Chapter 6

Mudrocks, Shales, Silica Deposits and Evaporites

Knut Bjørlykke

6.1 Mudrocks and Shales

Mudrocks and shales are the most abundant lithologies in most sedimentary basins. They are important because shales include source rocks for oil and gas, and recently large reserves of gas have been found in shales. Shales may therefore be reservoir rocks because they may have significant porosity and some (although small) permeability to flow gas. The rising production of oil and gas from shales (shale gas and shale oil) in recent years has led to a new interest in the primary composition and the properties of mudstones and shales as functions of the burial depth and temperature. The seismic image for sandstones also depends on the properties of adjacent shales.

There is however no precise definition for mud or mudrocks. It is used to describe fine-grained rocks with a relatively high content of clay-sized particles, mostly clay minerals but also other minerals. Carbonate mud is discussed under carbonate sediments. The upper limit for clay particles is 0.004 mm in the geological literature, but in the engineering literature (soil science) 0.002 mm is commonly used. Because clay minerals are essentially flat flakes, they have large surface areas, some minerals like smectite having several hundred m^2/g. Kaolinite minerals are much larger (>0.01 mm) and have much smaller surface area. There is a cohesion between small particles, and clay minerals also have a surface charge due to broken bonds in the mineral structure. This cohesion plays an important role in sedimentary processes of erosion, transport and deposition since most clastic sediments contain significant amounts of clay. The properties of clays are not only controlled by the mechanical strength of the grains but also by the composition of the pore fluid. This is also true during sediment compaction. Kaolinite has much lower surface charge than smectite and illite.

Mudrocks and shales are often treated as one lithology, but they vary greatly as a function of both mineral composition and grain-size distribution. A relatively large fraction of grains may be larger than clay size, but as long as the larger particles are floating in a finer matrix the properties are dominated by the clay-sized particles.

Here we will discuss siliceous (i.e. non-carbonate) mudrocks and clay. The clay minerals in mudrocks may have different origins:

(1) Clay minerals formed by weathering of igneous and metamorphic rocks.
(2) By erosion of older shales and mudrocks.
(3) From volcanic ash.
(4) By diagenesis on the seafloor and during burial.

The clay mineral assemblage produced by weathering depends on the composition of the rocks that are being weathered, and the climate. A humid climate will favour the formation of kaolinite. In a granite or gneiss, feldspar, mica and most other silicate minerals will dissolve and the aluminum and silica will precipitate as kaolinite, and after long periods of weathering, as gibbsite ($Al(OH)_3$. The quartz grains will be weathered out as sand and their grain size will reflect the quartz crystal size range in the parent rock (see Chap. 3). The result is a bimodal distribution of sand and kaolinitic clays.

In areas with mostly basic rocks like anorthosite, gabbro and basalts, weathering will only produce clay

---

K. Bjørlykke (✉)
Department of Geosciences, University of Oslo, Oslo, Norway
e-mail: knut.bjorlykke@geo.uio.no

K. Bjørlykke (ed.), *Petroleum Geoscience: From Sedimentary Environments to Rock Physics*,
DOI 10.1007/978-3-642-34132-8_6, © Springer-Verlag Berlin Heidelberg 2015

minerals, since there is no quartz which in more acid rocks forms most of the sand fraction. Minerals like basic plagioclases, pyroxenes and hornblende will quickly break down to clay minerals such as kaolinite, and after long periods of weathering gibbsite ($Al(OH)_3$.

6.2 Supply of Clay Minerals to Sedimentary Basins

While kaolinite is derived from humid climate weathering, smectite and illite are more typical of deserts because there is less flow of fresh (meteoric) groundwater. Chlorite is mostly derived from erosion of metamorphic rocks in relatively cold climates where weathering is slow. In warmer and wetter climates chlorite will break down, but may occur near basalts and basic volcanic rocks, particularly in the marine environment where chlorite is more stable. Volcanic ash consisting of glass and unstable volcanic mineral assemblages may alter to smectite, both on land and on the seafloor. In deep sea sediments, zeolites like phillipsite are common.

Erosion of older mudrocks and shales can produce nearly all types of clay minerals. Glacial clays are essentially mechanically ground down sedimentary, metamorphic or igneous rocks. Since there is very little chemical weathering, their chemical composition is nearly the same as the rocks eroded. Chlorite and illite are formed by disintegration of mica and metamorphic chlorite, and most of the quartz and feldspar is preserved. We find such clays accumulating in front of modern glaciers that terminate in lakes or the ocean. When the continental ice sheet withdrew from Scandinavia 10,000–9,000 years ago, thick glaciomarine clays were deposited in the fjords and sea. Subsequent postglacial isostatic uplift elevated the inland portions by up to 200 m above the present sea level.

Clay transported by rivers into lakes will remain suspended for some time (due to slow flocculation) and very finely laminated clayey sediments will be deposited. In lakes there is usually less bioturbation to destroy the lamination than in marine environments. Freshwater sediments tend to be finely laminated compared to most marine sediments.

Clay from rivers is not transported far offshore and we see from satellite pictures that there is clear water not so far from the delta front (Fig. 6.1). When the clay minerals come into contact with seawater, the salt content in the water will cause the clay particles to flocculate, which makes them sink faster to the bottom near to the river mouth. This is because clay minerals have a negative charge which prevents them from sticking together in freshwater. In seawater these negative charges are neutralised by the cations in seawater, such as Na^+, K^+, Mg^{++} and Ca^{++}. K^+ is most effective because it is not so strongly hydrated (surrounded by water molecules) as Mg^{++}, $Na^+$and Ca^{++} (Fig. 6.2).

