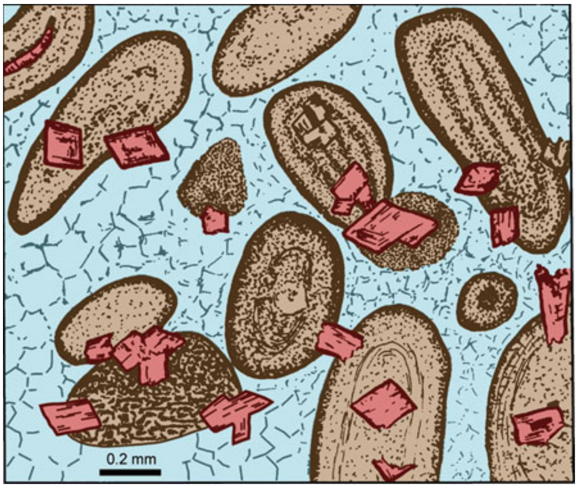

Fig. 5.57 Partly dolomitised oolite. The dolomite rhombs (*dark brown*) transect the oolite grains (*light brown*) and the surrounding spar crystals (*blue*), indicating a late diagenetic dolomitisation (modified from Greensmith 1978)

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

Mg^{2+} is more strongly hydrated than Ca^{2+} in seawater. The Mg^{2+} ion together with its surrounding water molecules, $Mg(H_2O)_6^{2+}$, 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 $MgCl_2 + NaCl + CaCl_2$. The main reason that 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 $\left(NH_4^+\right)$ 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. 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.

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 Late Diagenetic Dolomite

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.

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. 5.58).

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

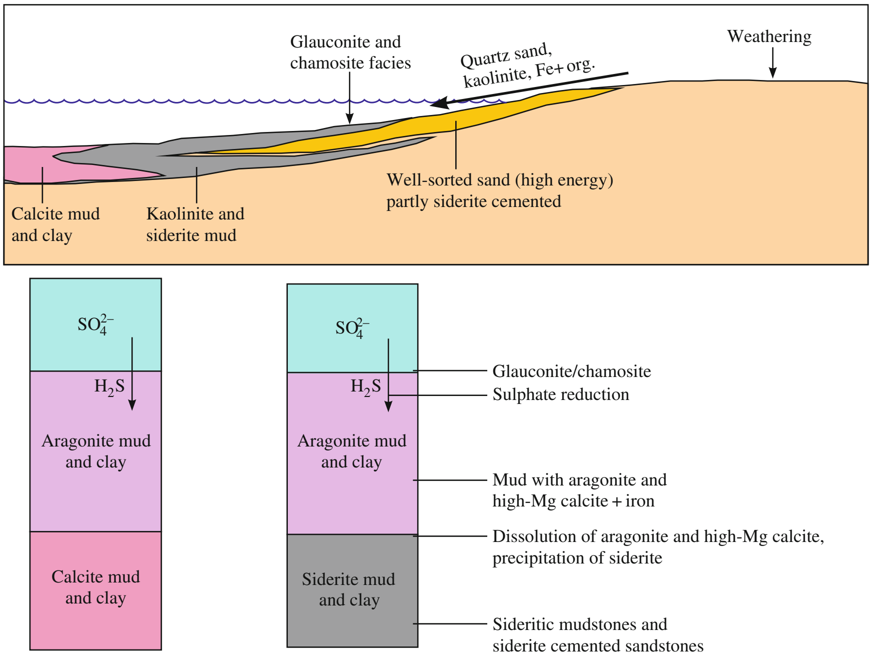

Fig. 5.58 Formation of sideritic limestones. During weathering large amounts of iron are released and transported as red fine-grained iron oxides. Reacting with organic matter iron oxide is reduced to Fe^{2+} and when aragonite becomes unstable, siderite ($FeCO_3$) is formed instead of calcite because siderite is most stable (lower solubility)

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 almost 40% of the oil reserves in the world. They are particularly common in the Middle East.

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*.

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