of their reduced solubility in the oxidised state. Iron may also be precipitated below the redox boundary as iron sulphides or iron carbonate (siderite), though iron carbonates will not form during sulphate reduction. This is because all the iron will be precipitated as sulphide, which has a much lower solubility than siderite. Manganese is not precipitated as sulphides because of the high solubility of Mn-sulphides, but may be precipitated as Mn-carbonate in the reduced zone.

At a depth where there is practically no more free dissolved oxygen in the porewater, sulphates can be used by sulphate-reducing bacteria. The reduction of sulphates produces sulphides such as pyrite.

The composition of clastic sediments is modified by the addition of new components produced locally within the basin:

(1) Biogenic carbonates and silica.
(2) Authigenic minerals precipitating near the seabed such as carbonates, phosphates, glauconite, chamosite, sulphides and iron and manganese minerals.
(3) Meteoric water-flushing causing leaching of feldspar and mica and precipitation of kaolinite beneath the seafloor.

4.5 Importance of Biogenic Activity

Bioturbation plays an important role in changing the textural composition of the sediments after deposition. The burrowing organisms eat mud and thereby oxidise organic matter and physically destroy the primary lamination. Sediments overturned by bioturbation become more exposed to oxidation at the sea or lake bottom. Bioturbation may reduce the porosity and permeability of sandy laminae by mixing clay with clean sand.

Bioturbation will also destroy thin clay laminae, which may significantly increase the vertical permeability and this may be very significant for reservoir quality. Undisturbed primary lamination may be evidence of rather rapid sedimentation giving little time for a burrowing bottom fauna to become established, or alternatively indicate strongly reducing conditions restricting the fauna. Black shales usually have well preserved lamination due to lack of burrowing organisms. The presence or absence of burrowing also influences the physical properties, particularly the difference in velocity and resistivity parallel and vertical to bedding (anisotropy) and this may be important for geophysical modelling.

Burrowing worms produce faecal material which may develop into smectite-rich clays, which in turn may develop into chlorite coatings, thus improving reservoir quality. Early diagenetic formation of coatings on quartz grains is extremely important due to its role in preserving porosity at greater depth.

Most clastic depositional environments have some organisms producing organic matter which, at least in part, is incorporated within the sediments. Both sandstones and mudstones nearly always contain significant amounts of biogenic material from calcareous, and sometimes also siliceous, organisms and this may later be an important source of carbonate and silica cement at greater burial depth.

Marine organisms composed of aragonite dissolve during relatively shallow burial and calcite precipitates either as replacements within the fossils (neomorphism) or as cement in pore space between the grains.

Carbonate cement in sandstones may form layers or concretions and in most cases is derived from biogenic carbonate, particularly from organisms composed of aragonite. Siliceous organisms composed of opal (e.g. diatoms or siliceous sponges) may be an important source of micro-quartz coatings on quartz grains at greater depth.

Carbonate cements in both mudstones and sandstones are mostly due to dissolution and reprecipitation of biogenic carbonate or early aragonite cement. There are usually no other major sources of carbonate cement. In the sulphate-reducing zone, carbonate concretions form, often with a negative δ^{13}C due to the CO_2 produced during sulphate reduction. Carbonate concretions in cores may be mistaken for continuous carbonate layers but it is possible to recognise that they are concretions (Walderhaug and Bjørkum 1998). Even if CO_2 is generated from organic matter, there are few Ca^{2+} sources available in sandstones or mudstones for making calcite. Leaching of plagioclase can supply some Ca^{2+}, which can be precipitated as calcite, but this can only account for very small amounts of the calcite observed in such sediments. The distribution of carbonate cement is related to facies and sequence stratigraphy.

The evolution of pelagic planktonic calcareous organisms in the Mesozoic drastically increased the supply of carbonate on the seafloor, including in deeper waters. Before then most of the carbonate was produced by benthic organisms restricted to shallow water facies. Upper Jurassic and younger sandstones often contain abundant calcite cement due to the “rain” of calcareous algae, foraminifera and other planktonic organisms settling on the seafloor. Silica-producing organisms may also be important for diagenesis and reservoir quality at greater burial. Organisms like siliceous sponges are composed of amorphous silica which at higher temperatures will be dissolved and replaced by opal CT and quartz. Diatoms and radiolarians may also be a major source of silica which will be precipitated as quartz. Diatoms appeared during the Cretaceous and have been a major source of amorphous silica during the Cainozoic. Diatoms can produce pure siliceous rocks like the Tertiary Monterey Fm of California, which is both a source rock and a fractured reservoir rock.