Clay minerals transported into marine sedimentary basins will also be subjected to sorting by grain size. Recent sediments in the Gulf of Mexico contain about 30–40% silt in addition to clay and compact rather

Fig. 6.1 Satellite photograph showing the distribution of clay *outside* the Mississippi delta. The limited extent of the delta mud is due to flocculation of the clay particles when freshwater is mixed with ocean water

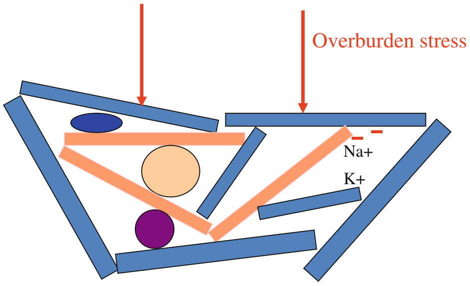

Fig. 6.2 Poorly compacted clays have a “house of cards” structure. Clay minerals have negative surface charges due to broken chemical bonds in their silicate structure. In freshwater there is repulsion between the clay minerals, keeping them in suspension. In seawater, cations like sodium and potassium help to neutralise these charges and the clays will form denser aggregates (flocculation)

efficiently from about 80% porosity on the sea floor to about 35–40% at about 500–600 m depth (Day-Stirrat et al. 2012). This may be due partly to poor sorting. Kaolinite is the coarsest grained of the clay minerals and will therefore be deposited in the most proximal parts of deltas and shorefaces while illite and smectite will be transported further out into the more distal parts (Fig. 6.1). As sedimentation progrades into deep water on a continental margin illitic and smectitic clay will form the base and grade upwards into more kaolinite-rich sediments (Bjørlykke 2011).

From deltas and the shelf edge, clayey sediments as well as sand may be transported down the slope by turbidity currents or debris flows. In the most distal shelf or deep-water facies, sedimentation rates can be very low and aeolian dust may make up much of the sediment deposited. This is particularly true offshore dry areas like the Sahara in West Africa. This mud is rich in fine-grained smectite and illite, often with iron oxides which may serve as an important nutrient for organic production in the South Atlantic Ocean. Volcanic ash may be deposited over large areas. During transgressions, extensive layers of mud may be deposited on shelves along the basin margin. This mud may later be eroded and supplied to the basin during periods of uplift, so that the prograding regressive sequences may be rich in clay. Weathering of basic rocks like anorthosites and gabbroid rocks proceeds rapidly and produces almost only clay minerals and very little sand, because of the lack of quartz.

6.3 Silica (SiO_2) Deposits

Silica which is liberated through weathering goes into solution as silicic acid (H_4SiO_4). Even if quartz and also feldspar have relatively low solubility, large quantities of silica are transported by rivers out into the sea. The total amount of dissolved silica added annually to the sea is estimated to be about 4×10^8 tonnes. Some silica is also introduced from the mid-oceanic ridges, but is probably of only very modest significance compared with the fluvial input. An equal amount of silica must be removed for the seawater composition to remain constant. Silica is removed biologically as biogenic silica, and through the formation of silicate minerals in the sea. Radiolaria and diatoms are particularly efficient at removing silica. As a result, even though quartz is only very slightly soluble in seawater (3–6 ppm SiO_2), surface water (seawater) is usually undersaturated with respect to quartz. This is because the organisms can precipitate silica from seawater even if the concentration of SiO_2 is far less than 1 ppm. While amorphous silica has a solubility of about 150 ppm, cristobalite and tridymite have a solubility of 6–15 ppm, depending on the degree of order in the crystals. The most important silica-producing organisms are:

Phytoplankton: diatoms and silicoflagellates
Zooplankton: radiolaria
Silica sponges

These organisms are built up of amorphous silica (opal A). The total production of organic silica in the oceans has been estimated to be from 2×10^{10} up to 10^{11} tonnes/year. The largest contribution comes from diatoms, and also a very large percentage (50–70%) of the total primary production of carbon (2×10^{10} tonnes/year) is ascribable to diatoms consisting of about 60% silica and 40% carbon.

The flux of silica into the oceans from the continents is far less than the organic production of siliceous organisms. The approximately 4×10^8 tonnes/year brought by rivers only represents about 1% of all organic silica precipitation. Some silica is added to the sea through submarine volcanism along the oceanic spreading ridges. Seawater is being circulated (convected) through hot basalt, dissolving silica and precipitating sulphides from the sulphate in the seawater. Even with this source of silica, the supply to the ocean water can not balance the amounts precipitated biologically. Since we must assume that the composition of seawater has been relatively constant, this means that only about 1% of the overall organic silica production is retained in sedimentary deposits. Most of the silica from plankton redissolves in the undersaturated seawater before it reaches the bottom, and some also dissolves on the seafloor and diffuses up into the water column. Consequently it is only when the rate of organic precipitation is higher than the rate of solution that we find deposition of organic silica.

Diatoms dissolve because seawater is undersaturated with respect to silica, and large quantities of organic material can thereby be released without oxidation taking place. Organic matter produced by the solution of diatoms thus constitutes a large part of the total organic matter accumulated. Phosphates, nitrogen and various trace metals are also released through the disintegration of plankton as they sink through the water column. These recycled nutrients can once more provide the basis for organic production when water

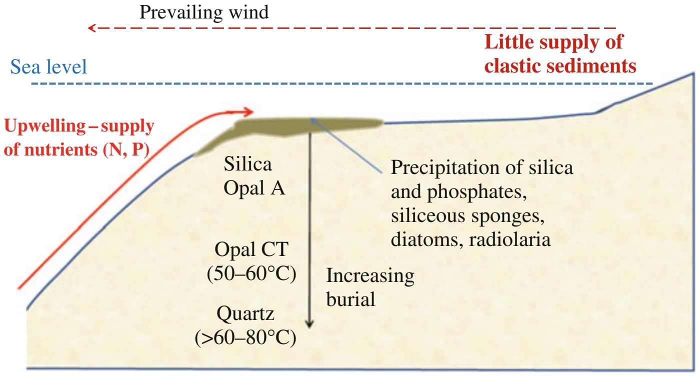

Fig. 6.3 Upwelling of water rich in nutrients causes biological precipitation of silica and phosphates. The silica deposits (opal A) will, when buried, be altered to opal CT and then to quartz

wells up to the photic zone (Fig. 6.3). The upwelling currents also prevent supply of clastic sediments from land, so that nearly pure silica can be deposited.

