolites may grow in layers parallel to bedding or develop dome-shaped, columnar or irregular structures. The stromatolite structures are often broken into polygons which are separated from each other by sediment-filled cracks. The cracks are the posthumous reflection of shrinkage cracks as a result of drying.

The slope of the sediment surface here is only 0.4 m/km and during powerful storms water is driven in over the sabkha and later evaporates. Anhydrite, dolomite, magnesite and halite may be precipitated, though the halite is easily dissolved again. The precipitation of gypsum and anhydrite leads to the water developing a higher Mg^{2+}/Ca^{2+} ratio, which favours the formation of dolomite and magnesite.

In the Persian Gulf green calcareous algae such as *Halimeda* and *Penicillus*, which are important producers of lime mud in the Bahamas, are for the most part absent. Chemical precipitation is therefore probably the most important process, particularly during periods when diatoms proliferate and raise the pH by consuming CO_2 and thereby reducing the solubility of calcite. On the continental shelf, biogenic carbonate accumulates in the form of shells of foraminifera, molluscs, ostracods, bryozoans and echinoderms. Especially in shallow water environments the skeletal material can be heavily affected by post-mortem micritisation if exposed on the sea bottom for some time. Along the outer edge of the shelf are reefs, built of coral species that are particularly well adapted to the high salinity.

Tidal channels connect the lagoons with the gulf. At the mouths of the channels there are ebb-tidal deltas with oolite banks in the shallowest parts (<2 m). In addition to oolites there are grains of bioclastic material. Tidal deltas of this sort would form good oil reservoirs because of the high primary porosity, and in the Mesozoic series we find similar reservoir rocks. Shoreface deposits are not as well sorted as we would normally expect as they consist of fine sand and lime mud. This is possibly because the shoreline is stabilised by plants which bind the sediments.

Gastropods are particularly important in the lagoons and the intertidal environment. On the beach, shrimps and crabs burrow and disturb the lamination in the sediments. The lagoons are surrounded by swamps with bushes and mangroves, or algal flats. Landward of the algal mat facies, which is most typically developed at the high water mark, the sabkha facies continues. The degree of evaporation is higher here in the supratidal zone and dilution with seawater rarer. The sulphates, especially gypsum or anhydrite, are precipitated within the sediment near the groundwater table. The sabkha flats pass landwards into drier areas dominated by aeolian sand.

The facies distribution we have just described, from the open marine lagoon to the supratidal environment, will form a characteristic vertical sequence in the event of relative sea level fall and progradation. Periods with transgressions and subsequent regressive outbuilding will result in a series of sequences (cycles), starting with shallow marine (subtidal) sediments and culminating with evaporites (anhydrite) at the top. These cycles are also found in the Mesozoic and the impervious anhydrite beds forms an ideal cap rock above oil reservoir rocks. Carbonate sand facies, pellet facies, and particularly oolites, make good reservoir rocks, while the marine muds are source rocks.

5.7.3.4 Evaporite Basins

In ocean areas with normal salinity, practically all carbonate deposition is through biological precipitation. This is because the biological precipitation is rather efficient so the sea water does not become saturated with respect to the most common carbonate minerals like aragonite and calcite. In areas with somewhat higher salinity, however, for example in the Persian Gulf, there may also be chemical precipitation of calcium carbonate. This is because there are fewer organisms to precipitate carbonate and because of evaporation concentrating the sea water. Here too this precipitation may nevertheless be linked to biological factors. Periods with algal blooms in the surface waters involve photosynthesis and consumption of CO_2. This raises the pH, creating oversaturation and thus favourable conditions for chemical precipitation.

Carbonates make up only a small percentage of the salt precipitated when seawater evaporates to dryness. However, they are among the least soluble of the common salts in restricted ocean basins where the salinity is too low for the more soluble salts to precipitate (e.g. NaCl). Carbonates together with sulphates like gypsum or anhydrite often form thick evaporite sequences. In highly saline basins with more intense evaporation and restricted circulation, the water will become enriched in Mg^{2+} and dolomite will form, perhaps also magnesite.

5.7.3.5 Carbonate Turbidites on Slopes Skirting Carbonate Platforms

Carbonate sand and mud which is stirred up during storms over shallow water may be transported over the shelf edge to continue downslope as turbidites or debris flows. Carbonate platforms may rise 2–3 km above the surrounding seafloor and the slope may be very steep (20–30°) because of the hard and stable carbonate rocks.

5.7.3.6 Pelagic Carbonate

Pelagic carbonate deposits consist largely of planktonic organisms (coccolithophores, foraminifera, pteropods etc.) which live in the upper part of the water column, sinking to the bottom when they die. How clean the carbonate deposits are depends on how much other biological sedimentation there is, e.g. from siliceous organisms like diatoms and radiolaria, and how rapidly clastic sedimentation takes place. Therefore, carbonate sediments commonly become concentrated on top of submarine highs where the siliciclastic sedimentation rates are low. This is often observed on seismic lines where the reflections become stronger on the top of submarine positive tectonic structures.

In the deep ocean much of the pelagic carbonate production is dissolved as the particles settle through the water column. The sedimentation rate is a function of productivity in the upper water layers minus solution as the dead organisms sink towards the seafloor. The dissolution of skeletal material is due to undersaturation of $CaCO_3$ in deep ocean water because this cold water can dissolve more CO_2 than warm surface water. The combination of low temperatures and increasing hydrostatic pressure with depth involves an increase in the pCO_2 and decrease in the pH. The CO_2 is produced by respiration and decay of pelagic organisms in the deep ocean. Below the depths where the rate of dissolution is equal to the rate of sedimentation of carbonate, no carbonate sediments accumulate. This is called the carbonate compensation depth (CCD) and varies from 1–2 km in cold water at higher latitude to 4–5 km in the warm water equatorial regions.

Since the planktonic carbonate organisms are very small, pelagic carbonate deposits form a fine-grained ooze of clay- and silt-size particles, with occasional larger fossil fragments. Large areas of the South Atlantic and Pacific are covered by sediment containing more than 50% $CaCO_3$ from planktonic organisms. Foraminifera and coccolithophores form the most important deep-sea carbonate deposits (Fig. 5.14).

Coccolithophores live mainly in the photic zone. In areas of high productivity, for example in the fjords of Norway, the concentration of coccolithophores may be several millions per litre, but 50,000–500,000 is a more normal level. Although they consist of low-Mg calcite, their size makes them relatively soluble in cold water. In consequence, although production is greatest at high latitudes, it is only at lower latitudes that large quantities of coccolithophores are able to accumulate on the seafloor.

Shallow, warm seas with little other carbonate production provide particularly favourable conditions for the deposition of purer coccolith deposits. The seas of northwest Europe in Cretaceous times were a good example. The climate in the Mesozoic was undoubtedly considerably warmer than today, and northwest Europe also lay further south. Chalk forms a characteristic rock which is exposed in Denmark, South England and France, and continues under the southern and middle sections of the North Sea. It is missing in the north, possibly for palaeoclimatic reasons, although it is found in northeast Ireland. Chalk sediments were probably deposited in water depths of not more than 100–300 m, mostly below the photic zone. Since chalk is a micritic limestone, one would not expect it to form a suitable reservoir rock. The Ekofisk and associated fields are in fact the world's only major oilfield in such rocks, and the low permeability of this fine-grained lithology creates problems for production.

Pelagic calcareous algae such as coccolithophores did not become common until the late Jurassic and early Cretaceous. Consequently we do not have chalk deposits from older periods. This is an example of where the rock type is totally dependent on which organisms were precipitating carbonate. During the Palaeozoic most carbonate production took place in shallow water, as there were no planktonic calcareous algae to form deepwater pelagic carbonates.

5.7.3.7 Lakes and Inland Seas

Carbonate sedimentation in lakes depends on the rate of weathering and supply of Ca^{2+} from older calcareous sediments and calcium-bearing silicate rocks in the drainage basin. If there is an ample supply of Ca^{2+} and CO_3^{2-} also lacustrine sediments may contain considerable amounts of carbonate, and particularly at lower latitudes we find pure carbonate deposits. In cold lakes the solubility of carbonate is high and the carbonate content in the bottom sediments will mostly be limited to a few species of bivalves and gastropods. Temperate lakes often accumulate calcareous muds called marls, which in some lake sediments contain dolomite. Algae and certain higher plants often play an important role in carbonate production in lakes.

The Dead Sea is a good example of an inland sea where carbonate is precipitated chemically due to strong evaporation. In Africa and other tropical areas, lakes will be subject to seasonal evaporation to dryness, and we may find alternating layers of biogenic carbonate and chemically precipitated carbonate. Here, too, algal blooms in the surface water layer play a major role in precipitating carbonate. Thicker beds of carbonate below lake floors can be associated with longer term climate variation. In Lake Victoria, the sediments older than about 12,000 years have high carbonate content. This is because the lake nearly dried up during the last glacial period, when rainfall in the region was lower than now.

5.7.3.8 Calcareous Tufa Deposits and Travertine

Tufa is the name of a porous and spongy calcareous deposit common in limestone areas, usually at the base of slopes where groundwater emerges at the ground surface. Accreted in thin layers which often incorporate vegetation, it can build up into deposits several metres thick. Travertine is a more massive, relatively dense and sometimes finely banded and laminated carbonate deposit associated with freshwater springs or precipitated as speleothems in caves. Both varieties are precipitated from freshwater supersaturated with respect to calcium carbonate. Groundwater flowing through carbonate rock contains CO_2 at a higher partial pressure than at the surface because of the lower ambient temperature and the higher pressure that is due to the weight of the overlying water column. The increased partial pressure of CO_2 promotes increased dissolution of calcium carbonate from the host rock. When the water flows out of the rock at the surface, or reaches a cave, it will regain equilibrium with atmospheric pressure, causing degassing of CO_2. The loss of CO_2 entails that the water may become supersaturated with regards to calcite, followed by precipitation of this mineral. This is particularly effective in summer when the water will quickly warm up once it emerges. Exposure to light will also cause biogenic precipitation (photosynthesis) by algae.

5.7.4 Meteoric Water Flow and Diagenesis

The introduction of meteoric water has a profound effect on carbonate sediments and their potential as reservoir rocks.

A proportion of the rainwater (meteoric water) falling on land infiltrates into the groundwater. The flow of groundwater ultimately is limited by the rate of recharge by rainwater, which determines the water table gradient. As long as the water table is above

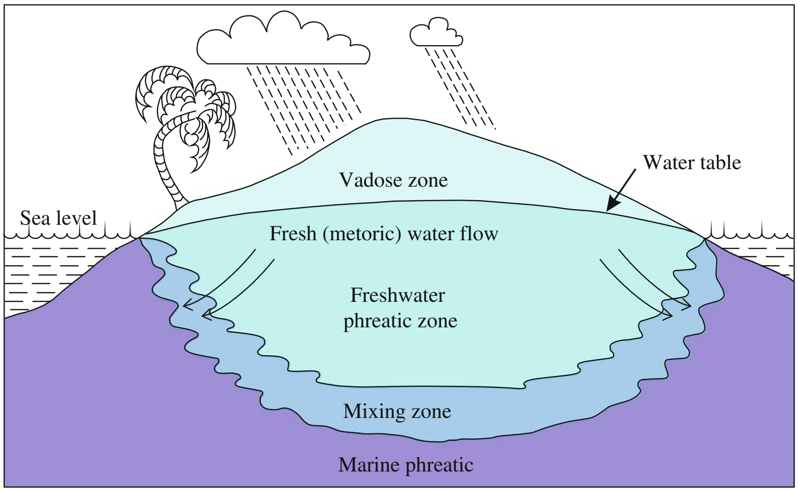


Fig. 5.49 Cross-section of an ideal permeable carbonate sand island showing the distribution of major diagenetic environments in the shallow subsurface. The vadose zone is situated near the surface above the water table, and the pore spaces are occupied by water and air. The pore spaces below the groundwater table are permanently water-saturated. The fresh interstitial waters float on the denser saline waters beneath. There is a mixing zone between the two water phases (modified from Scoffin 1987)

sea level the groundwater has the hydrodynamic potential to flow beneath the beach and out into the basin beneath the seafloor, floating on top of the more saline basin porewater (Fig. 5.49). The freshwater lens is floating like an iceberg in the sea. With a groundwater density of 1.00 g/cm^3 and the more saline water 1.025 g/cm^3, the ratio between the groundwater head and the depth of freshwater penetration is theoretically $1/(1.025 - 1.00) = 1/40$. A groundwater head of just 10 m can drive freshwater to a depth of up to 400 m below sea level. Shallow water carbonates deposited in coastal environments and around islands will thus in most cases be flushed by fresh groundwater after deposition. The diagenetic effects are greatest at shallow depth where the flow rates are highest.

