CHAPTER

5

Sedimentary Rocks

OUTLINE

Introduction to Mineralogy and Petrology
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5.1. FUNCTION, SIGNIFICANCE, CLASSIFICATION AND TRANSFORMATION

Sedimentary rocks are formed by one or in combination of the complex physical, chemical, biological and geological diagenetic processes of sediments. The sediments are deposited on or near the Earth's surface at a temperature and pressure appropriate to these conditions. The rocks are formed under specific processes derived from other preexisting rocks of igneous, sedimentary, and metamorphic origin, and/or as products of life activities of organisms or chemical secretion.

The title of sedimentary rocks (from the Latin sedimentum residue) suggests that these rocks are formed by deposition of inorganic and organic, solid or excreted material from aqueous solutions. However, the sedimentary rocks also include rocks originated by diagenetic chemical processes of existing sediments and sedimentary rocks (e.g. late-diagenetic dolomite and anhydrite, and some diagenetic siliceous sediment). While the term "sediments" usually cover nonlithified, and in some cases, soft deposits, the entitled sedimentary rocks mainly include lithified deposits in the form of solid rock, and all sediments and sedimentary rocks along.

The basic requirement for the formation of sediment is the existence of underlying materials, which are primarily in the evolution of Earth's rocky crust, composed of igneous, metamorphic and older sedimentary rocks. The deposition process continues at the Earth's surface with its evolution, so that the size and thickness of sedimentary cover increases in the rocky crust. The rock configuration changes by tectonic movements (global tectonics), volcanism and erosion. The sedimentary rocks also include residues resulted by accumulation of volcanic materials after its transfer and deposition by wind, water or ice, i.e. pyroclastic rocks.

The sediments and sedimentary rocks are divided into two basic groups with respect to the type of physical, chemical, biochemical and geological processes. There are mixed sediments and sedimentary rocks between these two distinct and different groups (Table 5.2).

1. Clastic (exogenous) sediments and sedimentary rocks.
2. Chemical and biochemical (endogenous) sediments and sedimentary rocks.

Clastic sediments and sedimentary rocks are divided according to size of clasts, regardless of their origin, except those ejected from volcanoes, as follows:

1. Coarse grain or gravel (rudaceous)
2. Medium-grain or sandy (arenaceous)
3. Fine grain and argillaceous (pelite).

Sediments that are generated by deposition of clasts ejected during volcanic eruptions belong to a special group of clastic sediments and called as "volcanoclastic" or "volcaniclastic" sedimentary rocks.

Special group of clastic sediments include residual sediment (residue) remaining after an intense chemical weathering of rocks.

Chemical and biochemical sediments and sedimentary rocks include the following:

1. Carbonate, e.g. limestone.
2. Evaporate, e.g. halite and carnallite.
3. Siliceous sedimentary rocks, e.g. sandstone.

The thick file of sediments moves down to deeper depth due to overlying accumulation of fresh sediments. The package at depth will be under the influence of elevated temperatures and pressures, making some components unstable and transform into new stable ingredients. The same sediments gradually transform or metamorphose under increasing pressure and elevated temperature at great depth.

It is experimented that the diagenesis with significant metamorphic changes takes place at a depth of 4−5 km, pressures up to approximately 2530 bar and temperatures below 220 °C. The temperature increase, due to geothermal gradient of 1 °C/33 m depth, corroborates the temperature of 200−220 °C at Central European depths of about 6600−7260 m. It also supports that the temperature increase in the Earth's crust is not an exclusive function of the depth of the overlay, but due to the proximity of magma, volcanism and other thermodynamic factors. Therefore, the depth at which the metamorphism starts will be very different from place to place. It can be safe to assume that the sedimentary rocks gradually transform or metamorphose into metamorphic rocks at great depths of covering supplemented by the rise of pressure and temperature above 220 °C (Fig. 6.9).

