Chapter 6

Shales, Silica Deposits and Evaporites

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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 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 mineral grains are essentially flat flakes, they have large surface areas, some like smectite having several hundred m^2/g. 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.

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. 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 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.

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K. Bjørlykke (ed.), *Petroleum Geoscience: From Sedimentary Environments to Rock Physics*,
DOI 10.1007/978-3-642-02332-3_6, © Springer-Verlag Berlin Heidelberg 2010

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, the inland portions of which became valleys through postglacial isostatic uplift.

Clay transported by rivers into lakes will remain suspended for some time 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).

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

Clay minerals transported into marine sedimentary basins will also be subjected to sorting by grain size. 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).

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

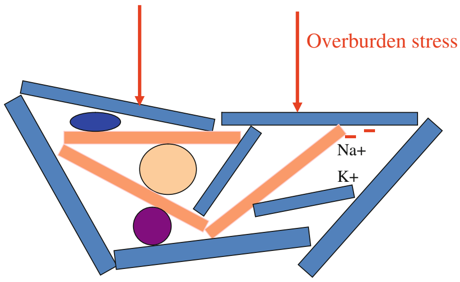

Fig. 6.2 Clay minerals have negative charges due to broken chemical bonds in their silicate structure. In freshwater there is repulsion between the clay minerals, keeping them in suspension. In seawater, cations like sodium and potassium help to neutralise these charges and the clays will form denser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

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.

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 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

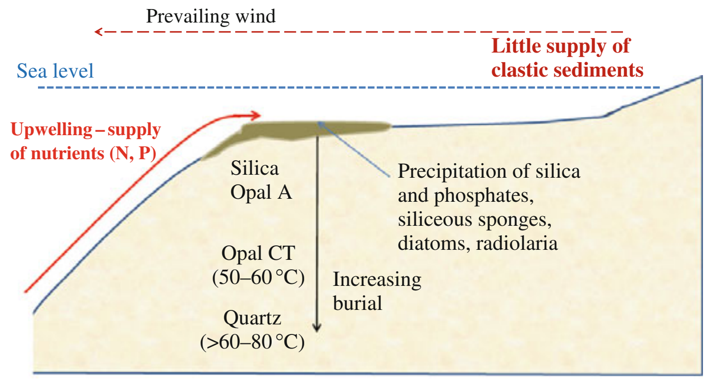

Fig. 6.3 Upwelling of water rich in nutrients causes biological precipitation of silica and phosphates. The silica deposits (opal A) will, when buried, be altered to opal CT and then to quartz

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.

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. They 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.

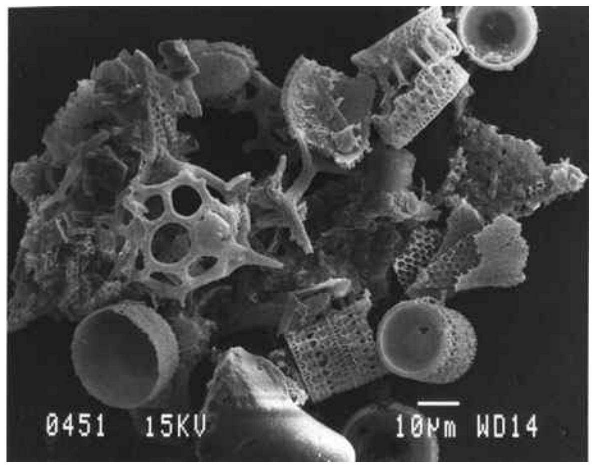

Fig. 6.4 Diatoms and radiolaria from Oligocene siliceous sediments from the North Sea basin (1,430 m depth). From Thyberg et al. (1999)

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.