However, coastal carbonate environments are usually rather dry and while carbonate platforms may have more rainfall, the islands on them may be small compared to the size of the platform. Both these factors tend to reduce the flux of meteoric water into marine carbonate sediments, although it may still be very significant, particularly when the sedimentation rate is low. More distal and pelagic facies may avoid this flushing altogether. On land and in the nearshore parts of the basin meteoric water may also be undersaturated with respect to calcite, in which case caverns are likely to develop.

When meteoric water flows through recent carbonate sediments it will be undersaturated with respect to aragonite but become rapidly supersaturated with respect to calcite. Aragonite will therefore dissolve first and calcite will precipitate (Fig. 5.50a). Gradually the meteoric water will reach equilibrium with low-Mg calcite, and calcite cement in the form of large crystals (block-shaped cement) may be precipitated (Fig. 5.51). This cement is very different from marine cements precipitated from modified seawater (without sulphate).

On land, the sediments above the water table are located in the *vadose* zone, where the pores are alternately filled with water and air as a consequence of intermittent meteoric water percolation. Partial desiccation results in an unequal distribution of the porewater with it primarily held near grain contacts, by capillary forces; as a result there will be a preferential cementation of pore throats giving a rounded pore geometry. This cement type is called meniscus cement (Figs. 5.50b and 5.51). Porewater will also collect on the underside of grains as pendant droplets and precipitate cement in this form, called pendant cement. Both

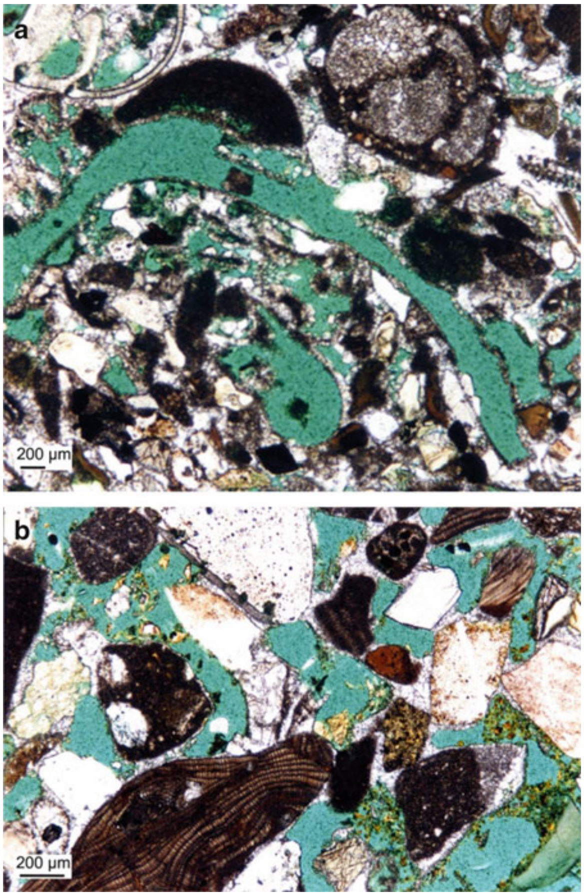


Fig. 5.50 (**a**) Mould after a dissolved mollusc (large, green-stained pore in the middle). After dissolution of the aragonitic shell the void is outlined by a micritic envelope. There is only a thin veneer of calcite spar precipitated in the mould at this early diagenetic stage. Thin section, plane polarised light. Quaternary, Rhodes, Greece. (**b**) Meniscus carbonate cement is concentrated at grain contacts resulting in pore rounding. This cement is diagnostic for freshwater vadose cementation. Primary porosity is stained blue. Thin section, plane polarised light. Quaternary, Rhodes, Greece

meniscus cement and pendant cement are characteristic of partial cementation in the vadose zone.

At sea level lowstands, particularly in the Quaternary, marine carbonate sediments were directly exposed to freshwater that caused rapid cementation. The sea level drop of more than 100 m during the glaciations exposed and cemented all carbonate sediments that had been in the photic zone during the preceding interglacial (highstand) periods. On modern carbonate banks soft sediments are therefore limited to the Holocene (postglacial) deposits, which normally are less than 2–3 m thick.

5.7.5 Shallow-Marine Diagenesis

5.7.5.1 Introduction

Lithification is the process which transforms loose sediment into solid rock. It occurs through new minerals (cement) being precipitated in the pore spaces binding together the primary particles. To cause carbonate cement to be precipitated, we must have porewater which is oversaturated with respect to a carbonate phase.

In general diagenetic processes are driven by a progression towards more mechanically stable grain packings and more thermodynamically stable mineral assemblages. This is also the case for carbonate sediments. During progressive burial the increasing overburden stress causes denser packing of grains so that the porosity is reduced. The reduction in porosity is then a function of the effective stress that may be expressed as the compressibility of the rock. Mechanical compaction is in principle instantaneous but there is usually some additional compaction with time at the same effective stress. This is called creep.

The mechanical compaction of carbonate sand and mud follows the same principles as for terrigenous sand and clay. In the case of carbonate sediments however, chemical processes involving dissolution and cement precipitation are much more important at low temperatures. This is because the kinetics of carbonate reactions are much faster at low temperature than is the case for silicate reactions. The prediction of porosity and permeability in carbonate rocks therefore also depends to a very large extent on chemical diagenesis at shallow depth. Porosity reduction in carbonates can therefore not be predicted solely on the basis of effective stress because it also depends on the primary mineralogical composition of the grains and textural relationships.

Cement formed in a marine environment is aragonite or high-Mg calcite, which forms needle-shaped crystals. High-Mg calcite can also precipitate as micritic cement. Early marine aragonite cement may grow as evenly distributed layers of aragonite needles perpendicular to the surface of the grains. This is

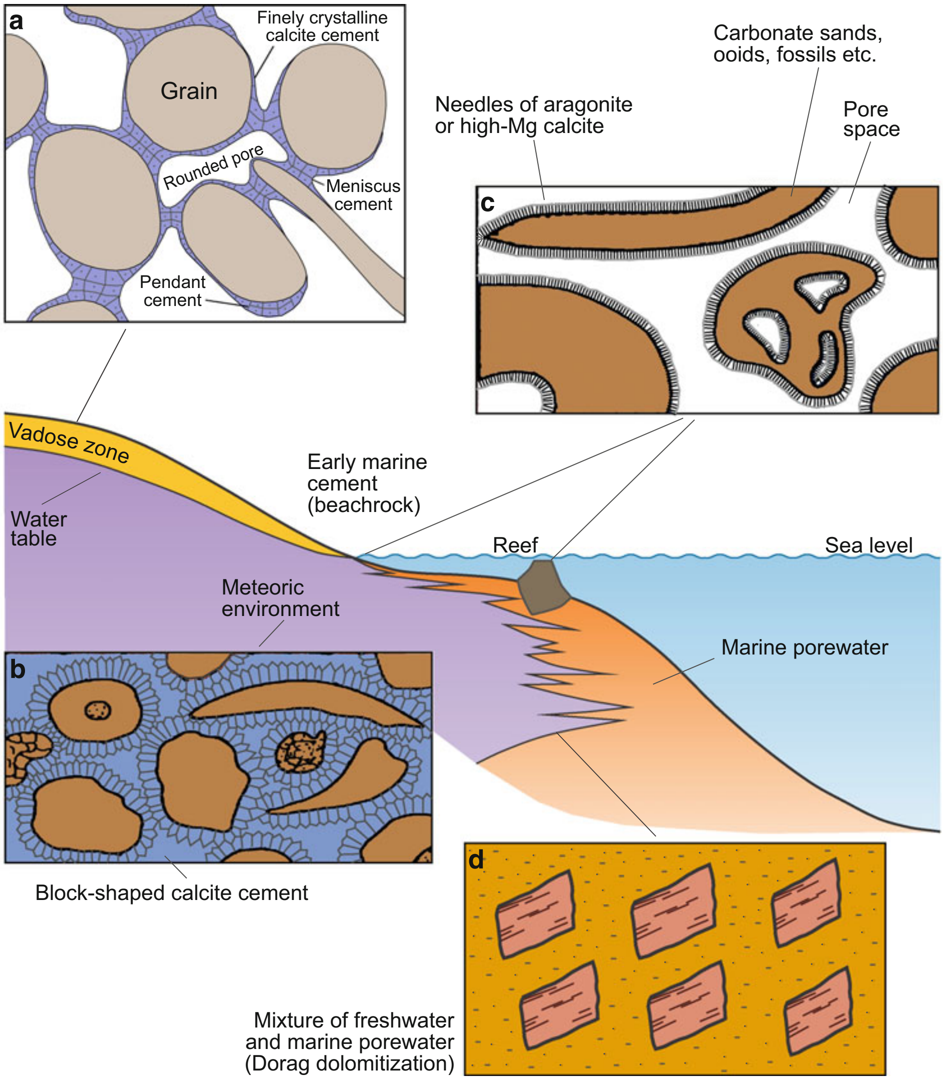


Fig. 5.51 Types of carbonate cement as a function of diagenetic environment. (**a**) Water is held near grain contacts in the vadose zone by capillary forces, and as a result cements form in these places (meniscus cement). In this way the pores will become more rounded due to the preferential cementation of the pore throats. Water will also collect at the underside of grains as pendant droplets, and after multiple phases of drainage and precipitation a cement with pendant form will be precipitated (pendant cement). (**b**) Phreatic calcite cement is typically clear and blocky shaped. (**c**) Early marine cements commonly consist of an isopachous fringe of acicular aragonite or high-Mg calcite. (**d**) Dolomite can be precipitated from a mixture of fresh and marine porewater

called isopachous fibrous cement because a layer of uniform thickness is formed (Fig. 5.52). Isopachous calcite cement may also be precipitated in meteoric (phreatic) porewater (Fig. 5.51).