Many of the mineral resources are sedimentary in origin. All mineral fuels, i.e. oil, natural gas, coal and oil shale, are confined only in sediments, except otherwise in some special cases. The oil and gas-filled pores in lithified sediments, coal and oil shale are sedimentary rocks. Many metallic and nonmetallic minerals are hosted by sedimentary rocks, e.g. majority of iron ore, and partly of manganese, copper, uranium and magnesium. In addition, many sedimentary rocks are directly used as raw material for obtaining cement (marl and limestone), glass (quartz sand), ceramic and porcelain (clay and kaolinite), bricks and tiles (clay), building materials like concrete (aggregates of limestone, dolomite or sandstone, gravel, and sand) or used as a technical, architectural and building stone (limestone, dolomite, and sandstone). All the mineral phosphate, nitrate and potassium fertilizers mineral, salts (halite and carnallite) as well as gypsum and anhydrite are of sedimentary origin. The sedimentary rocks are the excellent holders or the collectors of freshwater, which today, become the primary life essential of all humanity.

5.2. SEDIMENTARY ROCK FORMATION

Sedimentary rocks are, sediments, formed by the following precesses:

1. Sedimentation of solid residues (clasts) left over from weathering of older rocks (clastic sediment).
2. Biochemical and chemical secretion from aqueous solutions, as well as the deposition and accumulation of fossil evidence.
3. Skeletons and shells of organisms (chemical and biochemical sediments).

The formations of sedimentary rocks include the following:

1. Processes of physical and chemical weathering of older rocks.
2. Transfer or transport of materials in solid or dissolved state.
3. Deposition or sedimentation.
4. Complex processes of diagenesis and, significantly, the lithifaction.

5.2.1. Weathering

Weathering is the process of destruction of rocks on Earth's surface or shallow water due to:

1. physical or mechanical,
2. chemical, and
3. biochemical factors, or due to the effects of atmosphere, water, ice, climate and temperature changes, erosion, sunshine and life activity of organisms.

The first two, and the third factor of weathering, are closely related and interactive. The rocks are weathered out in two ways, by the action of water, especially water flows like a river, occasional torrents and storm tides and waves:

1. Mechanically because of the speed and power of water flows and water activities during the transmission of material.
2. Chemical dissolution due to the action of the weak carbon and humic acids.

5.2.1.1. Physical or Mechanical Weathering

The physical or mechanical wear and tear (deterioration and weathering) includes fragmentation and disintegration of existing minerals and rocks, without the formation of new minerals. The development is primarily caused by mechanical action of water, ice or wind, sunshine and frost. The process of grinding stones in finely dispersed particles is a basic element of physical weathering. This causes an increase in volume and decrease in density that facilitates and accelerates their chemical weathering because of the intensification of the oxidation and hydration of primary mineral constituents of the rocks. Products of the physical weathering are solid particles or clasts of different sizes:

1. Mud (0.004−0.063 mm)
2. Sand (0.063−2 mm)
3. Gravel (2−256 mm)
4. Boulder (>256 mm).

These materials may be transferred to a greater or lesser distances by water, wind or glaciers, or may remain in place.

Insolation (solar radiation energy) is the most important factor of physical weathering, especially in arid region (dry climate), i.e. in the deserts. The repeated changes of hot days and cold nights cause recurring expansion and contraction of certain mineral constituents of rock. The anisotropic properties of minerals are affected by various stresses causing to weakening of ties between the mineral, cracking and disintegration of rocks. This process is particularly intense in the surface areas of dark colored rocks, e.g. basalt (Fig. 4.37).

Absorption and *desorption* of water (hydration–dehydration) caused by large temperature differences that change the pressure of water vapor in the air and in the pores of rocks. It creates dissolution or extraction of minerals salts in the rock or enhances the strong hydration of some minerals (e.g. anhydrite in gypsum). The frequent volume change can result into complete destruction of rocks. The atmosphere is saturated with water vapor and decrease evaporation of water from the pores of rocks, specifically, at lower temperatures, typically at night. However, the evaporation of water from rocks increases at high temperatures during day and the pressure of water vapor in the air fall. These changes are caused by repeated dissolving and crystallization of salt. The rocks formed cavities during dissolving the salt, which further enhance its physical and chemical weathering. The crystallization of salts in the pores space makes destructive stresses due to increase in volume of the rocks. The hydration of anhydrite to gypsum increases the volume by 38%.