Opal A will decompose to opal CT which may consist of bladed crystals forming small spheres called lepispheres. Because more energy (temperature) is required to precipitate quartz, minerals like cristobalite and tridymite are formed. These are minerals which are stable at very high temperatures (1,000–1,500°C), but precipitate out instead of quartz at low temperatures, even though quartz is thermodynamically more stable.

This phase is called opal CT, sometimes also porcellanite. Opal CT will, when subjected to higher temperatures, slowly dissolve and the silica will be precipitated as quartz.

Amorphous silica (opal A) dissolves and is replaced by opal CT, usually at a temperature of around 50–70°C which corresponds to about 1.5–2 km of overburden at average geothermal gradients. The reason why amorphous silica (opal A) can exist so long despite being thermodynamically unstable, is that quartz does not crystallise at low temperatures. Opal CT is transformed into quartz at temperatures around 60–80°C. The change in acoustic impedence which accompanies the transition from opal A to opal CT and then to quartz (chert) may produce a significant seismic reflection. Because these reactions are controlled by temperature they tend to occur as horizontal zones that may be mistaken for a fluid contact (gas/water or oil/water).

Vast amounts of diatoms are found today round Antarctica, and the thick sediment accumulations there have a very high content of amorphous silica. In the North Sea too there are now large amounts of silica but there is little net accumulation. In the Tertiary sequence in the North Sea there are major silica beds. Those with the greatest extent are associated with ash layers from Eocene volcanicity related to the opening of the Norwegian–Greenland Sea and consist of radiolarians and diatoms together with altered volcanic sediments (ash) with abundant smectite. Well-cemented silica beds of Eocene age are called Moler in Denmark, and Balder Formation in the North Sea where it generates a very prominent seismic reflector.

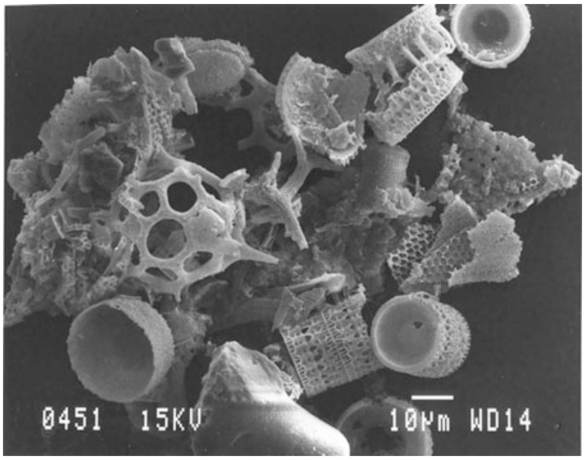

Fig. 6.4 Diatoms and radiolaria from Oligocene siliceous sediments from the North Sea basin (1,430 m depth). From Thyberg et al. (1999)

In the Oligocene there are also nearly pure silica beds, and where they are buried to less than 1,500–1,600 m, fossils of opal A such as diatoms are exceptionally well preserved (Fig. 6.4). The silica is still opal A. When altered to opal CT most of the primary structures are gone.

When opal A and opal CT dissolve, the water becomes oversaturated with respect to quartz which then begins to crystallise at a large number of points (nucleii). It thus forms microcrystalline quartz, known as "chert". The dark colouration is due to organic material. In Europe, flint is the best known variety of chert which is abundant as concretions in the Upper Cretaceous Chalk. Cherts are formed of silica which has been finely distributed in the sediment, largely as sponges and radiolaria often concentrated along special horizons. Because small particles with a large specific surface are highly unstable, they will dissolve and silica will be precipitated in nodules which are massive structures with a small specific surface and in consequence thermodynamically more stable.

Novaculite is more or less synonymous with light, laminated chert which contains less organic material. Porcellanite is a term applied to more contaminated silica (chert) which has the appearance of unglazed porcelain. Laminated chert is very common in Palaeozoic and Mesozoic sequences immediately above oceanic seafloor (ophiolites) near spreading ridges, sourced from water circulating through the basalts. This chert may be white, grey or dark, depending on the content of organic matter or traces of iron, magnesium etc.

Chert containing oxidised iron has a reddish colouration and is called jasper. Jasper may form on the seafloor near the spreading ridges. When water circulates through the spreading ridges it carries away iron which then oxidises in the seawater and produces the red colour. When mixed with silica which is precipitated mostly by organisms, chert is formed. Jasper is found on top of obducted ocean floor basalts in nappes of Ordovician age in western Norway.

Chert has also been found during ocean drilling, overlying present ocean floor of Cretaceous or Tertiary age. Although all amorphous silica has been converted to quartz, it is often possible in chert to detect the remains of organic particles, e.g. radiolaria, especially in Palaeozoic chert deposits. Younger silica deposits are chiefly precipitated by diatoms. In areas with upwelling, silica may also be deposited in relatively shallow water. The Monterey Formation in California is a well-known example of chert formed in an upwelling zone. Around the Pacific Ocean similar chert of Upper Miocene age is found. The Monterey Formation is both an important source and reservoir rock for oil in California, especially in the Ventura Basin. It is a source rock on account of the organic matter produced by the diatoms. After the transformation to opal C and quartz, the rock fractured due to tectonic folding, so that it became a fractured reservoir (Fig. 6.5).


Oil seep in chert. Santa Maria, north of Santa Barbara

Fig. 6.5 Monterey chert with oil seeps, California

Subjected to 1–2 km of overburden, amorphous silica is converted to quartz and the rock becomes brittle and fractures during folding and faulting to form good fractured reservoirs.