The relative growth rate of the cement will depend on the chemical composition of the substrate and its microstructure. The greater the accordance between the substrate and the cement, the higher the growth rate will be. Calcite cement that grows out from echinoderm fragments will have a fast growth rate because both will have an identical lattice structure. The cement precipitates as syntaxial rims in optical continuity with the single calcite crystals of echinoderm plates, such that twin lamellae and cleavage planes transgress skeletal plates and cement overgrowths (Fig. 5.53). This style of cementation, called syntaxial

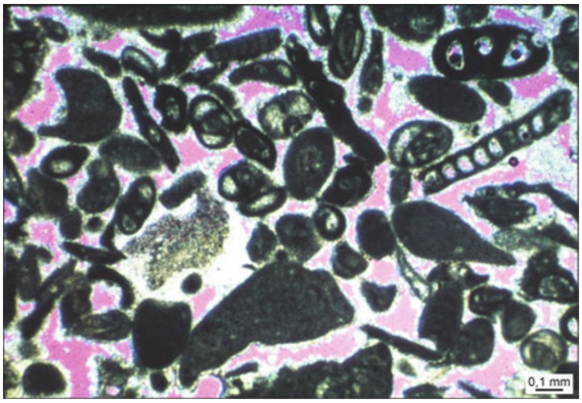


Fig. 5.52 Beach rock dominated by foraminifera and lithoclasts cemented with an isopachous rim of acicular aragonite cement. The pink areas are voids filled with stained epoxy. Thin section as viewed in plane polarised light. Recent, Bahamas

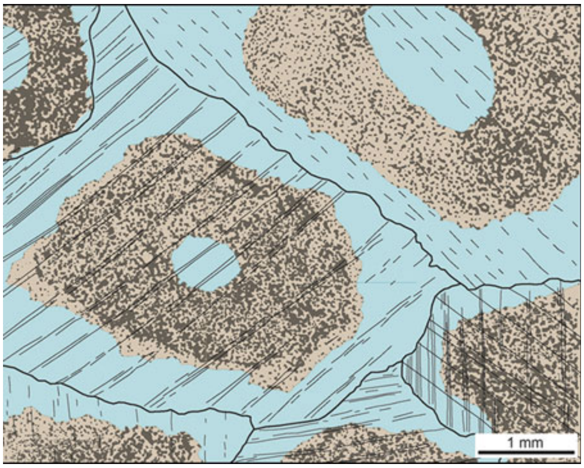


Fig. 5.53 Crinoidal limestone. Dusty looking crinoid ossicles with syntaxial calcite cement. The cement is in optical continuity with the echinoderm plates, with twin lamellae transgressing skeletal plates and cement (modified from Greensmith 1978)

or epitaxial cementation, often completely obliterates porosity in echinoderm-rich rocks. The volume of syntaxial overgrowth on echinoderm fragments is generally greater than the volume of cement crystals that have started their growth on multicrystalline fossil fragments or terrigenous material. In extreme cases, so much syntaxial cement may surround the echinoderm fragments that other grains will also become incorporated (poikilotopic crystal growth).

When calcite replaces earlier aragonite or high-Mg calcite by neomorphism, we sometimes see “ghosts” of the earlier crystals. Radiaxial fibrous cement mosaics frequently form as a result of replacement of high-Mg calcite cement but also may form by direct precipitation of aragonite. These are mosaics of calcite crystals with optic axes that converge away from the substratum (cavity wall) on which they grew. They contain twin laminae which are convex towards the substratum.

Calcite cement formed early in oxidised porewater will contain practically no iron, since Fe^{3+} is not soluble in the oxidised state. Only Fe^{2+} can substitute for Ca^{2+} in the calcite structure, and the formation of ferroan calcite therefore requires reducing conditions. Calcite precipitated in the sulphate-reducing zone is free of iron (non-ferroan), however, since all the available Fe^{2+} will form sulphides. Calcite formed at greater depths under reducing conditions will normally contain some iron and manganese, depending on the availability of such ions in the porewater at the time of formation availability of such ions in the porewater at the time of formation (Fig. 5.54a,b) At temperatures of about 100°C and above, iron-rich carbonates like ankerite $(\mathrm{Ca(Mg,Fe)(CO_3)_2})$ become increasingly stable and are often found in minor quantities.

When a particle, e.g. a fossil, which consists of aragonite, is dissolved and replaced by calcite, this can occur by means of two different processes (Fig. 5.55):

A. By complete dissolution of the particle leaving a mould (secondary cavity) showing the outline of the original grain. The mould can subsequently become filled with low-Mg calcite, either entirely or partially depending on the supply of pore fluid supersaturated with calcite. This secondary precipitate has a highly characteristic texture. A narrow zone of small prismatic crystals develops along the periphery of the cavity. The crystals become larger and more equidimensional towards the centre of the cavity; this is called a “drusy mosaic” (Bathurst 1975).
B. Through gradual dissolution of aragonite and simultaneous precipitation of low-Mg calcite. This reaction mechanism, *neomorphism*, will to some extent preserve primary structures.

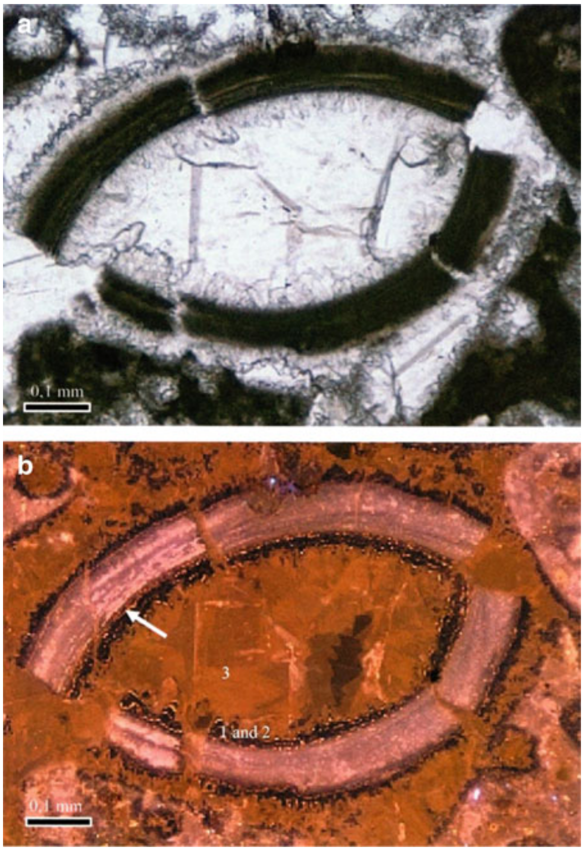


Fig. 5.54 (**a**) shows a well cemented limestone with an articulated ostracod in the middle. From this transmitted light view it is not possible to differentiate between the three different cement generations which are clearly visible with cathodoluminescence microscopy (**b**). Cement generations 1 and 2 have been precipitated before compaction of the fossil, because these cements are missing on the broken surfaces which are due to early burial compaction of the sediment. The third cement generation (3) is a post-compaction precipitation filling the remaining primary porosity and cracks in the fossil. Thin section as seen in plane polarised light and cathodoluminescence. Upper Tertiary, Iran. (Photographs courtesy of Torleiv Torgersen)

5.7.5.2 Beach Rock

The tidal zone on sandy beaches in tropical areas is commonly cemented by aragonite or less commonly by high-Mg calcite to produce "beach rock". On modern beaches the lithified zone may be about 0.5 m in thickness containing embedded bottles or other artifacts indicating that cementation has been very rapid by geological standards. Cementation takes place *in situ* beneath a thin sediment cover and is due to a combination of high flux of water due to wave action and rise in ionic concentration due to evaporation of seawater as it drains through the beach at low tide.

5.7.5.3 Hardground

A combination of dissolution and precipitation of carbonate sediments close to the seabed may produce a well-cemented surface called a "hardground". This can be recognised by evidence of borings and/or encrustations of hard bottom faunal elements such as calcareous algae, sponges, corals, serpulids, crinoids and oysters. Hard grounds are best developed in areas of slow sedimentation and high current activity. Long exposure on the seafloor can also lead to impregnation with minerals such as iron hydroxides, phosphorite and glauconite.

5.7.5.4 Cementation in Modern Reefs

Modern reefs have a very high porosity, made up of everything from small cavities to large caverns. It was previously believed that this primary porosity was preserved in older reefs. Boring and blasting into modern reefs, however, has revealed that the primary porosity is rapidly reduced because the hollows are rapidly filled up with fossil fragments and lime mud, and/or become more or less cemented by early marine cement. Reefs can therefore only make good reservoir rocks if secondary porosity develops through the dissolution of fossils or cement. This may happen by the reef being exposed above sea level to groundwater percolation and also by flow beneath the seabed of meteoric water from land. Aragonite or high-Mg calcite will then dissolve particularly easily and low-Mg calcite will precipitate. This diagenetic process may not significantly increase the overall porosity, but merely redistribute it.

Marine cementation commences early in reefs. The parts most exposed to waves, where water flux is greatest, will undergo rapid marine cementation. In the interior and landward parts there are less marine cement and more secondary porosity due to subaerial exposure and freshwater flushing. Skeletal material of primary aragonite may dissolve as calcite precipitates in the open framework porosity. Thus the porosity to a large extent becomes mouldic due to dissolution of many of the reef-building organisms.

Early cementation of aragonite or high-Mg calcite reduces porosity but the cementation produces a mechanically much stronger rock. The potential for preserving the remaining porosity is therefore higher than in uncemented carbonate sand. Furthermore, pressure solution may be reduced because the cement increases the contact area which reduces the stress per grain contact.

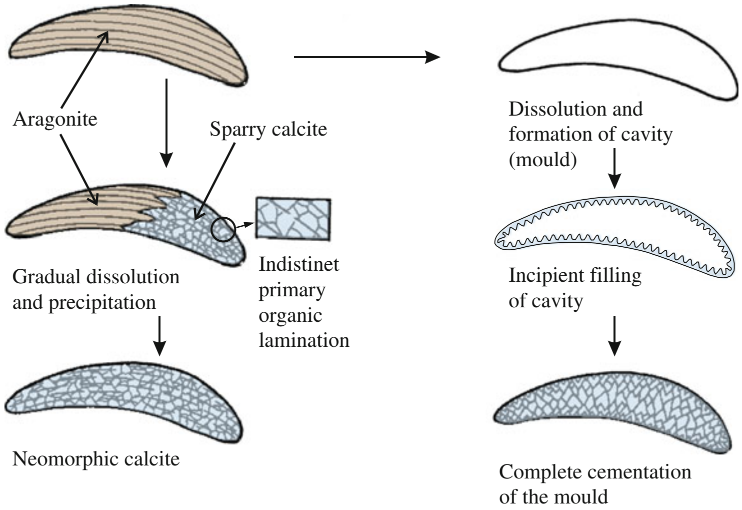


Fig. 5.55 Two types of conversion of aragonite to calcite. *Left*: neomorphic replacement of the grain. *Right*: complete solution of the grain and later precipitation of sparry calcite. If oil or gas is introduced before the moulds are cemented up the porosity may be preserved (modified from Bjørlykke 1989)

5.7.5.5 Reefs as Reservoir Rocks

The properties of reefs as reservoir rocks vary greatly and depend very much on the type of reef building organisms. These have varied through time and depend also on the environment. The fossils determine the initial mineralogical composition of the reef structures and hence the burial diagenesis.

The coarse carbonate block deposits (talus) down the slope in front of the reef (the fore-reef facies) and bioclastic sand behind the reef experience less water flow and tend to develop less marine cement. These facies constitute better reservoir rocks in terms of primary porosity.

Reefs are often surrounded by organic-rich terrigenous mud which may form a good source rock during burial. The reefs themselves may be good hydrocarbon traps, because they rise up from the seabed and thereby constitute structures which may become sealed if the reef drowns and is covered by terrigenous mud (Fig. 5.56).

5.7.6 Burial Diagenesis

Early cementation by calcite cements reduces the primary porosity but the cement may strengthen the grain framework and thus reduce compaction. Statistically, however, porosity clearly decreases as a function of burial depth (Schmoker and Halley 1982), although the porosity/depth function varies greatly with the lithology. The loss of porosity in carbonate sediments is partly a result of mechanical compaction of the carbonate mud and grains, just as in terrigenous mud and sand, but with an important difference. Unlike silicate reactions, carbonate reactions are relatively fast even at low temperatures and chemical compaction is therefore important both at shallow depth and low temperature, as well as at deeper burial depth and higher temperature.