Freezing–thawing is at temperate climates in the high mountains of rocks saturated with water. This exerts high pressure and great stress due to increased volume of ice compared to the volume of water. Such stresses can destroy the hardest rocks. The intensity of destruction is subject to freezing of high-porosity rocks that are already tectonically fractured.

Erosion is the process of destruction of relating parts of the Earth's surface with accessibility of streams, ice and wind. The river erosion is strongest with torrential water flows. The water carries a large mass of rock debris. The quantity of material transfer will be more and the size of individual pieces will be larger at the highest speed of the water flow. The water swirling along with rock material will impose strong impact on the rocks at the bottom and sides of the river bed. The tear-off pieces collapse into the river and become part of its course. The rock materials crumble, fall-apart, and crush in such a transfer situation. Thereby, the large pieces gradually become sandy and the final product of these processes results in grain sizes of tiniest powder (silt).

Denudation is the name for the processes of erosion, leaching, stripping, and reducing the mainland due to removal of material from higher to lower areas like valleys, river valleys, lakes and seas with a permanent filling of low lands.

Glacial erosion is among the most devastating factors of physical weathering of rocks on Earth's surface. The ice and rock carried by glaciers acted as sandpaper which moves down the valley, smoothing and widening them, leaving U-shaped profiles for the valley cross-sections. There will be, finally, large steep-walled bowls called "glacial cirques" at the heads of these valleys. A sharp-sided ridge separates them when glaciers carve out valleys next to each other.

Abrasion wave activity is more intense as greater as their speed and strength. The abrasion is stronger with larger grain sizes, larger quantity of material transfer, and the weaker ground rock strength. Abrasion on the seacoasts depends on the strength of the waves, which can move the heavy stone blocks of several hundred tons in the stormy weather. The high waves hit the rocky shore and destroy rocks due to the power of water and waves. The hydraulic effects of water contained in the hollows and crevices of coastal rocks crack and break the massive boulders into pieces (Fig. 5.1). In the activity of waves and moving of rock material by mutual collision and friction of the fragments of the original angular remain form well-rounded grains of sand and gravel. The rocky debris becomes smaller all the while.

FIGURE 5.1 Strong action of wind and wave of Pacific Ocean crack, break and split the giant hard rock mass to smaller fragments of sand and silt along West Coast Highway to San Francisco. *Source: Soumi.*

FIGURE 5.2 Chemical weathering by surface oxidation process of rain and seawater on basalt. The dark gray/black color has changed to reddish forming open erosion cavities, Mumbai coastal area, India.

5.2.1.2. *Chemical Weathering*

The chemical weathering occurs mainly due to the action of water, carbonic acid and oxygen on the minerals and rocks, where they are chemically susceptible to changes. As a consequence, some disappear and some appear as "authigenic" minerals, which are stable under conditions prevailing in the Earth's surface or just below the surface. The chemical weathering in action of water and water as a mild carbonic acid is hydration. The same process with action of oxygen is oxidation.

Hydration is the process of receiving H^+ ions and the release of alkali elements (Na, K, Li, Ca, Mg, Sr) and silicon (Si). A great amount of alkali liberates during the chemical weathering of rocks, transfer by water in dissolved, mainly ionic, but partly in collide state over long distances in rivers, lakes and seas. The same water excretes new minerals in the favorable physical and chemical conditions. The weathering products of some rocks in the hydration and carbonation generate soils that are very different in different climatic zones.