The Monterey Formation contains organic-rich shales and phosphate deposits. This is a very common association when sediments have been deposited in upwelling areas with a limited clastic supply. Transformation of amorphous silica to quartz appears to depend on the chemical environment (temperature, pH, ionic strength, Mg concentration). Clay minerals reduce the conversion rate. Because of its high organic content the Monterey formation has recently been considered to have a potential for production of shale oil. It is however not clear if this will be permitted for environmental reasons.

In soils, however, quartz may precipitate at low temperature near the surface, forming *silcrete* resulting in very hard ground.

Precambrian chert deposits typically occur in conjunction with banded iron formations (BIFs). It is uncertain whether there were organisms which could precipitate silica in Precambrian times, or whether Precambrian chert was chemically deposited. There are no definite indications of biological precipitation of Precambrian chert, and since silica must also have been added to the oceans, we must assume that the ocean was saturated with respect to silica, and that there may have been inorganic precipitation of silica.

Silica deposits may also be formed in lakes by freshwater diatoms. In lakes along the rift systems of East Africa, there are thick deposits of diatomite which are exploited for use in insulating materials. A great deal of CO_2 is taken from the lake water by diatoms and other algae for photosynthesis, and the water therefore becomes strongly basic (pH 9–10). This increases the solubility of silica, thus increasing the corrosion of silicate minerals. Examples of this are found, for instance, at Lake Turkana in Kenya. Volcanic rocks and water from hot springs are also important sources of silica.

Chemical precipitation of silica may also take place in evaporite basins, and in ephemeral lakes which dry up between rainy seasons.

6.4 Evaporites

Evaporites consist of minerals which have crystallised out through evaporation of water. This can happen in many ways:

1. Evaporation of seawater in completely or partly cut-off marine basins.
2. In lakes which have little or no outlet and a high evaporation rate.
3. Through evaporation of seasonal precipitation which collects in topographical depressions without outlets (playas).
4. In soil profiles or sandy sediments, through evaporation of groundwater.
5. In arctic areas, the sublimation of ice and the freezing of seawater to ice both increase the salt concentration of sea water, and evaporite minerals such as gypsum may be precipitated.
6. Through solution and precipitation of salts from older evaporite deposits.

The formation of evaporites is therefore not an unambiguous indication of a high temperature, but most evaporite deposits (salt) form in the climatically dry belts about 20–30° from the equator. Evaporites contain a number of salt minerals which are too soluble to be precipitated in normal marine or continental environments. The most important are:

Chlorides
Sulphates
Alkaline carbonates
Ca-Mg carbonates
Borates
Nitrates
Silica deposits
Iron deposits

6.4.1 Marine Evaporite Environments

Although the salt content of seawater varies somewhat in the different parts of the world's oceans, the composition of seawater is relatively constant. The table below shows the percentage composition of dissolved salts in seawater which add up to a salinity of 35‰. To the right are the percentages of the various salts obtained through evaporation.

Percentage by weight of salts in seawater

Ion	Percentage in seawater	Salt	Percentage by weight of common salts after evaporation
Na	30.64	NaCl	77.76
Mg	3.76	$MgCl_2$	10.86
Ca	1.20	$MgSO_4$	4.74
K	1.09	$CaSO_4$	3.60
C1	55.21	K_2SO_4	2.47
SO	7.70	$MgBr_2$	0.22
CO	0.21	$CaCO_3$	0.35
Br	0.19		
	100.00		100.00

By evaporating seawater one can therefore determine the relative amounts of different salts. An evaporite basin will often have some supply of seawater, such that the evaporation is not total. As a result, evaporite deposits may accumulate carbonates and sulphates, while the chlorides remain in solution.

When seawater evaporates, carbonates are among the first salts to precipitate, but the amount of carbonate in solution is very small. When the volume of seawater is reduced to 1/3–1/5, both $CaCO_3$ (aragonite) and $CaSO_4 \cdot 2H_2O$ (gypsum) have precipitated. Only when the volume is down to 1/10 will NaCl (halite), quantitatively the main constituent, be precipitated (Fig. 6.6). $MgSO_4$ and $MgCl_2$ will be precipitated at the same time. Polyhalite $\left(Ca_2K_2Mg(SO_4)_5 \cdot 2H_2O\right)$ commonly precipitates when the seawater has been reduced to 1/20. KCl (sylvite) and bromides are among the most soluble

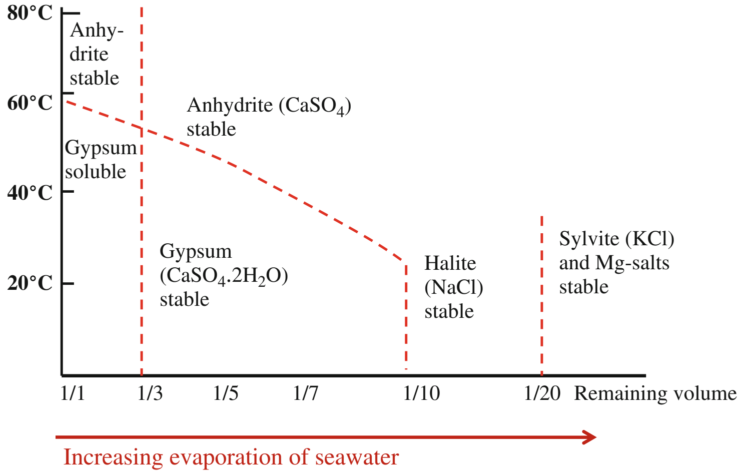

Fig. 6.6 Stability of salt minerals as a function of progressive evaporation of seawater and temperature

salts, and are hence the last to precipitate. If the salt concentration increases with evaporation, this is the sequence of salt deposition. During periods with greater circulation and supply of normal seawater the salt concentration will fall, and there will be cyclic salt deposition and solution. Chlorides (NaCl, KCl) will dissolve in moisture from the air unless the humidity is very low.