Aragonite and high-Mg calcite are metastable minerals in the marine environment. They precipitate because low-Mg calcite, which is the thermodynamically stable calcium carbonate phase, fails to precipitate. This is probably due to the poisoning (inhibiting) effect of sulphate on calcite precipitation (Kastner 1984). During burial both aragonite and high-Mg calcite dissolve and are replaced by low-Mg calcite, but we do not know how fast this reaction is in marine sediments. This thermodynamic drive for dissolution and compaction is almost independent of stress. The dissolution of aragonite fossils or cements may cause grain framework to collapse, whereas high-Mg calcite is replaced by calcite that retains much of the original texture so that the grain framework is conserved.

The solubility of carbonate grains is also a function of effective stress and thus burial depth. Pressure

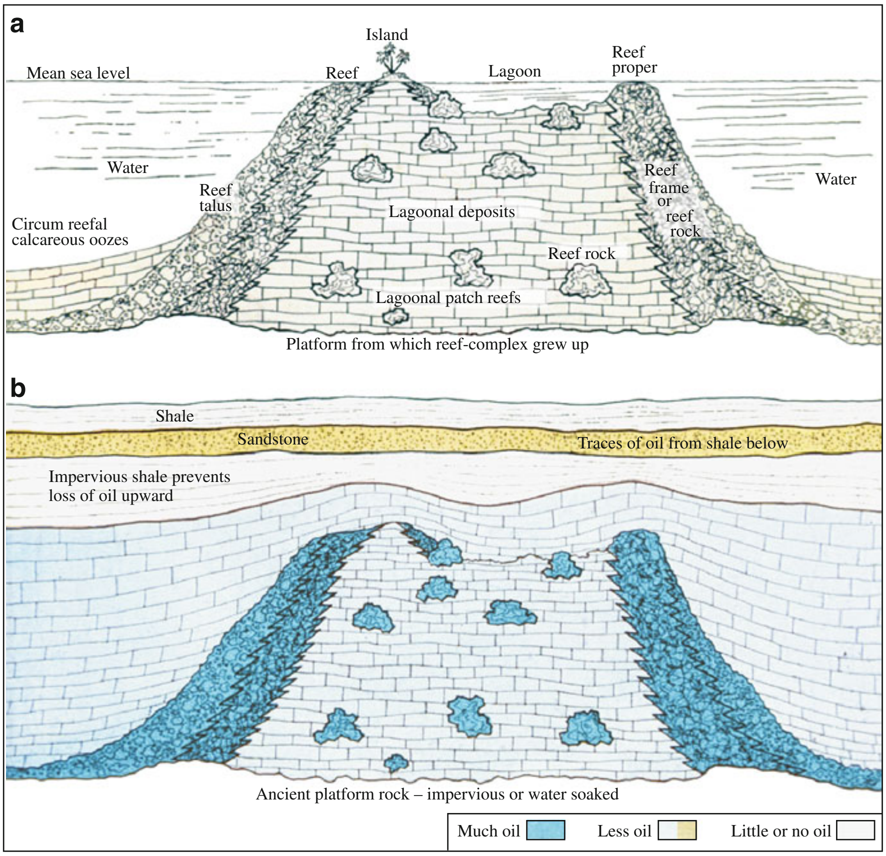


Fig. 5.56 (**a**) Vertical cross-section through a carbonate platform from which a reef complex grew up. (**b**) Micritic limestones in the lagoon have low porosity and permeability and oil and/or gas will mainly be present in reef and reef talus facies. The reef has been building into the deep ocean producing a steep submarine slope. The red algae is a strong reefbuilding organism while the more delicate green algae live in the protected lagoonal environments. In the supratidal environment we find blue-green algae and offshore carbonate is precipitated by planktonic algae (coccolithophores)

solution will often be concentrated at particular horizons where there has been some enrichment of clay particles which increases the rate of solution. Stylolites, which are surfaces where a considerable amount of solution has taken place, will then form. The horizon will be enriched with finely divided silicate minerals and other insoluble material in the limestones (Fig. 5.57). Where carbonate, usually calcite, is dissolved due to pressure solution, the dissolved material tends to be precipitated in the neighbouring pore spaces. When the pores between stylolites are filled with cement, dissolution along the stylolite ceases. Stylolites may have a relief from 1–2 mm up to several tens of centimetres and a spacing of typically 1–5 cm. As the rate of solution

Fig. 5.57 Cross-section of a stylolite. The *dark colour* is due to insoluble material within the limestone (such as clay minerals, pyrite and organic matter) which is concentrated in the seam. The amplitude (the distance between top and bottom) may be taken as a minimum measure of the thickness of the dissolved carbonate layer

along the surface varies, a very irregular relief develops which may be taken as a minimum measure of the thickness of the carbonate layer dissolved.

The carbonate dissolved at grain contacts and along stylolites is transported to the adjacent sediments by diffusion. Here the carbonate will usually re-precipitate in the pores, with a possible reduction in porosity of up to about 20%. Investigation of interbedded layers of limestone and dolomite (the rock is also called dolostone) show that the former is more susceptible to pressure solution than the latter. Dolostone usually has a strong framework of interconnected dolomite rhombs. Stylolites are therefore especially well developed in carbonates that are almost exclusively calcitic. Some late diagenetic dolomite rhombs may precipitate along developing stylolite surfaces as a result of a dynamic system with pressure gradients on a microscopic scale.

CO_2 and organic acids generated from decomposing organic matter are rapidly neutralised. The pH decreases with depth because of the increasing amounts of CO_2 that can be dissolved in the porewater as the pressure increases. The solubility of calcite increases with increasing pressure but at normal hydrostatic pressure gradients temperature is the overriding factor determining the solubility gradients. Calcite precipitates only very locally during upwards flow, where there are abrupt pressure drops.

Compaction-driven flow is normally directed upwards and since the solubility then is reduced, dissolution rather than precipitation will occur. The capacity of compaction-driven porewater to transport carbonate is in any case rather limited because of the low solubility gradients and moderate fluid fluxes at greater depth.

5.7.7 Classification of Carbonate Rocks

Early petrologists often subdivided limestones according to the size of the dominant mechanically deposited grains: Calcilutite (grains <63 μm), calcarenite (grains between 63 μm and 2 mm) and calcirudite (grains >2 mm). Later Folk's (1959, 1962) classification was widely accepted because of its applicability to a wide range of carbonate rock types and the ease with which its terms could be utilised and understood. Folk's classification is based on the idea that, in principle, the sedimentation of carbonate sediments is comparable to that of terrigenous material. However, today most workers prefer to use the classification by Dunham (1962) because it is not based on the composition of the matrix but on the nature of the framework, which is more applicable in revealing the depositional processes.

5.7.8 Folk (1959, 1962) Classification

Disregarding admixture of terrigenous material, Folk (1959, 1962) distinguished between three basic components of limestones:

1. Sediment grains (allochems). The principal allochems are: skeletal grains, ooids, peloids and fragments of carbonate rocks (intraclasts or extraclasts).
2. Microcrystalline lime mud (micrite) comprising clay-size particles (grain size <4 μm). In modern carbonate environments such as the Bahamas most of the mud consists of micron-sized needles of aragonite produced by green algae like *Halimeda* and *Penicillus*. These are transported as clay fraction material.
3. Sparry calcite cement (sparite) which is carbonate crystals that have been diagenetically precipitated in the pore space after deposition. While the carbonate mud and some of the grains have a brown stain due to organic material, the cement stands out as clear and transparent in thin section.

Almost all carbonate deposits contain more than one type of material, and Folk's classification is based on the relative proportions of the three endmembers: allochems, microcrystalline lime mud and sparry calcite cement (Fig. 5.58). Allochems represent the framework of the rock making up the bulk of most limestones. The matrix between the allochems may consist of lime mud if there is little bottom current. In limestones this mud may have recrystallised into small calcite crystals (microcrystalline mud), which is called *micrite* and is thus an indicator of a low-energy environment.

Deposits consisting of well-sorted allochems have primary porosity which may be filled with cement during diagenesis. The cement is precipitated from aqueous solutions and consists of clear, transparent crystals (spar) which are easy to distinguish from micrite, which tends to be brownish because of the organic

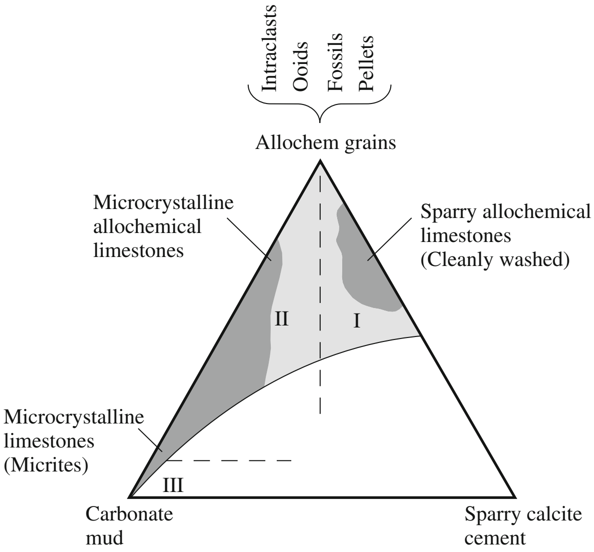


Fig. 5.58 Triangular diagram showing the three major textural types of limestones. *Shaded areas* depict the most commonly encountered limestones. *I*. The limestones consist chiefly of allochemical constituents cemented by sparry calcite. The relative proportions of sparry calcite cement and allochems varies within rather restricted limits depending on the packing and shape of the allochems, which are important factors for the pore volume. *II*. These limestones also consist of a considerable proportion of allochems, but in these cases the currents were not strong enough or persistent enough to winnow away the micrite. In these deposits the restriction of packing imposes a certain maximum on the amount of allochems, but there is no minimum. Therefore the content of allochems may vary from about 80% down to almost nothing in clean carbonate mud. *III*. Limestones consisting almost entirely of micrite with little or no allochems or sparry calcite (modified from Folk 1962)