Oxidation is a very significant factor of chemical weathering of rocks. The oxidation process changes the primary color, porosity, volume, and mineral composition of rocks (Fig. 5.2). The oxidation zone is the deepest in rocks of areas where the basic water is deep below the surface. The oxidation occurs mainly above the basic level of groundwater table in areas with steep relief and warm climate. The rainwater enriched with oxygen (which causes oxidation processes) penetrates into the depth of the pores of rocks. In the deeper layers, water gradually loses oxygen with more and more saturation of dissolved cations and anions, and loses the oxidizing effect. The effect of oxidation processes on color change of rocks can be seen best in fresh outdoor shoots of dark gray sediments along and around the tectonic cracks, crevices or open layer spaces. The transition in dark tan or reddish color can be seen along zones of circulation of oxygen-enriched rainwater. Such color change is the result of oxidation of Fe^{2+} to Fe^{3+} with the formation of goethite (yellow-brown color) or hematite (reddish color), and oxidation of organic matter.

The easily oxidized mineral constituents of rocks are sulfides, such as, pyrite (FeS_2), hematite (Fe_2O_3) or goethite (α-FeO,OH), and from other constituents of rocks and organic matter.

The chemical weathering depends on the climate. The heat, daytime and annual temperature fluctuations and humidity significantly accelerate the abrasion. The increase in temperature by 10 °C accelerates the flow of chemical reactions up to 2–2.5 times more. The chemical weathering is related to the Earth's surface, shallow area and underwater. The weathering process can be under the influence of the atmosphere, water and seawater. The main factor of chemical weathering of rocks is water that contains dissolved CO_2 and dissociates to the free $[H]^+$ and $[HCO_3]^+$ ions, representing a mild carbonic acid ($CO_2 + H_2O = H_2CO_3$). The content of free $[H]^+$ ion determines its chemical activity and the share of water acts neutrally (pH = 7), acidic (pH = 1–7) and alkaline (pH = 7–14).

The process of formation of new mineral directly depends on the pH of the water. Kaolinite is the most important mineral in the zone of weathering and occurs in acidic pH ~5. Montmorillonite occurs in the weak alkaline solution at pH >7. The water in the chemical weathering has a significant role in transferring large amounts of easily soluble anions and cations. The large amounts of silicic acid (H_4SiO_4) or Si ions that are released during the weathering of silicate minerals are equally significant.

If the pressure of CO_2 increases in the atmosphere, it will increase its solubility in the water creating an increase in acidity of water, i.e. its conversion into weak carbonic acid. Such water is chemically very aggressive toward many petrogenic minerals intensively destroying carbonates, feldspars and amphiboles.

The effect of water containing dissolved carbon dioxide on calcite is very fast and powerful process (Fig. 5.3). The soluble calcium hydrogen carbonate occurs in water, which can be illustrated by the following chemical reaction:

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

$$\underset{\text{Calcite}}{\ } \underset{\text{dissociation carbonic acid}}{[H]^+ + [HCO_3]^-} \longrightarrow \underset{\text{calcium hydrogen-carbonate}}{Ca(HCO_3)_2}$$

The effects of water on feldspars are leaching of alkalis, liberation of Si and combination with H_2O in the silicic acid to form kaolinite. It is a well-known process of kaolinitization:

$$\underset{\text{orthoclase}}{2KAlSi_3O_8} + 10H_2O + CO_2 \longrightarrow \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + \underset{\text{silicic acid}}{4H_4SiO_4} + 2K^+ + (CO_3)^{2-}$$

Kaolinitization process is an example of chemical weathering, hydration and the leaching of mineral constituents of parent rock and generates new or authigenic minerals. The formation of new minerals is called "autigenesis". The most common authigenic minerals formed during the chemical weathering are clay minerals and the aluminum hydroxides. The minerals

FIGURE 5.3 Chemical weathering of limestone in association of rain and seawater with erosion of surface leaving large open cavities, Mediterranean Sea at west bank of Alexandria, Egypt.

from kaolinite group generate during weathering of rocks with large precipitation. It forms weak acidic solution in the soil at pH of 5 and contains enough dissolved silicon in water in the form of silicic acid (H_4SiO_4).

5.2.1.3. *Biological Weathering*

Biological weathering takes place under the influence of life activities of organisms. The organic processes involve biological dissolution of rocks from bacterial activity, humic acids and bioerosion or destruction. The changes occur by the growth of roots, and drilling of organisms (shells, lichens, cyanobacteria, algae and the fungi) in the rock on which they cultivate. The bioerosion of carbonate rocks (limestone and dolomite) caused by cyanobacteria, lichens and fungi has particularly significant role. The large areas where these organisms live, and their prolonged activities during the geological period destroy significant amount of rock with the formation of massive quantity of very fine-grained carbonate detritus of limestone sludge (Section 5.7.1.2).