Biogenic carbonate is in most cases the main source of calcite cement. The distribution of such cement must therefore be linked to sedimentary facies, more specifically to biological productivity relative to the clastic sedimentation rate. Environments with low clastic sedimentation rates, particularly submarine highs, often have high organic carbonate production.

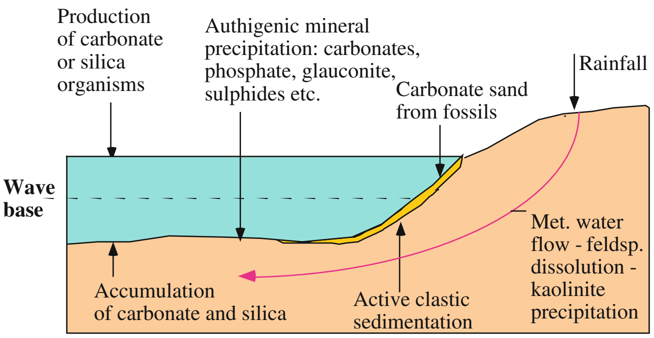
4.6 Meteoric Water Flow and Mineral Dissolution

Meteoric water is rainwater which infiltrates the ground. Initially this water is distilled water and therefore undersaturated with respect to all minerals. The reactions between meteoric water and the land surface are an important part of the weathering process. Rainwater contains carbon dioxide (CO_2) and sulphur dioxide (SO_2) from the air and is therefore slightly acidic, producing carbonic acid (H_2CO_3) and sulphuric acid (H_2SO_4).

Some of the rainwater seeps down to the groundwater, and as long as the groundwater table is above sea level, meteoric water will flow along the most permeable beds into the basin. Meteoric water will first dissolve carbonates and then slowly dissolve unstable minerals like feldspar and mica (Fig. 4.3).

Decaying organic matter in the ground produces CO_2 which is added to the groundwater, making it more acid. Humic acids generated by decaying plants also hasten the weathering reactions. At the same time this acidity is neutralised by weathering reactions with silicate minerals like feldspar and the dissolution of carbonates which consume protons (H^+). As the groundwater reacts with minerals and in some cases with amorphous phases, it will approach equilibrium with many of the minerals present and this will happen first with carbonates. In the case of silicate minerals these reactions are very slow so the porewater may remain under- or supersaturated for a long time with respect to silicate minerals like quartz and feldspar.

Depending on the elevation of the groundwater table and the distribution of permeable layers (sandstones), the flow of meteoric water can extend beneath the seafloor far out into sedimentary basins. Reactions between meteoric water and minerals occur in the



The primary clastic composition is modified by:
1) Meteoric water leaching and precipitation of kaolinite.
2) By addition of biogenic carbonate and silica.
3) By precipitation of authigenic minerals on the the seafloor.

Fig. 4.3 Diagenetic processes in shallow marine environments. Sandstones deposited in these environments will be flushed by meteoric water flow and/or from the delta top, causing dissolution of feldspar and mica. Calcareous fossils and early carbonate cement may be a very important addition to the composition of the sandstones. The occurrence of siliceous organisms such a sponges can strongly influence reservoir quality at depth ground and are a kind of subsurface weathering along the groundwater flow paths. Leaching by meteoric water is generally strong in fluvial and alluvial sediments. Even within dry river beds there is a focused flow of groundwater.

The groundwater level represents the head (potentiometric surface) for groundwater flow and groundwater therefore has a potential to flow through sediments or other aquifers far below sea level.

The rates of leaching of minerals like feldspar and mica and the precipitation of kaolinite are functions of the flux of groundwater flowing through each rock volume per unit of time. These are in principle weathering reactions similar to those which take place during normal weathering in a humid climate. Cations like Na^+ and K^+ are stripped from silicate minerals like feldspar and mica and brought into solution.