Periods of increased evaporation and hence high salt concentration may alternate with influxes of seawater with a more normal salt concentration, producing cycles representing changes in salinity. These are called evaporite cycles. In many evaporite basins the salt concentration has been sufficiently high for gypsum to be precipitated, but not high enough for chlorides (see Fig. 6.7).

The stability of the various salts during evaporation can be determined experimentally, or estimated through physical chemistry calculations. However, it is clear that certain metastable mineral phases can also be formed. Calcium sulphate may precipitate both as a hydrated mineral, $CaSO_4 \cdot 2H_2O$ (gypsum), and as a non-hydrated mineral $CaSO_4$ (anhydrite) (see Fig. 6.8). Which of these two phases forms as a result of oversaturation of calcium sulphate depends on the temperature, salinity and water vapour pressure. In a solution of $CaSO_4$ alone, anhydrite forms only at temperatures of over 60°C, but as the concentration of other salts increases, anhydrite may form at temperatures down to 25–30°C (Fig. 6.6).

Gypsum is the mineral which normally forms in marine evaporites, but anhydrite is also observed in modern evaporites in supratidal zones. This is true, for example, of the sabkha deposits in the Persian Gulf. These are black algal muds in the supratidal zone, where temperatures may be up to 80°C, and anhydrite is deposited in the sediment. In patches of open water where the temperature is lower, gypsum forms instead.

Evaporite sediments have formed (or preserved) in the sedimentary record throughout geological history, but appear to have formed more abundantly during certain periods, particularly the Permian. In Northern Europe and the North Sea we find thick evaporites from this period in what is called the Zechstein Sea, which serve as a cap rock for the gas in the underlying Permian aeolian sandstones.

The lighter salt layers will flow upward and gradually form large mushroom-shaped or columnar structures. The prerequisite for initiating this salt dome formation, however, is that the salt beds must be at least 100–200 m thick. Salt domes are common in Northern Germany, Denmark and the southern part of the North Sea, where they may form oil or gas traps. During the Permian, NW Europe was in the dry belt 20–30°N, similar to the Sahara today.

Surveys of the bottom of the Mediterranean Sea have revealed the existence of considerable evaporite deposits in Upper Miocene sequences. Adjacent land areas also have numerous localities where salt beds of this age (Messinian salt) have been preserved. This can indicate that the Straits of Gibraltar were closed

Fig. 6.7 Layers of gypsum in sabkha

for large parts of the Tertiary and that the Mediterranean Sea was a vast desert inland sea 2,000–3,000 m below sea level at that time.

6.5 The Sabkha Model

"Sabkha" is the Arabic term for the large flat areas around the Persian Gulf. This area extends from the tidal zone, forming an 8–10 km wide belt with a very low seaward gradient of only about 0.4 m/km. The sabkha flats were created by carbonate sediments infilling lagoons, chiefly during the Holocene. For the last 4,000 years there has been a gradual regression in the area. The climate is very dry (30–100 mm annual precipitation), but this is nevertheless sufficient to cause groundwater from surrounding areas to flow out to the sea. The groundwater flow is extremely slow, only a few centimetres a year, but is nevertheless responsible for the diagenetic environment containing porewater of continental origin. During storms and high tides, marine water floods the sabkha. Some runs off, some evaporates and some filters down into the sediment and mixes with the groundwater. Relatively large amounts of gypsum are then formed. The remainder of the water is highly enriched in magnesium, and dolomite is formed. Evaporation will increase the salt concentration of the porewater, and if it is intense enough, chlorides (halite) are precipitated in addition to gypsum. However, halites will dissolve easily the next time salt water flows in over the sabkha. Moisture in the air will also help to dissolve halite on the surface, so that it is not preserved in the bedding series.

Fig. 6.8 Gypsum crystals growing on the sabkha surface

The sediments which are deposited alternate between gypsum-carbonate and some clastics. A conspicuous lamination develops because of algal growth (cyanobacteria), which does not get destroyed because there is no bioturbation in this salt environment.

Although it is hot, up to 50–80°C on the sabkha, evaporation is limited where there is no open water because of the low permeability within the sediments. When the water table sinks, the evaporation rate rapidly declines. Thick layers of sediments with gypsum make up much of the Sabkha sediments (Fig. 6.8).

Whereas the rate of evaporation from open water in the Persian Gulf is about 124 cm/year, it is only about 6 cm/year in the sabkha. We therefore have only moderate "evaporite pumping" where chlorides are precipitated above the water table and sulphates below the water table. The chlorides deposited will, however, redissolve as the overburden increases and the relative position of the water table rises. In some semi-arid regions, e.g. the Coorong region of Australia, dolomite lakes form which evaporate to dryness in the summer (ephemeral lakes). Evaporite minerals deposited in summer will redissolve during the winter rains, and will not be preserved in the bedding series.

6.6 Marine Evaporites

Evaporation from the surface of the sea will cause the salinity of the water in a basin to increase. If there is little wave or current action, the warm surface water will not mix quickly with the underlying, colder water. If the salt concentration increases, the density will increase and the surface water will sink to greater depths and mix with the water there, despite being warmer. To create a high salinity basin we must have physical barriers reducing or totally blocking the connection to the open ocean, and the evaporation must be greater than the total amount of freshwater added to the basin by precipitation, rivers and groundwater. If the evaporation is lower than the supply of freshwater it will develop into a freshwater basin.

An evaporite basin with a limited connection to the open sea may not dry out; it can then accumulate large amounts of gypsum, but not more soluble salt like halite (NaCl). The Mediterranean has enough seawater exchange through the Straits of Gibraltar to prevent the formation of evaporites in the Mediterranean today.