5.2.2. Sediment Transport

The transfer of detritus, i.e. solid materials or clasts remaining after the physical and chemical weathering, primarily takes place by water, and lesser part by wind and glaciers.

5.2.2.1. *Fluvial Processes*

The transfer of detritus by flowing water is the most natural way of transport and deposition of sedimentary rock. The flow of water can be orderly, laminar or turbulent. Laminar movement of water is gentle with certain parts of the fluid move in the parallel layers. The movement of detritus is also parallel to the flow of water without mixing. In turbulent or vortex movement, the main flow of water changes the speed and also the direction of flow. The turbulence movement of water carries large masses of fluid mixed with debris material due to the difference in the speeds and whirling motion. The detritus can be carried by dragging, suspension, sediment flow, underwater sliding and gravity flow. This is similar to rock transfer in air by landslides and avalanches.

The particles and grains will slide or roll on the bottom during the material transfer. The grains moves in short jumps during transmission, i.e. hitting in the bottom and bounce off the bottom back in the fluid. The detritus finally settle when the energy of water (or wind) is so much limited that it can no longer move. The transfer with the suspension is possible only if the intensity of turbulent water movement is greater than the speed of deposition of material by the action of gravity. The fine grain of clay-dusty (mud) or clay-sandy-dusty detritus transmits mainly in suspension. The flow of sediments is the movement of a mixture of unbound sediment and water. The underwater sliding includes sliding of poorly bound sediment down the slope on the bottom of the nearly flat or a little wavy surface. The sedimentary body originated by sliding (Section 5.3.1.5) in the lower and upper parts shows a strong deformation of primary inner and outer stratification or slump structure. The deformation in central part of such body can be weak and strong in the lower and upper part. There is always a clear angular discordance toward the basement and roof (Fig. 5.17).

Blurry or turbidity currents are flow of material mixed with water under the influence of gravity moving down the slightly inclined (1−3°), but long underwater slopes. The blurry or turbidity current of material forms due to the increase mixing of solid particles with water and differences in effects of gravity on large grains and small particles. The large grains (gravel) move forward with greater acceleration and accumulate in the bottom. The smaller grains (sand) lag increasingly behind in stream, and the smallest particles (dust, silt and clay) left behind suspended in the tail of currents. The suspension raises high above the bottom due to the turbulence of water. The coarse grains move faster up to 60 km/h compared to the smaller particles. The larger grains are increasingly separated from the small grains and accumulate in the frontal part of the flow and in its bottom. The finer materials that are lagging behind in the suspension are lifted above the bottom. In this way, the current or flow separates coarse material on the forehead, medium material in the middle and fine material in the tail end. The granulometric differentiation takes place horizontally and vertically (large grains in bottom, small in suspension above the bottom). The sediments of special structure, "turbidites," are common in flysch facies and are created from such distributed material within the turbidite current. These structures are deposited as sedimentary fan-shaped bodies (Figs 3.8 and 7.9) as shown in more detail in Section 7.2.5.

The detrite flows or debris flows are defined as more or less cohesive laminar flows of relatively dense sediment–fluid mixture of plastic types or clasts containing at least 4% clay component. The stability of the sediments is disturbed by extruding of fluids and clay, and thus initiates its movement down the slope. The debrite flows can be initiated by seismic shocks or can develop as a result of rapid accumulation of debris or formation of gases in sediments that cause local increase of pressures. When the gravity force is no longer stronger than the internal friction of sedimentary masses, or when there is no exceeded pore pressure, the flow suddenly stops or "freezes". The detrite flows can move down the slope angle $>1°$ with the speed of up to 20 cm/s.