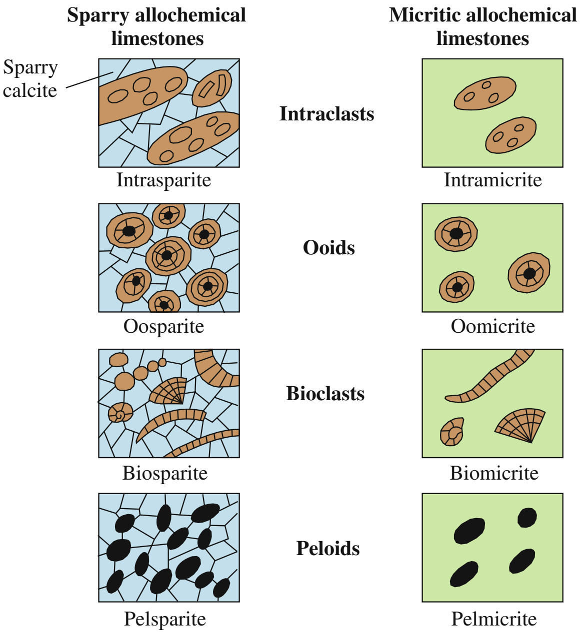


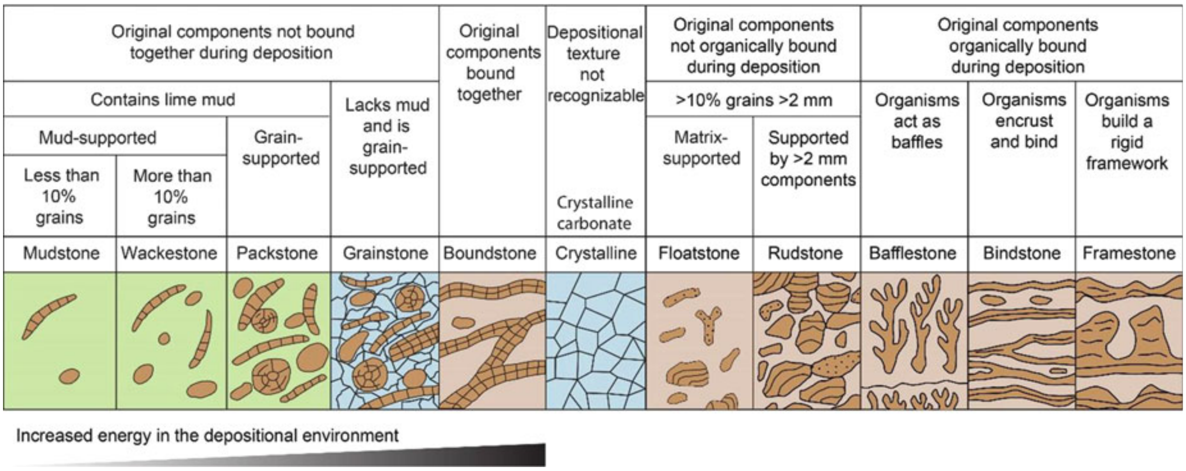
Fig. 5.59 Somewhat simplified schematic representation of the constituents that form the basis for Folk's classification of carbonate rocks (modified from Tucker and Wright 1990)

content. *Sparite* is thus a term for well-sorted carbonate sand, originally with high primary porosity, which has later been filled with calcite cement (spar). As such it normally represents a high-energy environment. Thus the relative proportions of micrite and sparry calcite cement indicate the degree of "sorting" or current strength of the environment during deposition.

As illustrated in Fig. 5.59 there are two parts to the rock name classification. The first part is contributed by the abbreviated allochems' name based on the dominating type of allochem. The second part reflects the void-filling material (micrite or sparry calcite). Biosparite, for example, means that the carbonate rock is dominated by fossil fragments without any matrix, but cemented with sparry calcite cement. Oomicrites and pelmicrites are sediments consisting of oolites or pellets with a carbonate mud matrix. Intrasparite consists of carbonate fragments eroded inside a basin to form well-sorted carbonate deposits. Sediments with a considerable percentage of grains larger than 1.0 mm are called rudites. A coarse-grained bioclastic sparite would thus be classified as biosparrudite.

If the allochems are found in a matrix of carbonate mud (micrite) the rock is termed biomicrite, oomicrite, intramicrite or pelmicrite. These sediments represent low-energy environments where neither currents nor wave action separate the mud from the grains. Micrites normally have too low porosity and permeability to be reservoir rocks. While the carbonate mud may initially have high porosity this is strongly reduced by mechanical and chemical compaction. Micrites may, however, become tectonically fractured, thus increasing their porosity and particularly their permeability. Secondary porosity due to dissolution of aragonite and high-Mg calcite fossils may also improve the reservoir quality of micrites.

Carbonate sediments deposited in environments with sufficient wave or current energy to separate the grains from the muddy matrix can be well-sorted with



Original components not bound together during deposition				Original components bound together	Depositional texture not recognizable	Original components not organically bound during deposition		Original components organically bound during deposition		
Contains lime mud			Lacks mud and is grain-supported			>10% grains >2 mm		Organisms act as baffles	Organisms encrust and bind	Organisms build a rigid framework
Mud-supported		Grain-supported				Matrix-supported	Supported by >2 mm components			
Less than 10% grains	More than 10% grains				Crystalline carbonate					
Mudstone	Wackestone	Packstone	Grainstone	Boundstone	Crystalline	Floatstone	Rudstone	Bafflestone	Bindstone	Framestone

Fig. 5.60 Dunham (1962) classified carbonate rocks according to depositional texture (modified from Tucker and Wright 1990). The classification was later expanded with different autochthonous and allochthonous types of reef limestones by Embry and Klovan (1971, see also James 1984). See text for explanation

an initial pore space of about 40% between the grains (or even more if the skeletal material shows irregular growth forms). These sparry deposits are potential reservoir rocks if they only become partly cemented with calcite spar. The presence of petroleum may retard the precipitation of carbonate cement.

5.7.9 *Dunham (1962) Classification*

Working for Shell Oil, Dunham (1962) developed a classification which was more oriented to the needs of the oil industry, and this simple classification has become the most widely used today. His classification is also based on the depositional texture of the limestone, but the fundamental criterion is not the composition on the matrix as in the Folk (1959, 1962) classification, but the nature of the framework (whether it is mud-supported or grain-supported), see Fig. 5.60. Mud is defined as carbonate particles with a grain size <20 µm.

Mud-supported deposits imply deposition in a low energy environment. Limestones with very few grains (<10%) floating in a mud matrix are classified as mudstones. Mudstones with more than 10% grains, but still mud-supported, are classified as wackestones. Grain-supported limestones indicate deposition in a high energy environment. They are classified as packstones or grainstones, the former having a mud matrix, the latter a greater or lesser amount of calcite cement in the intergranular pores. The term boundstone is used where the fabric indicates that the original components are bound together during deposition (e.g. as in reefs). It is equivalent to the term biolithite in the classification of Folk (1959).

The textures of carbonate deposits correspond in many ways to those we observe in clastic terrigenous sediments. Mudstone corresponds to clay, and wackestone and packstone correspond to greywackes. Grainstones are well sorted with little matrix. We distinguish between grain-supported and matrix- or mud-supported sandstones. Mud-supported sandstones will be subject to compaction of the matrix between the grains, and have many of the plastic properties of fine-grained sediments (muds). The degree of compaction will depend on the proportion of grains.

Grain-supported carbonates have a framework of grains which rest upon one another. Compaction cannot take place without the grain framework being deformed. This may take place by the grains being packed more tightly through mechanically crushing due to the force exerted by the overburden, or being chemically dissolved, particularly at the contacts between grains (pressure solution). The mechanical strength of carbonate fragments from fossils may be relatively low, but that of thick-shelled fossils and ooids is high. The contacts between grains will initially be very small, for example round ooids will only have very limited areas of contact. As the overburden increases, the pressure per unit area at the contact points will be very great. Pressure solution will then occur at the contact points, so that the contact area expands and the pressure per unit area decreases.

The distinction between grain-supported and mud-supported rocks is not simply a function of the ratio of grains to mud, because carbonate grains have widely different and often highly irregular shapes. Rocks composed of spherical grains (e.g. ooids) may need a grain content of about 60% to achieve grain support, whereas rocks with highly irregular grain shapes may form a self-supporting framework with a grain content of only 20–25%.

Mudstones, wackestones and packstones would all be poor reservoir rocks because of the carbonate mud in the matrix. In the case of packstones the grains form a grain-supported fabric but the matrix is still carbonate mud. Grainstones represents well-sorted carbonate deposits with good porosity and permeability, which may serve as a good reservoir if cement precipitation is not too advanced. This is the carbonate equivalent of well-sorted siliceous sand. Boundstones are rocks bound together by organisms (fossils) as in reefs, and they may also have high porosity and permeability.

Embry and Klovan (1971) extended the classification of Dunham (1962) with different types of autochthonous and allochthonous reef limestones (Fig. 5.60). The autochthonous types are bafflestone that contains in-place stalked fossils that trapped sediment by baffling the currents, bindstone that contains in-place large lamellar or tabular fossils that encrust or bind loose sediment together, and framestone that contains in-place large frame-builders forming the rigid framework of the reef. The autochthonous types contain more than 10% particles larger than 2 mm; the matrix-supported type is floatstone while the clast-supported is termed rudstone.

5.7.10 Dolomitisation

The term “dolomite” is used to designate both a mineral and rocks in which this mineral is the main constituent (Figs. 5.61 and 5.62a,b). To avoid confusion, the term “dolostone” has been introduced for the rock, but has not been widely adopted.

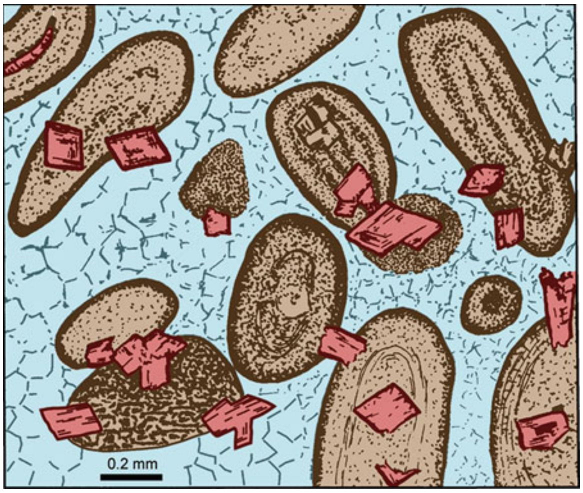


Fig. 5.61 Partly dolomitised oolite. The dolomite rhombs (*dark brown*) transect the oolite grains (*light brown*) and the surrounding spar crystals (*blue*), indicating a late diagenetic dolomitisation (modified from Greensmith 1978)

The mineral dolomite $(\mathrm{CaMg(CO_3)_2})$, consists of layers of $\mathrm{CO_3^{2-}}$ groups separated by alternating layers of $\mathrm{Mg^{2+}}$ and $\mathrm{Ca^{2+}}$. This is a highly organised structure (trigonal rhombohedral) and the organisation of more or less pure layers of $\mathrm{Mg^{2+}}$ and $\mathrm{Ca^{2+}}$ leads to high kinetic energy being required for the crystallisation of dolomite. This is particularly true at low temperatures, and so far it has not been possible to synthesise low temperature dolomite (<100°C) in the laboratory.

Dolomite is in most cases not formed directly, but as a secondary mineral as a result of reactions between different forms of $\mathrm{CaCO_3}$ and $\mathrm{Mg^{2+}}$. The reaction

$$2\mathrm{CaCO_3} + \mathrm{Mg^{2+}} = \mathrm{CaMg(CO_3)_2} + \mathrm{Ca^{2+}}$$

is dependent on the $\mathrm{Mg^{2+}/Ca^{2+}}$ ratio. The dolomitisation process will only proceed with a supply of magnesium maintaining a high $\mathrm{Mg^{2+}/Ca^{2+}}$ ratio.

$\mathrm{Mg^{2+}}$ is more strongly hydrated than $\mathrm{Ca^{2+}}$ in seawater. The $\mathrm{Mg^{2+}}$ ion together with its surrounding water molecules, $\mathrm{Mg(H_2O)_6^{2+}}$, cannot easily enter a crystal position at surface temperatures. However, the hydration decreases with increasing temperature and this is a factor often cited in favour of explaining late burial dolomitisation.