6.7 Tectonic Control of the Formation of Evaporite Basins

Partial or complete severing of marine basins occurs as a result of tectonic uplift of barriers. Rifting and incipient spreading of the ocean floor provide ideal conditions for the formation of evaporite basins, as marine basins may be partly or entirely cut off by horsts or by volcanoes and lavas. The Red Sea used to be an active evaporite basin but gradually the connection with the Indian Ocean has become too large.

Rifting, and spreading of the ocean floor in connection with the formation of the Atlantic Ocean, led to the accumulation of thick evaporite series in the dry regions and freshwater lakes in the wetter parts. In Jurassic and Lower Cretaceous times early seafloor spreading resulted in the formation of a series of evaporite basins in the area between Africa and South America south of the equator, and in the Gulf of Mexico and North Africa north of the palaeo-equator. Where they were sufficiently thick, they formed diapirs which greatly influenced further sedimentation and the structural development of these parts of the continental shelf. As seafloor spreading continued, such that the Atlantic Ocean widened and the ocean floor basalts cooled and subsided more rapidly, the opportunities for forming closed basins diminished. After the mid-Cretaceous no major evaporite basins formed in this region. The salt is an ideal cap rock and both in the Gulf of Mexico and offshore Brazil large reservoirs of "sub-salt" oil have been found.

6.8 Evaporites in Lakes and Inland Seas

Basins with no outlet are formed particularly in tectonically active areas. In East Africa we find numerous freshwater evaporites in the rift basins where the climate is sufficiently arid, and at the end of the Cainozoic during the Mio-Pliocene there were many landlocked lakes and inland seas in connection with rift valleys. Since the chemistry of river water is quite different from that of seawater, such "continental" evaporites are quite different from marine series. The composition will vary according to the types of rocks and the weathering in the drainage area around the lake. Lake evaporites normally contain large amounts of carbonate, particularly sodium carbonate and a number of other salts, hence the name "soda lakes". The mineralogical composition of these soda deposits is very complex. Two important minerals are trona $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ and gaylussite, $CaCO_3 \cdot Na_2CO_3 \cdot 5H_2O$. If there is volcanism in the area, as is often the case around rift valleys, this will modify the composition of the water, both by weathering of ash and lava and by the direct addition of volcanic water (springs) rich in dissolved salts.

In playa lakes there may be total evaporation of seasonal rainfall resulting in thin layers of carbonates, including dolomite and sulphates. Signs of dessication and wind reworking will be common. Salt and clay particles in the dried-out lakes will tend to be transported by the wind, to form small dunes. Water from occasional rains in deserts will often collect between large aeolian dunes and form interdune lakes and sabkhas.

6.9 Evaporation of Groundwater

Where groundwater evaporation exceeds rainfall there is net upward transport to the surface of the soil and salts have to precipitate out in the soil profile. This can happen in the vadose zone near the sea, or inland where evaporation is high and the groundwater has flowed from another area. Gypsum and chlorides exert great crystallisation power, and can push aside the sediment matrix so that large euhedral crystals form. In brown soil types such as prairie soils, where the rainfall is high enough to prevent the accumulation of more soluble salts, a layer of carbonate (caliche) is commonly formed and in drier areas also gypsum. When such soils are eroded the broken up caliche will form pebbly conglomerates.

Evaporites from older geological periods are easily dissolved by groundwater or surface water. The Dead Sea is an example of an evaporite basin where water flowing into the basin is already rich in dissolved salts. This is because the Jordan river runs through evaporite sediments of Cretaceous and Tertiary age. In addition, water of volcanic origin enters the rift valley through faults and fractures.

6.10 The Stability of Gypsum and Anhydrite During Burial Diagenesis

Higher pressure and temperature will favour the stability of anhydrite, which has a more compact structure than gypsum. Gypsum formed in evaporite environments will therefore turn into anhydrite when there is sufficient overlying sediment, usually at depths ranging from just under 1,000 to 3,000 m. When anhydrite-bearing sediments are uplifted and come into contact with groundwater due to erosion of overlying sediments they will gradually, depending on the water circulation, hydrate to gypsum which is then the stable phase. The loss of water resulting from the transition from gypsum to anhydrite leads to a volume reduction (compaction) of 38%, and the transition from anhydrite to gypsum leads to a corresponding increase (expansion) of 60%. The volume increase can produce near-surface deformation and faulting in basins where evaporites have been uplifted due to erosion or diapirism. This compaction and expansion creates serious geotechnical problems in those areas of Europe, e.g. Switzerland and Germany, where evaporite deposits are common. Sulphates are rather stable and are not easily reduced to sulphides inorganically; this requires sulphate-reducing bacteria. However in evaporite deposits which have been buried to depths where the temperature has exceeded 80°C, sulphate-reducing bacteria have not survived and the rocks are then pasteurised. The reduction of sulphides like gypsum and anhydrite will then be very slow even at shallow depth.

6.11 Iron- and Manganese-Rich Sediments

Iron and manganese share many similarities in their geochemical behaviour in sedimentary environments. Both elements are poorly soluble in the oxidised state because they form hydroxides and oxides: $Fe(OH)_3$, $Mn(OH)_4$, Fe_2O_3 and MnO_2. In the reduced state they occur as Fe^{2+} and Mn^{2+} and are then much more soluble. Both iron and manganese can be precipitated as carbonate ($FeCO_3$, $MnCO_3$), either as separate minerals, or as part of calcite, dolomite or ankerite. They are therefore not very soluble in basic solutions with low redox potentials, but are quite soluble at low pH values and in the reduced state. Consequently we can precipitate iron and manganese in two ways: (1) through oxidation, (2) by changing the solution from acid to basic.

Fe^{2+} forms iron sulphides with very low solubility while manganese sulphides are far more soluble and therefore more soluble in porewater which is reducing and acid. Based on these geochemical considerations, we can predict a great deal about the deposition of iron and manganese in sediments. As silicates and other minerals dissolve in the oxidising environment during weathering, the concentration of insoluble iron oxides ($Fe(OH)_3$) and manganese ($Mn(OH)_4$) will increase, along with aluminium ($Al(OH)_3$), and constitute a major part of laterite.