The sediments formed by precipitation of detrite flows are called "debrites". The typical debrites are mainly composed of clasts of different sizes: coarse granular debris, with a diameter of several millimeters up to tens or even hundreds of meters, and medium granular to fine-grained muddy matrix in such a mutual ratio that the clasts have matrix support (clasts "floating" in fine matrix). Coarse blocks in debrite and debrite breccias are known under the name "olistolith" (Fig. 7.8; Section 7.2.5). The clasts that originate from the strong physical weathering or erosion of rocks outside participation area belong to extraclasts, and which originate from erosion of older sedimentary rocks inside the participation area called *intraclasts*.

5.2.2.2. Aeolian Processes

The wind can carry substantial amounts of material of small dimensions to long distances, especially in areas of bulk material with a dry arid climate or in deserts. The area is characterized by lack of moisture and vegetation. The main activity of the wind in the desert consists in puffing away, blowing up and transfer of sand and dust grains of a certain size depending on the intensity and wind speed. On the other hand, the grains are sorted from coarse to smallest particles in weakening of power and speed of wind. The regular wind usually does not carry sand-size grains far away and only the strongest winds can move larger sand grains by jumping on the ground and thereby transport sand in the direction of the wind and settles in the form of sand dune.

In contrast, the strong wind or air vortex currents can lift fine sand and dusts high off the ground and transfer to very long distances. The wind can pick up the smallest dust thousands of feet high in the air and carry it hundreds of miles far away from where it was raised. The wind, except in deserts, puffs sand and dust from river flood plains, upper delta plains and low coastal sea areas, especially low coastal areas above high tide level. All this material is redeposited closer or further from the original place in the form of special sediments and sedimentary bodies, which are known as *aeolianite*, aeolian dunes and mega-dunes or loess (Section 5.5.4.1.4).

5.2.2.3. *Glacial Processes*

The glaciers carry and transport large amount of materials by erosion and scraping of the sides and bedrock on which it descend in lower areas. Material transported by glaciers is not sorted because of its incorporation in an ice mass. There is no possibility of selection of detritus on grain size. Therefore, sediments deposited from glacier's transportation are extremely poorly sorted and contain smallest particles and up to several decimeter-diameter blocks, and even feet, as it is the case with diamictite (Section 5.5.2). The coarse and fine-grain detritus can be transported in the form of iceberg that floats on rivers, lakes or seas. Such material is deposited on the river, lake or sea bottom, after the gradual melting of icebergs and more often in their grain size. The mineralogical composition differs significantly from the usual lake or marine sediments.

The role of the glaciers in the transfer of material is limited only to areas with permanent ice and snow cover, particularly on high mountains with glaciers and moraines. A part of ice and snow melts during the summer and the rock debris accumulates in the form of moraines.

Moraines are composed of materials of different sizes and different types of sediments and sedimentary rocks (till, tillite, and diamictite). The sliding speed of glaciers is very different, depending on the angle of slopes, ice thickness, the width of the surface over which it moves, roughness and climate changes, particularly of temperature. In general, the speed of glaciers can be of only a few millimeters and up to several meters per day. The accumulated material can still carry with the water that originates from melting of ice in the forehead. These are fluvioglacial flows that have high energy and can strongly erode the surface.

5.2.3. Deposition

The deposition of material transferred by water, wind or ice begins to cease at a time and place when the power of water or wind or ice becomes too weak to continue moving all the materials. The glacier moves down on lower region and starts melting. The deposition processes are very complex and form different types of layer and shapes of sedimentary bodies (Section 5.3 and Chapter 7). There are three main ways of settling of material and sedimentary filling of space namely aggradation, progradation and retrogradation (Fig. 5.4).