Experiments show that in the absence of sulphate, dolomite forms rapidly in solutions with $\mathrm{MgCl_2} + \mathrm{NaCl} + \mathrm{CaCl_2}$. The main reason that

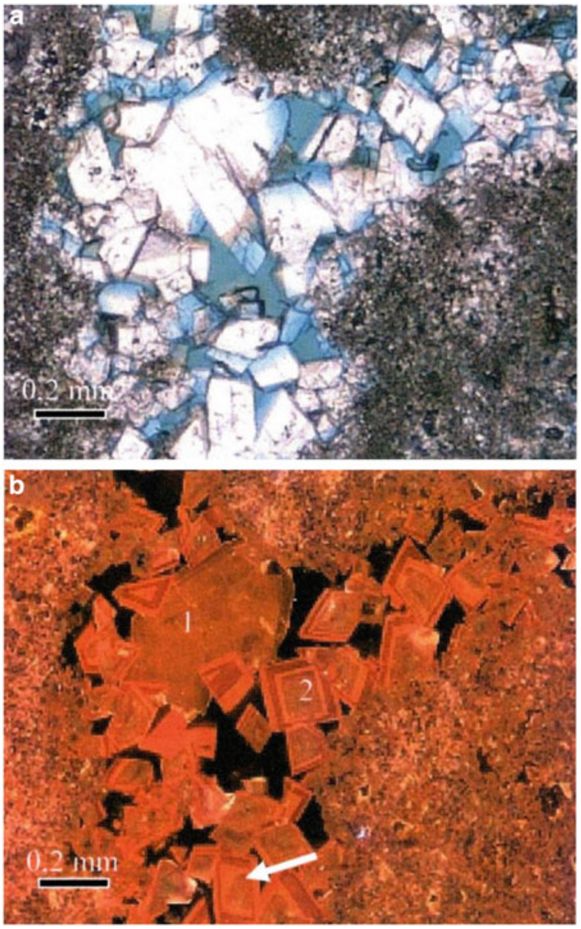


Fig. 5.62 (**a**) Partly cemented secondary cavity in a limestone as seen in plane polarised light. The remaining porosity has been impregnated with blue coloured epoxy. (**b**) The same area viewed with cathodoluminescence microscopy. The cement consists of brown luminescent calcite (1) and zoned dolomite crystals (2). The zoned dolomite crystals have both euhedral and irregular cores (arrow) with a brown luminescence, while the periphery is characterised by thin zones of reddish luminescence. Upper Tertiary, Iran. (Photos courtesy of Torleiv Torgersen)

dolomite is not common in modern marine environments is that the sulphate ion (SO_4^{2-}) is very efficient at preventing dolomitisation. Consequently dolomitisation takes place more easily when there are few sulphate ions (Baker and Kastner 1981). For this reason dolomite is formed in a number of lakes and in brackish zones with mixing of salt- and freshwater (Dorag model). In a microbial sulphate reduction zone, the SO_4^{2-} concentration will be lower and ammonium (NH_{4^+}) can be formed by nitrate-reducing bacteria. The sulphate is reduced to hydrogen sulphide (H_2S), which may react with dissolved reduced iron (Fe^{2+}) to form metal sulphides such as pyrite (FeS_2). NH_{4^+} can replace Mg^{2+} adsorbed on clay minerals. In this way magnesium is liberated for dolomitisation.

5.7.10.1 Models

Dolomitisation means that $CaCO_3$ is dissolved and dolomite precipitated. The conditions for this are:

1. That calcium carbonate becomes unstable, and that the solution is supersaturated with respect to dolomite.
2. That Mg^{2+} is added to the solution so that dolomitisation can continue.
3. That an inhibitor such as sulphate is absent or at least in low concentration.

Solution of calcium carbonate takes place most easily if we have aragonite at the outset. Fine-grained carbonate mud has a large specific surface which enables it to react more rapidly than massive carbonate.

The dolomitisation process is accelerated if the sediment concerned has a high permeability and a high rate of percolating porewater containing magnesium, though if carbonate sediments already contain a good deal of magnesium, dolomitisation will be able to proceed without any addition of Mg^{2+}. This applies, for example, to carbonate sediments rich in high-Mg calcite as in reefs. We often find thin dolomite beds or finely divided dolomite in shales, and this may be due to a supply of Mg^{2+} from clay minerals.

Seawater is a highly complex solution. We cannot simply predict the way in which it will react from the concentrations found through chemical analyses. Some of the Mg^{2+} and Ca^{2+} is associated with Cl^- through ion pairing, and must be excluded from calculations regarding activities involving carbonates.

Theoretical calculations indicate that dolomitisation should occur when the Mg^{2+}/Ca^{2+} activity ratio is about 0.6. Although these figures are somewhat uncertain, it is clear that seawater, in which the Mg^{2+}/Ca^{2+} ratio is 5.6, is oversaturated with respect to dolomite. The fact that dolomite does not form is ascribable to kinetic reasons, one probably being the high SO_4^{2-} concentration, and only when the ratio is over about 7 will dolomitisation take place in seawater. In freshwater the ion strength is lower, and here dolomite can be formed at lower Mg^{2+}/Ca^{2+} ratios because there is very little sulphate. However, freshwater contains little magnesium, so Mg^{2+} must be supplied by mixing with seawater and large amounts of seawater must circulate through the limestone. A steady percolation of freshwater alone will not lead to any great degree of dolomitisation, because freshwater will displace the magnesium-rich salt water, and the mixing zone will be too small.

Seawater is the only source of magnesium for large scale dolomitisation, except in evaporite sequences where Mg-rich evaporite minerals can dissolve and add Mg^{2+} to the porewater. The seawater which circulates inside atolls and reefs is reducing and therefore low in sulphate, at the same time having abundant magnesium. Reef and atoll facies therefore offer favourable conditions for dolomitisation. Dolomitisation of large volumes of limestones would require vary large sources of magnesium and it is only very near to the surface that seawater can flow with sufficient fluid fluxes to supply enough Mg^{2+} to cause pervasive dolomitisation. Freshwater has a low sulphate content which makes it easier to precipitate dolomite but it does not explain the supply of such large quantities of Mg^{2+}.

Hydrothermal circulation of seawater will cause dolomitisation but that will be limited to the flow path controlled by fractures and permeable layers. Very little of the flow will penetrate tight rocks, i.e. micritic limestones.

Massive and extensive dolomites are likely to be formed at shallow depth near the surface or seafloor in marine basins. This is favoured by high salinity and evaporitic conditions.

Dolomite showing fluid inclusion and textural evidence of having formed at higher temperatures may have been recrystallised at greater depth.

5.7.10.2 Evaporite Model for Dolomitisation

Dolomite is often associated with evaporite environments. The first definite example of dolomite being formed today was found in evaporating sediments in a supratidal environment in the Bahamas in about 1960. It is clear that when seawater evaporates, and aragonite and also gypsum ($CaSO_4 \cdot 2H_2O$) are precipitated, the composition of the fraction still in solution will become increasingly enriched in magnesium, and dolomite will only be precipitated at high Mg^{2+}/Ca^{2+} ratios. In addition magnesite ($MgCO_3$) may form. This explains why dolomite is important in most evaporite sequences. However, evaporite minerals are very soluble, particularly chlorides, and often are not preserved; gypsum may also dissolve and be replaced by carbonate. Dolomite might therefore have been deposited in an evaporite environment despite the fact that we do not find any of the original highly soluble salts preserved. For this reason it is important to look for indirect evidence of evaporite conditions and solution, including replacement of evaporite minerals.

The most important indicators of evaporite conditions are:

1. Absence of ordinary marine fossils, apart from stromatolites which can tolerate high salinity. In Palaeozoic and younger deposits stromatolites are typical of evaporites, because under normal marine conditions cyanobacteria have too much competition from other organisms.
2. Breccias which may have been formed through solution of underlying salt deposits so that beds collapse and form a *collapse breccia*. Such breccias are characterised by angular fragments from an overlying bed, for example of carbonate, which have fallen down into a solution cavity.
3. Pseudomorphosis (replacement) of evaporite minerals, e.g. halite (NaCl) and gypsum ($CaSO_4 \cdot 2H_2O$). Evaporite minerals, which are disseminated through a matrix of less soluble minerals such as carbonates, are often replaced through pseudomorphosis so that the crystal form may reveal the original mineral. The cubic halite crystals are typical, and the characteristic swallow-tail twins of gypsum crystals are easily recognised even if they have been replaced by other minerals.
4. C*hickenwire structure*. Anhydrite often forms very characteristic nodules or continuous layers which look like chicken wire. Even if the anhydrite layers are converted to calcite, these structures may be preserved.
5. Authigenic quartz and feldspar. Evaporites are often associated with microcrystalline quartz (chert) and chalcedony. A high content of authigenic feldspar and zeolites is also typical of many evaporites. With low-grade metamorphism (200–300°C) zeolites will dissolve and be replaced by feldspar.

5.7.10.3 Constraints on Diagenetic Dolomite Formation

While early diagenetic dolomite is normally relatively fine-grained, late-diagenetic dolomite usually forms larger crystals, often well-defined dolomite rhombs. The smaller crystals are formed by rapid crystal growth under conditions of high supersaturation. The larger crystals are formed by slow crystal growth from a few nucleation centres at a very low degree of supersaturation combined with deep burial.

As mentioned previously, hydration of Mg^{2+} decreases with increasing temperature, making Mg^{2+} more readily available for the dolomite structure. Dolomite might then be formed at very low Mg^{2+}/Ca^{2+} ratios; at about 80°C the ratio can be as low as 0.1. Although dolomite can precipitate in solutions with low Mg^{2+}/Ca^{2+} ratios, the question remains of how sufficient magnesium is added for the dolomitisation to take place. The amount of magnesium in solution in the deeper part (>2–3 km burial depth) of sedimentary basins is in most cases very low and is far from adequate as a source for large-scale dolomitisation. Water from compaction of mudstones and shales is probably also insufficient to supply much magnesium for dolomitisation. Primary high-Mg calcite will be a source of Mg to form dolomite at depth.

There is only a little magnesium in the porewater of sedimentary basins apart from in the vicinity of evaporites. Probably most of the dolomitisation occurs near the surface where the magnesium comes from seawater. Fine-grained dolomite, formed at an early stage, may be dissolved at depth and recrystallise as coarser-grained dolomite, in which case there is no need to postulate a magnesium supply deep in the basin.

We often find dolomite enriched along stylolites, probably because dolomite is less soluble than calcite and the solution and precipitation round a stylolite will concentrate clay minerals which, in turn, may release some magnesium.

If the composition of the porewater later shifts towards a low Mg^{2+}/Ca^{2+} ratio, dolomite may dissolve and calcite reprecipitate. There are a number of cases where distinctly dolomite-type rhombs are found to consist of calcite. One common cause of reversed dolomitisation – often called *dedolomitisation* – is porewater coming from gypsum which is dissolving. This gives the porewater a high Ca^{2+} concentration. However, many people have recommended that the term "dedolomitisation" should be dropped, and the positive term "calcitisation" be used instead.

5.7.10.4 The Significance of Dolomitisation

For many years there has been intensive research into the processes which lead to dolomitisation. A great deal remains to be learnt, however, before we really understand the precise conditions for dolomitisation so that we can predict the extent of dolomite in sedimentary basins. The reason for this great interest is that dolomitic carbonate rocks are very important reservoirs for oil and gas. The dolomitisation process may create secondary porosity because dolomite has a greater density than calcite so if an identical number of mol dolomite is precipitated as in the original calcite, we would get approximately 12% smaller volume and an equivalent increase in porosity. The dolomitisation process assumes, however, that calcium is removed and magnesium introduced, and there is then no reason why there should be an increase in porosity proportional to the difference in density, since there is no reason why the same number of mol dolomite should be precipitated as were removed by the calcite dissolving. Since dolomitisation involves large-scale percolation of porewater, we may also have net increase in the porosity associated with this process.