These reactions can be written as below:

$$\begin{array}{llll} 2K(Na)AlSi_3O_8 + 2H^+ + 9H_2O = & Al_2Si_20_5(OH)_4 + & 4H_4SiO_4 & + 2K^+(2Na^+) \\ \text{Feldspar} & \text{Kaolinite} & \text{dissolved silica} & \text{dissolved cations} \end{array}$$

$$\begin{array}{ll} 2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O = & 3Al_2Si_20_5(OH)_4 + 2K^+ \\ \text{Muscovite} & \text{Kaolinite} \end{array}$$

We see from these reactions that low K^+/H^+ ratios will drive the reactions to the right. Dissolution of feldspar and mica and precipitation of kaolinite require that the reaction products, Na^+, K^+ and silica, are constantly removed and that there is a supply of new freshwater which is undersaturated with respect to feldspar and mica. Without a through flow of water these reactions stop because the reaction products on the right hand side of the equations are not removed. Groundwater must flow into the ground and up to the surface again or on to the seafloor. A clay coating on feldspar often remains and the dissolved aluminium and some of the silica is precipitated as kaolinite, so there is a rather small increase in porosity and reduced permeability (Fig. 4.4a). The pores between the kaolinite crystals may be too small (Fig. 4.4b, c) to be filled with oil so that the oil saturation is reduced in kaolinite-rich sandstones (see Chap. 20).

The silica released from feldspar dissolution can normally not be precipitated as quartz because of the low temperature near the surface, but remains in solution even if the porewater is highly supersaturated with respect to quartz. Silica must, however, also be removed along with potassium by the flowing water. If the silica concentration in the porewater increases too much, kaolinite is no longer stable and smectite will precipitate instead. This happens in sediments rich in volcanic material or biogenic silica and where the flux of meteoric water is low. In a desert environment evaporation of groundwater may increase the silica concentration and make smectite more stable.

The porewater does not have to be acidic for kaolinite to form, but the K^+/H^+ ratio must be low. If the pH is high the K^+ concentration has to be correspondingly lower. Authigenic kaolinite may also form in impure limestones as a result of meteoric water flushing, and the porewater is then certainly not acidic. Even if there is only a small amount of carbonate it will buffer the composition of the porewater.

The average groundwater flux is determined by the rainfall and the percentage of water infiltration into the ground. In moderately humid climates the rainfall may be 1 metre/year and the infiltration in the order of 0.1–0.3 metres/year. High-permeability subsurface pathways (aquifers) focus the flow. The aquifers may be sand or gravel beds in muddy sediments. Meteoric water may penetrate deeply into sedimentary basins because of the potential created by the head of the groundwater table but the flux of meteoric water decreases strongly in the deeper parts of basins.

The meteoric water will gradually become less undersaturated with respect to minerals like feldspar and mica and its leaching capacity will gradually diminish. The most intense mineral leaching will therefore occur near the surface or at relatively shallow depth beneath the seafloor. In areas with low sedimentation rates the total flow of water through the sediment will be higher because the sediments remain longer at shallow depth. If the sediment stays in the zone intensively flushed by meteoric water, the amount of feldspar leaching will be high. In basins with high sedimentation rates, synsedimentary faulting