Aggradation is the deposition process in which depositional area fills with vertical stacking of sediment from the thick layer of water, as for example the case of deposition in the deep water far away from shore. The new sediment settles just above the previously deposited material (Fig. 5.4(A)). Aggradation is simply the increase in land elevation step by step due to the deposition of new sediment in areas in which the

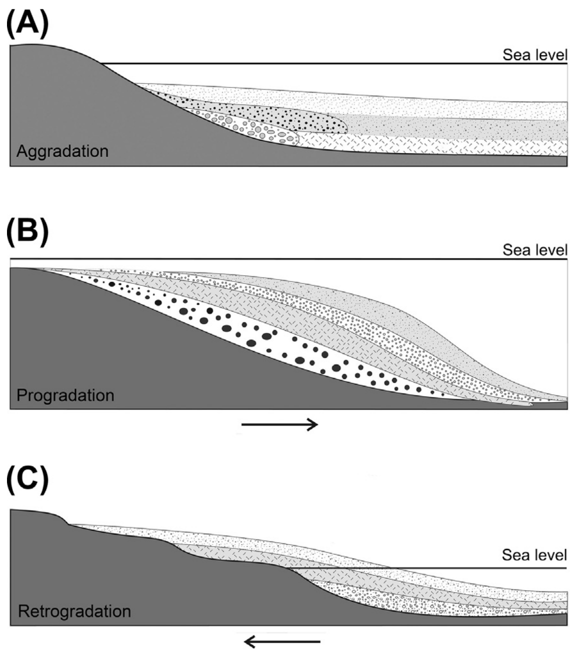

FIGURE 5.4 Three chief processes of debris settling from the moving of solid–liquid-mix materials and sedimentary feeling such as (A) Aggradation, (B) Progradation, and (C) Retrogradation.

supply of sediment is greater than the amount of material that the system is able to transport, often resulting subsidence. It typically includes lowland alluvial rivers, deltas and fans.

Progradation is the deposition process in which the depositional area fills most of its edges toward the center. The material deposits from the coast and moves progressively further toward the center of the depositional area (Fig. 5.4(B)). Progradation is the growth of river delta farther out into the sea over time, such that the volume of incoming sediments is greater than the volume of the delta that is lost through subsidence, sea level rise and/or erosion. The youngest sedimentary depositional units are usually not in its entire propagation deposited on the previously deposited units. The younger units settle on sediments deposited by aggradation rather than progradation, providing that portions of deposition by aggradation are significantly smaller than those formed in progradation. The consequence of progradation deposition is depositional sequence in which it does not always match the progradation sediment units. Progradation is the most prominent process of deposition in river deltas, turbidity fans, the deposition of fragments of skeletal organisms in coral and other reefs. The progress of coral reefs and other similar sediments deposits on the slope of the ridge. Progradation is very common in the tertiary deposits of Pannonian Basin, and has an important role in mutual relations between collector and isolator rocks in the oil and gas fields (Fig. 5.24).

Retrogradation is a process of deposition in which sedimentation area expands due to relative or global lifting of sea level, i.e. sinking of depositional area or rising of global sea level. Retrogradation is generally characteristic for the transgressive cycle during which the shallow-sea sediments precipitate farther and farther toward the mainland along with the influx of sea and coastline moving increasingly into the mainland (Fig. 5.4(C)). In this way over the initially deposited shallow marine sediments precipitate sediments of deeper and deeper waters. In other words, the process is the landward change in position of the front of river delta with time and occurs when the volume of the incoming sediment is less than the volume of the delta that is lost through subsidence, sea level rise and/or resulting erosion.

The gradual decline in the power of water precipitates the largest or larger particles first, and then all the finer particles. The major part of coarse river sediments deposit in alluvial fans (Section 7.2.2; Figs 7.1 and 7.2), deltas (Section 7.2.2; Figs 7.3 and 7.4), and the fine-grained sediments on the flood plains in floods, i.e. discharge from the river bed. A huge amount of sand and muddy sediments accumulates on the tidal plains and the sand deposits on the shallow sandbanks and sandy beaches (Section 7.2.3) and in the turbidity range (Section 7.2.5).