Bogs, such as we find in the Scandinavian highlands, have conditions ideal for such precipitating iron ("bog iron"). Water seeping through bogs will have low Eh and pH, and iron-containing minerals from underlying rocks will be dissolved by humic acids, transported in the reduced state and precipitated through oxidation where the water flows out of the bog.

Porewater in sediments and sedimentary rocks is normally reducing. This is because most sediments contain reducing agents, particularly organic material. Only the upper 0–20 cm below the sea (lake) floor are oxidised. The depth to which the groundwater will be oxidising depends on the supply of oxygen, i.e. the oxygen content and rate of flow of groundwater compared to the consumption of oxygen due to oxidation. Desert sediments contain little organic material which can function as a reducing agent, and the groundwater will therefore remain oxidising longer. This can explain the red colouration of desert sediments which is due to trivalent iron.

The redox boundary, which normally lies just below the sediment/water boundary on the ocean bottom, represents an important geochemical trap. The concentration of elements on each side of this boundary is very different because of the different solubility of elements in the two separate chemical environments. A high concentration gradient of Fe^{2+} and Mn^{2+} on the reducing side of the redox boundary leads to a diffusion and precipitation of oxidised iron and manganese immediately above the boundary. At a depth where there is little oxygen in the porewater, sulphate-reducing bacteria consume the oxygen in the sulphate ions to form H_2S. The sulphate concentration in the porewater declines rapidly downwards causing a downwards diffusion. H_2S is an acid which can release (leach) iron bound in various clastic minerals to form FeS (machinawite), which is black and easily oxidised, and then pyrite (FeS_2) which is a little more stable. If the sediments have a high silica content, chamosite may also be formed. Glauconite must be formed right at the redox boundary, since it contains both bivalent (Fe^{2+}) and trivalent (Fe^{3+}) iron. Uranium and vanadium, which have low solubility in the reduced state and are more soluble when oxidised, will be able to diffuse downwards and be precipitated in the reducing zone below the redox boundary.

Manganese will not be as easily trapped in the sulphate-reducing zone, as Mn^{2+} does not form such stable sulphides as Fe^{2+}, and it will therefore have a greater tendency to be precipitated in the oxidised zone.

During breaks in sedimentation, or slow sedimentation, porewater expelled by compaction will cross the redox boundary and this may cause the precipitation of iron and manganese on the seafloor. *Manganese nodules* are concretions of manganese and iron hydroxides and oxides found on the seafloor, particularly in the ocean basins (South Atlantic and Pacific). They also contain relatively high concentrations of metals like Ni, Cu, Zn and Co and there have been plans to mine these deposits. The nodules grow by very slow concentric accretion in a pelagic ooze. Plankton is capable of accumulating very high concentrations of metals from seawater and when the organisms dissolve, the planktonic ooze becomes very rich in these metals, which will be precipitated together with the manganese hydroxides in the concretions.

Iron and manganese are virtually insoluble in oxygenated sea water, and consequently cannot be transported in ordinary solution. However, rivers can carry a good deal of iron and manganese adsorbed onto organic particles or as clay-sized iron oxides which in many cases may produce a red colour.

Iron can be precipitated not only by oxidation, but also in the reduced state in a basic environment. Thin carbonate laminations in shales represent a local high-pH environment, where reduced iron which is normally soluble can be precipitated:

$$Fe^{2+} + CaCO_3 = FeCO_3 + Ca^{2+}$$

This reaction occurs at relatively low Fe^{2+}/Ca^{2+} ratios because iron carbonate (siderite) is less soluble than calcite. If there is sulphur present, iron will first form the sulphide, however, and iron carbonate will not be stable. Siderite is therefore most typically formed in freshwater basins, and not directly in the sulphate-reducing zone in marine sediments. Siderite can also be formed below the sulphate-reducing zone, for example by reaction between aragonite and iron in the sediment.

6.12 Phosphorite (or "Phosphatic Deposits")

Phosphorites are sedimentary layers in which phosphate minerals are the main components, mainly apatite $Ca_5(PO_4)_3(F, Cl, OH)$. These crystals may contain fluor (F^-), chlorine (Cl^-) or hydroxyl (OH^-). Fluorapatite $Ca_5(PO_4)_3F$ is the most important in marine sediments. We also have francolite $(Ca, Na)_5(F, OH)(PO_4, CO_3)_3$, where some carbonate has substituted for phosphate and where sodium substitutes for calcium. Iron apatites such as strengite ($FePO_4 \cdot 2H_2O$) are also relatively common minerals in secondary (weathered) phosphatic deposits.

Phosphorite rocks are an important source of fertilizer. Large deposits such as those found in Morocco, Spanish Sahara and Senegal in West Africa, and in Florida, are of great commercial value. Understanding how phosphate deposits form is therefore a matter of considerable economic interest. In most sedimentary rocks phosphorus is a trace element, and very special conditions are necessary for phosphate enrichment to take place. These deposits therefore tell us something important about the environment of deposition.

Guano deposits are formed on land from bird or bat excrement in which the phosphate gradually becomes concentrated as the other organic components are leached out. For the phosphates to be preserved, the rainfall must not be too high, because it will dissolve phosphate sediments on land. We also have freshwater phosphatic deposits, but it is the marine ones that are the most important.

The first prerequisite for marine phosphate deposits is that sedimentation must proceed very slowly, i.e. there must be virtually no clastic sedimentation. In consequence we find phosphate beds associated with major or minor breaks in sedimentation, or with periods of very slow sedimentation. It has long been known that phosphate is formed in areas with strong upwelling and high organic productivity. We have good examples of this along the edge of the continental slope off Chile and Peru. Water welling up from great depths brings with it nutrients which are liberated when marine organisms disintegrate in deeper water. When the water flows up to the surface the nutrients are consumed by organisms, mostly plant plankton, which provide a high primary production. These organisms contain about 1% P (dry weight), which is an enrichment of 140,000 compared to dissolved phosphorus in ordinary seawater.