Micritic limestones have in most cases too low porosity and permeability to be regarded as reservoir rocks except when fractured. Tectonically fractured limestones may become cemented in relatively short geologic time before the migration of petroleum. Fractured dolomites are, however, more stable and likely to remain open longer because of the lower solubility of dolomite.

5.7.11 Formation of Carbonate Sediments Rich in Siderite and Chamosite (Ironstones)

Iron carbonates like siderite ($FeCO_3$) are stable carbonate phases with rather low solubility (Berner 1981). In the presence of sulphides, however, most of the iron will be precipitated as iron sulphides (i.e. pyrite or marcasite). Precipitation of siderite and other iron carbonates is therefore restricted to settings where the porewater has a low content of reduced sulphur (sulphides), as in freshwater and below the sulphate-reducing zone.

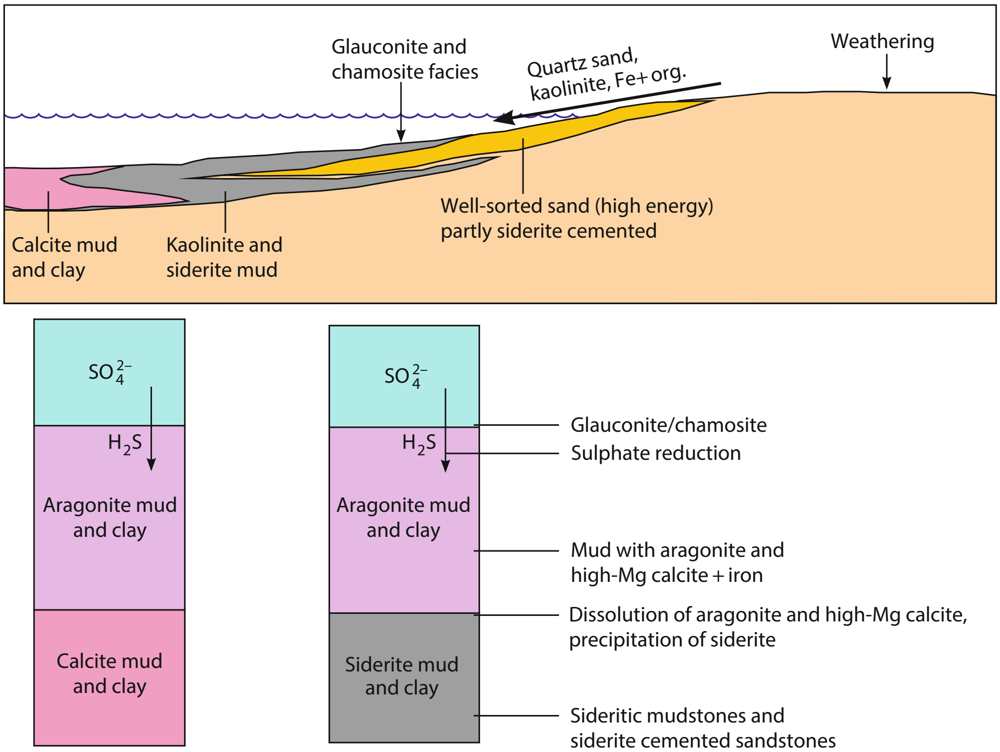


Fig. 5.63 Formation of sideritic limestones. During weathering large amounts of iron are released and transported as red fine grained iron oxides. Reacting with organic matter iron oxide is reduced to Fe^{2+} and when aragonite becomes unstable, siderite ($FeCO_3$) is formed instead of calcite because siderite is most stable (lower solubility)

There is almost no iron in solution in oxidised water and iron can therefore not be taken from seawater. During weathering on land, however, large amounts of iron may be released and transported as small particles of iron oxides, hydroxides or adsorbed on clay and organic matter. These are often concentrated in the distal parts of deltas where clastic sedimentation is low (Fig. 5.63).

Most of the iron supplied by rivers will be reduced just below the seafloor by small amounts of organic matter. It may precipitate at the redox boundary as iron oxides or as glauconite or chamosite. In carbonate sediments, aragonite may be partly replaced by siderite instead of calcite if iron is present. Because of the lower solubility of siderite all the available iron will be exhausted and precipitated as siderite before calcite can begin to precipitate.

Iron-rich sediments are typical of mixed carbonate and clastic sedimentary sequences. On carbonate platforms like the Bahamas there is little supply of iron because it is not connected to a source on land. All clastic iron-rich sediments are trapped in the deep water around the carbonate platform and there is practically no iron in the seawater covering the platform. Only small amounts of aeolian dust with some iron are transported to the Bahamas from Africa (Sahara).

5.8 Carbonate Reservoir Rocks

5.8.1 Introduction

Carbonate reservoir rocks are mostly limestones and dolomites and these rock types contain about 50% of the oil reserves in the world. They are particularly common in the Middle East accounting for many of the giant reservoirs, the majority of which have been in production for several decades.

Carbonate reservoir rocks differ in several important aspects from sandstone reservoirs:

1. The sediment particles are in most cases produced locally within the basin by biological production (fossils) or by chemical precipitation.
2. The mineralogy and the textures depend very much on the organisms precipitating the carbonates.
3. Carbonate minerals have higher solubility than silicate minerals in porewater, and also higher reaction rates at low temperature. Dissolution of grains and precipitation of cements may therefore be important also at shallow depth (<2 km).
4. The reservoir quality is highly dependent on the porosity, which may be of different types. The porosity in carbonate rocks may be pore space between grains (*intergranular porosity*) or porosity within grains (*intragranular porosity*), commonly fossils. These primary porosity types are usually strongly modified even at shallow depth during burial. Well-cemented carbonate rocks may be brittle, particularly during uplift, and tectonic fracturing may produce important *fracture porosity* and permeability.
5. Fractured carbonate reservoirs are very important both in limestones and dolostones (a rock of dolomite).

The most important porosity types in carbonate rocks are the following:

A. *Primary porosity* is the pore space that existed in the sediment just after deposition prior to diagenetic alteration. During burial the primary porosity is reduced by compaction and cementation.
   1. *Primary intergranular porosity* (pore space between carbonate grains)
      Intergranular porosity (inter-particle porosity) is the preserved primary pore space between grains. Pore shapes may vary considerably and are homogeneous only when the enclosing particles are of uniform size and shape (e.g. well-sorted ooids). The porosity increases with better sorting and more irregular grain shapes, attaining values up to approximately 60%. Also carbonate mud, just after deposition, has high intergranular porosity (70–80%) between the small mud particles, but the permeability is low and in most cases this porosity is rapidly reduced by mechanical compaction during early burial.
   2. *Intragranular porosity* (porosity inside grains)
      Intragranular porosity (intra-particle porosity) consists of pore space that occurs within grains. It is commonly formed by the decay of organic material within carbonate skeletons (e.g. foraminifera, corals and bryozoans).
   3. *Growth-framework porosity* (porosity inside a rigid framework produced by fossils)
      Growth-framework porosity is developed between and within organisms during the in-place growth of a carbonate framework. Typical examples are reef corals with uneven and patchily developed pores between the branches or between different colonial organisms.
   4. *Shelter porosity*
      Shelter porosity is often found below large plate-like grains which have acted as umbrellas protecting the pore space beneath from being filled with finer material. Typically porosity may be preserved below the convex side of molluscs and brachiopod shells. Organic material which is later decomposed may have produced shelter porosity which can be preserved if there is early cementation.

B. *Secondary porosity* is pore space produced by dissolution of grains or cement after deposition. Secondary porosity may therefore be regarded as an addition to the primary porosity. This requires a net transport of carbonate in solution out of the rock. If aragonite dissolves and the same amount of calcite precipitates inside the rock, no porosity is gained, though the distribution of pore space and the permeability may change drastically. Meteoric water is capable of dissolving both aragonite and calcite and transporting the dissolved material out from a limestone so that the net porosity is increased. At greater burial depth however the porewater is nearly always in equilibrium with calcite which is present in most marine sediments. The potential for significant net dissolution and formation of secondary porosity is therefore very limited.
   1. *Mouldic porosity*
      Mouldic porosity is formed by the selective dissolution of grains, particularly skeletal material with a primary aragonitic composition. Whole fossils or grains like ooids may dissolve after the precipitation of cement in the primary pores. These secondary pores thus become moulds of the dissolved structures. Mouldic porosity may also form by dissolution of fossils from a matrix of carbonate mud which has been

lithified. In the Jurassic Smackover Formation of Arkansas, USA, oomouldic porosity was created by the dissolution of ooids during freshwater flushing (More 1989).

2. *Fenestral porosity*
   Fenestral porosity consists generally of small elongate to equant pores which are typically 1–10 mm in diameter. These characteristic pores are often arranged in layers within the sediment and are most commonly encountered in algal mats facies where they have been produced by decaying organic matter or by desiccation.
3. *Breccia porosity*
   Breccia porosity may form by the collapse of a rock due to dissolution (e.g. dissolution of evaporites or limestone dissolution during karst weathering) or tectonic deformation.
4. *Fracture porosity*
   Fracture porosity commonly forms due to folding, faulting, salt doming, differential compaction, salt dissolution or fluid overpressure. Carbonate sediments often become cemented at shallow depth and may fracture and dilate so that fracture porosity is produced. Open fractures will gradually be filled with cement but fractures in dolomite may remain open longer than those in limestones.
   Shrinkage porosity is a special type of fracture porosity formed during early diagenesis when sediments may shrink i.e. due to dewatering. Septarian fractures in limestone concretions are also a kind of shrinkage fracture.
5. *Vuggy, channel and cavern porosity*
   Vuggy, channel and cavern (karstic) porosity are not fabric selective, i.e. they cut across grains and/or cement boundaries. The pores are of irregular size and shape and may or may not be interconnected. Many vugs are solution-enlarged moulds where evidence of the precursor grain has been destroyed by dissolution of the neighbouring matrix. Vuggy pores are commonly 1 mm–1 m in diameter. Cavern porosity commonly relates to meteoric (karstic) leaching and is differentiated from vuggy porosity by the larger pore size (man-sized or larger). Karst is formed by dissolution related to underground river systems and can therefore be very extensive and form large oil reservoirs.

5.8.2 Some Examples of Carbonate Reservoirs

5.8.2.1 Grainstones

Well-sorted carbonate sands (grainstones) are good reservoirs if the porosity is not reduced too much by cementation. The sand grains are usually ooids or fossil fragments. If the grains are mainly of low-Mg calcite, most of the porosity tends to be primary porosity which gradually fills with cement during burial. The source of most of the cement is then normally pressure solution along stylolites or grain-grain contacts.

Precipitation of early carbonate cement reduces the stresses at grain contacts and strengthens the grain framework. The mechanical compaction may therefore be reduced. When many of the grains consist of aragonite they may dissolve, producing secondary porosity while the dissolved carbonate fills the primary porosity. Dissolution of aragonitic ooids and fossils produces moulds which have very little communication between them and such mouldic reservoirs are characterized by rather high porosity but low permeability.

5.8.2.2 Fractured Reservoirs

The term fracture is used for any break in a rock and includes cracks, joints and faults. In many cases the fracture is less permeable than the matrix, but some may also be partly or totally open. Open fractures formed by extension are common during uplift and folding. Well-cemented limestones and dolomites tend to have brittle properties and faulting may produce a breccia with good permeability.

The rock fragments produced by the brecciation take the stress and prevent the fault plane from closing. Movements (off-set) along the fault plane have a similar effect. The porosity and permeability produced in carbonates is, however, temporary because it may relatively rapidly be filled with carbonate cement. Filling of open fractures by oil or gas will retard or inhibit calcite cementation and thus contribute to the conservation of the porosity. This is particularly true if the rocks are relatively oil-wet.