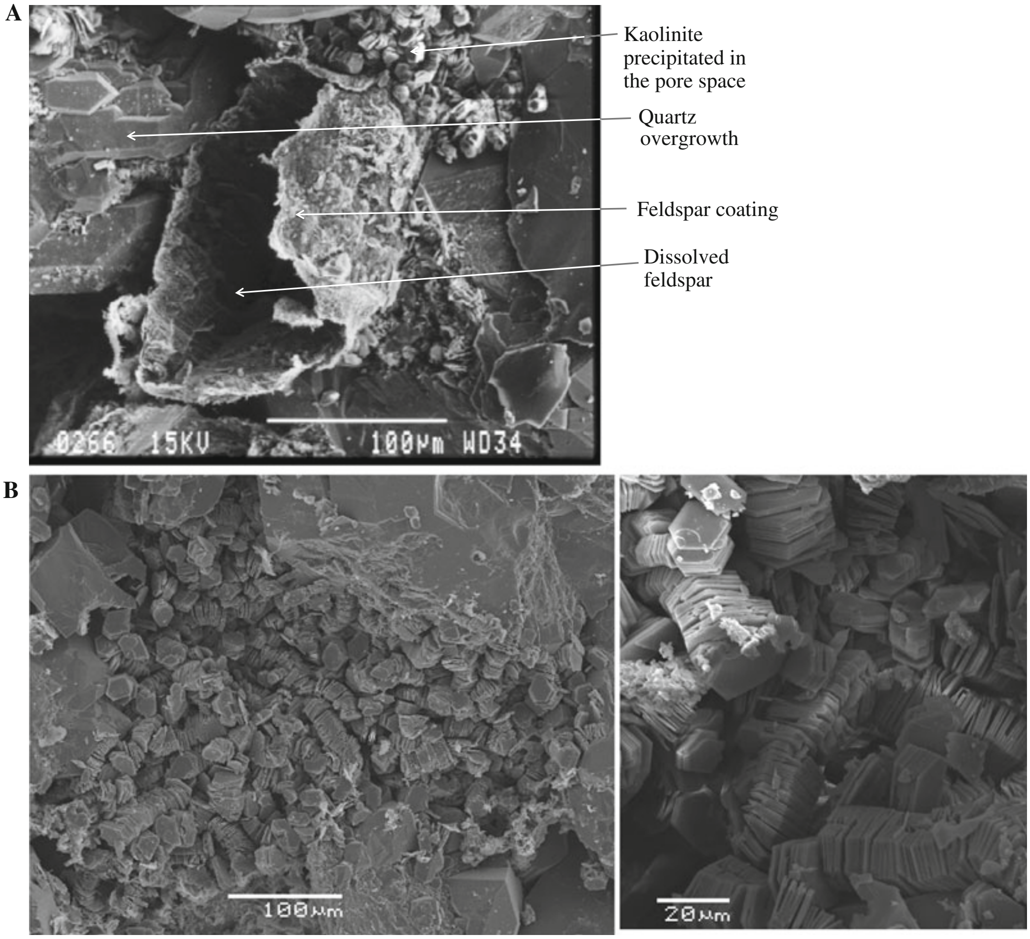


Fig. 4.4 (**a**) Scanning electron microscope picture of a sandstone (Brent Group) from the North Sea. The scale is 0.1 mm (100 µm). In the centre of the picture we see a cavity left by a dissolved feldspar grain. A clay rim around the feldspar remains undissolved, outlining the primary grain morphology. In the *upper part*, authigenic kaolinite crystals are forming small (10–20 µm) booklets. They have formed from the silica and aluminium released when the feldspar was dissolved by meteoric water. To the *left*, authigenic quartz is growing on clastic quartz. Note the relatively large pores between quartz and feldspar grains and the small pores between kaolinite crystals. (**b**) Pore-filling authigenic kaolinite. We see that the pores between the kaolinite crystals are very small – only 1–2 µm (from T.E. Maast unpublished)

(i.e. growth faults) may disconnect sand bodies from the main freshwater aquifers. The degree of feldspar leaching could then be used as an indication of the conductivity in the reservoir.

River water and groundwater is usually supersaturated with respect to quartz but undersaturated with respect to amorphous silica. About 10–30 ppm dissolved silica is common in groundwater and shallow porewater while the solubility of quartz at 20°C is only 4–5 ppm, showing that quartz does not form at low temperatures. In very alkaline water (i.e. E. African lakes), quartz may precipitate at low temperatures.

The early burial history of sandstones is not well studied for the simple reason that cores are not normally taken at depths shallower than 1–1.5 km in offshore basins, while onshore, erosion may have removed most of the youngest sequence. Looking at sandstone thin sections one can often get the impression that kaolinite is precipitated at a relatively late stage because it is a pore-filling mineral that may subsequently be surrounded by quartz cement. More detailed textural studies and isotopic evidence indicate that the kaolinite is formed early and may be enclosed in quart cement. Pore-filling kaolinite must, however,