Organisms with an amorphous silica skeleton (e.g. diatoms and radiolaria) will readily dissolve in seawater, and in some cases carbonate (calcite and particularly aragonite) will also dissolve, resulting in further phosphate enrichment. Phosphate minerals then crystallise out of the phosphate-rich sediments and often replace other minerals, e.g. carbonate. Apatite is a heavy mineral (specific weight 3.18) and may also be enriched mechanically by weak traction currents.

Apatite will often crystallise out as concretions in bottom ooze, and erosion by traction currents may concentrate these nodules into a conglomerate. On the continental shelf, phosphate forms at depths of between 100 and 400 m, i.e. below the photic zone. However, phosphate nodules and massive beds of fine-grained phosphate mud (phosphate micrite) may also form in lagoons where the water is less clear. These phosphate deposits will be easily eroded even as a result of minor regressions, and form conglomerates of phosphate mudstone (micrite). Today phosphate deposits are forming only in a few areas with strong upwelling, but in previous geological periods we find very extensive phosphate beds, often associated with transgressions. The transgressions will hold clastic sediment back for a while, enabling biogenic matter to be concentrated. Phosphate beds are often associated with other authigenic (formed *in situ*) minerals which take a long time to form, particularly glauconite and also manganese deposits.

In Florida there are large phosphate deposits of mid-Tertiary age, and the same beds are exposed on the floor of the continental shelf off South Carolina (Blake Plateau), where the manganese-rich phosphatic deposits total 10^9 tonnes.

Marine phosphate deposits may also be formed by fossils with a phosphatic skeleton, for example fish. These deposits may also be extensive, and are often called "bone beds".

Phosphate minerals such as apatite may contain considerable amounts of uranium and rare-earth metals which substitute for calcium. Weathering of phosphate deposits will lead to oxidation of uranium to UO_2^{2+}, which is soluble in the form of uranyl ions, and uranium may be precipitated again in the reduced state (UO_2) when it comes into contact with organic matter. This is why black shales and source rocks tend to have rather high radioactivy.

Weathering of phosphate sediments will initially cause solution of carbonate and carbonate-containing apatite so that the sediments become enriched in fluorapatite. As calcium is removed through solution of calcite by rainwater, the sediment will become richer in iron and aluminium, and iron and aluminium phosphates will form. Phosphate deposits are also formed through weathering of phosphate-bearing igneous rocks. Carbonatites from the East African rift system contain a high percentage of apatite, and when carbonate is dissolved during weathering, apatite becomes concentrated and forms phosphate deposits which are also rich in iron minerals. There are many types of apatite deposits and even if there is a high demand for phosphate in fertilizers it is unlikely that they would be exhausted in the next few centuries.

Further Reading

Abtew, W. and Melesse, A. 2013. Evaporation and Evaoptranspiration. Meaurements and Estimations. Springer Verlag, 206 pp.

Aplin, A.C., Fleet, A.J. and Macquaker, J.H.S. 1999. Muds and mudstones: Physical and fluid-flow properties. Geological Society Special Publication 158, 190 pp.

Bjørlykke, K. 2011. Open-system chemical behaviour of Wilcox Group mudstones. How is large scale mass transfer at great burial depth in sedimentary basins possible? A discussion. Marine and Petroleum Geology 28, 1381–1382.

Bjørlykke, K. 2014. Relationships between depositional environments, burial history and rock properties. Some principal aspects of diagenetic processes in sedimentary basins. Sedimentary Geology 301, 1–14.

Chamley, H. 1989. Clay Sedimentology. Springer, New York, 623 pp.

Day-Stirrat, R.J., Flemming, P.B., You, Y., Aplin, A.C. and Pluijm, van der, B.A. 2013. Modification of mudstone fabric and pore structure as a result of slope failure; Ursa Basin, Gulf of Mexico. Marine Geology v 341, 56–67.

Day-Stirrat, R.J., Flemming, P.B., You, Y., Aplin, A.C. and Pluijm, van der, B.A. 2012. The fabric of consolidation in the Gulf of Mexico mudstones. Marine Geology. v. 295–298, 77–85.

Delisle, G., Teschner, E., Faber, E., Panahi, B., Guliev, I. and Alliev, C. 2010. First approach in quantifying fluctuating gas emission and methane and radon from mud volcanoes in Azerbaijan. In: Wood, L.J. (ed.), Shale Tectonics. AAPG Memoir 93, pp. 211–224.

Schieber, J., Eier, W. and Sethi, P. 1998. Shales and Mudstones. Schweizerbartsche Verlagsbuchhandlung, Stuttgart, 384 pp.

Thyberg, B.I., Stabell, B., Faleide, J.I. and Bjørlykke, K. 1999. Upper Oligocene diatomaceous deposits in the northern North Sea – Silica diagenesis and paleogeographic implications. Norsk Geologisk Tidskrift 79, 3–18.

Thyberg, B., Jahren, J., Winje, T., Bjørlykke, K., Faleide, J.I. and Marcussen, Ø. 2010. Quartz cementation in Late Cretatceous mudstones, northern North Sea. Changes in rock properties due to dissolution of smectite and precipitation of micro-quartz crystals. Marine and Petroleum Geology 27, 1752–1764.

Weaver, C.E. 1989. Clays, Mudrocks and Shales. Developments in Sedimentology 44, 818 pp.

Wood, L.J. 2010. Shale Tectonics. AAPG Memoir 93, 238 pp.

Yang, Y. and Aplin, A.C. 2010. Permeability-porosity relationships for mudstones. Marine and Petroleum Geology 25, 1692–1696.