Fractures in limestones are commonly cemented by diffusion of carbonate from the adjacent matrix. Flow of water upward along the fault plane will cause dissolution of calcite rather than precipitation because of the retrograde solubility with respect to temperature.

In carbonates where the fractures are mostly open and forming a three-dimensional fracture network, the effective permeability can be very good. However, fractures are often formed during several phases of tectonic deformation and then only some of the fractures may remain open. The overall drainage during production is then more difficult to predict.

Fractured carbonate reservoirs often consist of dolomite. Well-cemented massive dolomite is rather brittle forming large fracture networks when subjected to tectonic forces.

Fractures in dolomite may be preserved longer than in limestones. This is because dolomite is both mechanically stronger and less soluble than calcite so that it will take longer for the fractures to be cemented up. For this reason we may find dolomite reservoirs at great depth (5–6 km) and also in uplifted basins. Fractured reservoirs may have very high permeability so that the reservoirs can be produced even if the average porosity is low.

5.8.2.3 Chalk

Chalk is a pelagic sediment where calcareous algae (coccolithophores) are dominant. Coccolithophores consist of low-Mg calcite and are therefore mineralogically stable during early diagenesis. The presence of aragonitic skeletal material is fairly meagre, so these mineralogically unstable fossils are not an important calcite source for early cementation. During periods with little pelagic sedimentation seafloor cementation may form hardgrounds. These are often encrusted by bivalves, boring organisms, bryozoa and sponges and may be mineralised by glauconite and phosphate.

For the most part the chalk is rather pure $CaCO_3$ but more clay-rich intervals like the Plenus Marl occur in the North Sea reservoirs, forming a tight low-permeability zone. Thin clay laminae enhance pressure solution and often develop into stylolites. The dissolution of calcite by pressure solution is the most important source of carbonate cement.

During diapirism of the underlying Zechstein salt (Upper Permian) the chalk became unstable and was reworked by gravity flows (turbidites and debris flows). The eroded sediments were already somewhat cemented and the debris flow units have proved to be better reservoir rocks than the primary chalk deposits. The early cementation may have strengthened the grains or aggregates of grains so that compaction during burial was reduced. In addition, the salt doming has produced fracturing in the chalk and these fractures have been essential in increasing the overall reservoir permeability.

Early filling of oil and gas in carbonate rocks like the chalk will retard calcite cementation and tend to preserved porosity compared to water-saturated chalk.

5.8.2.4 Carbonate diagenesis and reservoir properties

The initial mineralogical and textural composition determines the loss of porosity by mechanical and chemical compaction during burial. Since most carbonate sediments have been precipitated biologically both the mineralogy and the textural properties are primarily controlled by the organisms and later reworking. The content of unstable minerals, mainly aragonite and Mg calcite, and also the grain size ranging from mud to very coarse material, reflects the organisms that precipitated the carbonate.

In carbonate mud, aragonite will in most cases be replaced by calcite, producing a dense microcrystalline limestone. High contents of Sr are evidence of primary aragonite content.

Sediments containing almost only calcite, like the coccolliths making up chalk, will be rather stable chemically and also mechanically because the overburden stress in these fine-grained sediments is distributed on so many grain contacts. This is why the chalk in the Ekofisk Field may preserve 30% porosity at 2.5–3.0 km depth (Fig. 5.64).

Carbonate sand representing a coastal facies is likely to be flushed by freshwater, dissolving aragonite and precipitating calcite. This process may create karstic porosity and also enhanced porosity in sandstones.

At greater depth however the bulk chemical composition of carbonates does not change significantly except when influenced by hydrothermal activity (Bjørlykke and Jahren 2012, Ehrenberg et al. 2012). Below the reach of meteoric water flow the porewater flow is very low, limited by the rate of compaction (See Chap. 4).

In marine sedimentary basins there is nearly always some calcite, also in sandstones and shales and the porewater is therefore in equilibrium with calcite. This reduces the potential for dissolution, transport of solids in solution and precipitation both by advective flow of porewater and by diffusion, because the concentration gradients are so small.

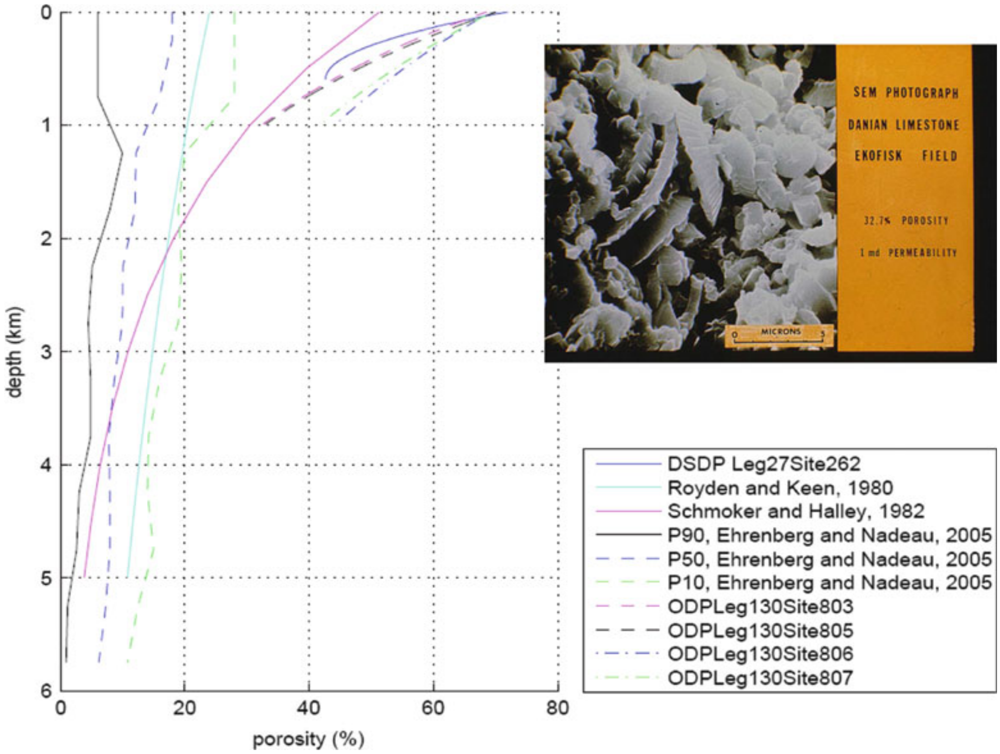


Fig. 5.64 Compaction curves for carbonates in sedimentary basins .The rate of porosity loss as a function of depth varies greatly with the initial textural and mineralogical composition. Chalk with little aragonite and high-Mg calcite preserve much porosity due its stable mineralogy (calcite) and fine grained composition.

Most black shales (source rocks) contain some carbonate layers or concretions which would neutralise organic acids and CO_2 generated during maturation of kerogen. In the absence of carbonate, black shales would generate acid porewater but this would be neutralised rapidly in contact with sediments containing calcite.

To increase the porosity of a 100 m thick limestone by 1%, 1 m^3 of calcite would have to be removed in solution (Fig. 5.65). This would require 27 000 volumes of porewater assuming 100 ppm) undersaturation with respect to calcite. Even if the porewater contained relatively high concentrations of organic acids, very large fluxes would be required to produce a significant net increase in (secondary) porosity (Barth and Bjørlykke 1993).

The potential for increasing the porosity of carbonate sediments is therefore very low except due to meteoric water flushing at rather shallow depth. Even if meteoric water can flow in porous carbonate sediments far offshore the porewater will rather quickly approach saturation with respect to calcite. Nearly all the dissolution will occur in the proximal parts where the meteoric water is recharged.

Early calcite cementation due to dissolution of aragonite may produce hard and mechanically stable limestones at shallow depth. Mechanical tests of shallow carbonates offshore Australia show that they would undergo very little mechanical compaction (strain) if subjected to stress of 40–50 MPa, corresponding to burial depth of 4–5 km (Croizé et al. 2010). This means that most of the porosity reduction would be chemical. In the case of sandstones, chemical compaction is mostly controlled by temperature due to the kinetics of quartz precipitation. In carbonates temperature is less important and the compaction rate is a very complex function of the distribution of stress on grain contacts and along stylolites.

In conclusion prediction of porosity in carbonate rocks must be based on the primary sediment composition and facies relationships, controlling chemical and mechanical compaction.

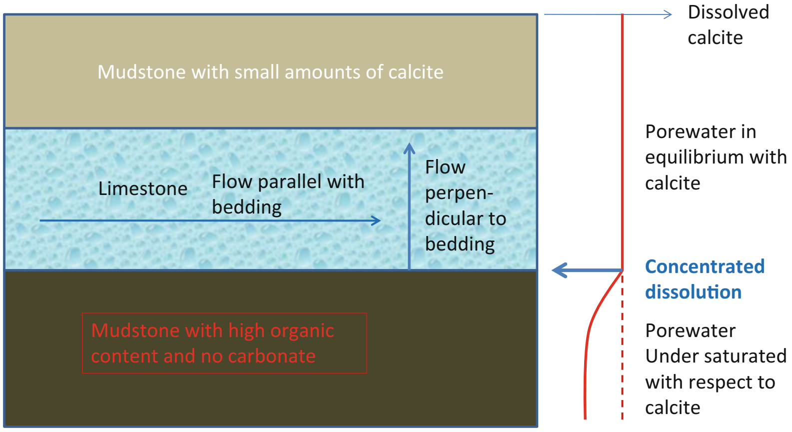


Fig. 5.65 Most marine sediments including sandstones and shales contain some carbonate and the porewater is nearly always in equilibrium with calcite. Most source rocks also contain some calcite. Black organic rich shales will produce some organic acids but these will be neutralized at the base of a limestone because of the high reaction rates of carbonates. Porewater undersaturated with respect to calcite can not create significant secondary porosity inside a limestone.

5.9 Summary

Limestones are mostly organically precipitated except in evaporitic environments. The evolution of calcareous organisms determines to a very large extent the initial grain size and mineralogy of the sediments, which in turn strongly influences the properties of carbonate reservoirs. The depositional environment is very important in controlling primary sorting of carbonate sand and the distribution of framework builders like reefs.

Limestones compact mechanically as a function of effective stress, but mineral dissolution and precipitation (chemical compaction) may also be important at shallow depth (0–1 km). Thermodynamically unstable aragonite dissolves at rather shallow depth which may cause the formation of secondary mouldic porosity and early cement. Sediments consisting of mostly calcite will compact mechanically until pressure solution becomes an effective compaction process. Grain-to-grain dissolution and stylolites then provide the sources of cement reducing the primary porosity.

Dolomite forms in most cases near the surface under evaporitic conditions, and under reducing condition in contact with seawater (as in reefs and atolls) where the sulphate content is low. Dolomitisation of calcite requires dissolution and reprecipitation and a large-scale supply of magnesium and there is no reason that this in itself should cause increased porosity even if dolomite is denser than calcite.

Dolomite is both mechanically and chemically more stable (less soluble) than calcite and therefore preserves more of its porosity during burial. Extensional fractures formed tectonically will tend to stay open longer in dolomite than in limestones and may therefore form important reservoirs.

Carbonate sediments may compact both mechanically and chemically also at shallow depth and low temperatures. Early cementation due to dissolution of aragonite and precipitation of calcite cement will increase rock strength and prevent further mechanical compaction. Carbonates are very complex with respect to reservoir properties. This is because of the great variation in the primary composition of the sediments, which may be precipitated chemically or biologically by many different types of organisms. Expertise is required in disciplines ranging from palaeontology to mineralogy and complex diagenetic reactions.

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