The turbidity current carries huge amounts of assorted sedimentary material down the slope and arrives on the flat bottom first. It, fairly and quickly, deposits majority of the large grains at that area from the head of turbidite flow within minutes or hours. All the sands and even finer grains are deposited in next few days and weeks, and the remaining tiny particles of clay from the tail of turbidite flow settle only a few hundred or even thousands of years duration. In such deposition of turbidite flow crop-up fan-shape sedimentary body or “turbidity fan” with proper vertical and lateral sorting of grains and particles, specific layered shapes and textural—structural features (Section 7.2.5). These sediments are known as “turbidites”. Large quantities of coarse granular debris deposit by gravitational flows at the foot of steep cliffs or mountain ranges in the form of talus on land or debrites under the sea (Fig. 5.24; Section 7.2.4).

The alluvial fan, lake and marine deltas, tidal plains, shallow-sea sandbank, as well as turbidity fans and debrites are the most important sedimentary bodies with characteristics of oil and gas collectors. Large amounts of calcium carbonate can be deposited on the bottom of waterfalls and in freshwater lakes through the life processes of plants in the form of calcareous tuff (Section 5.7.1.3.2; Fig. 5.43, etc.). Materials created by direct excretion of minerals from the water, either inorganic or organic, or biogenic processes precipitate in the sea. Similarly, large quantity of skeletons and shell of organisms (Section 5.7.1) settle down in shallow and warm seas. In this way, carbonate platforms are formed with different shapes and types of carbonate sedimentary bodies, which can also be an important reservoir rocks for oil and gas (Section 7.3.1). The deeper seas/oceans are favored location for deposition of the finely grained pelitic sediments (Section 5.5.4), the carbonate mud (Section 5.7.1.1.2), and the silicon sediments (Section 5.7.4).

The sediments and sedimentary rocks receive special shapes and the textural–structural features as a result of different mechanisms of transport and deposition of material, lithification or diagenetic processes. The exploration geologists, and especially sedimentologists, can reliably determine the conditions and the environments of deposition of sediments and the rocks deposited in geologic past through systematic study. The inferences can logically be experimented to demonstrate the depositional environment and process (Fig. 5.5).

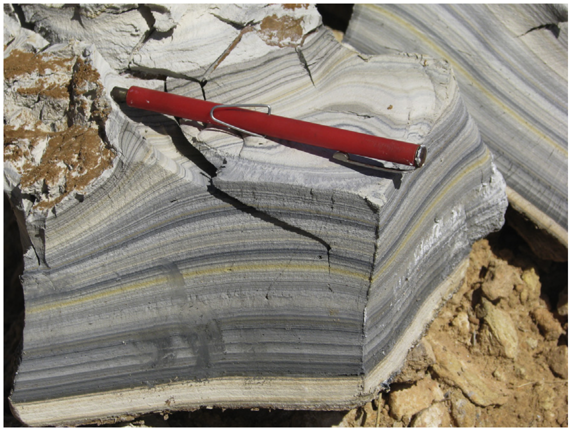

FIGURE 5.5 Alternate thin layers of extremely fine-grained calcium carbonate (light and white) and metallic minerals (sphalerite, galena and pyrite—gray, yellow and orange) deposited within week duration out of fine clayey diamond drill cuttings passing through zinc-lead mineralization in limestone host rock. The deposition occurs within the drill-sump of return water. The particles settle in rhythmic layers due to difference of Sp. Gr. between limestone and metallic minerals and dried fast at day temperature of ~50 °C. The recently formed compact sediment resembles laminated limestone. Image is taken at drill site of Lennard Shelf Exploration Camp, Meridian Minerals Limited, Western Australia in midsummer of 2011 by the Author.

5.2.4. Lithification

Lithifaction is a complex set of physical and chemical processes known as *diagenesis*. These are processes by which bulk, soft, water-saturated loose deposits gradually become solid sedimentary rock. The major diagenetic processes of lithifaction include compaction and cementation.

Compaction is the process of mechanical compression or packing of soft, loose, porous and water-soaked sediment with increasing pressure due to the weight of new sediments, i.e. due to increased depth of the overlay. The older compact sediments fall deeper under the increasing amount of new sediments, so that water eliminates with compaction flow and rises into the upper layers causing chemical diagenetic changes—the secretion of new minerals. The compaction results decrease in porosity of the sediments and its gradual solidification with the changes in mineral composition, and excretion of new mineral resulting in cementation of the sediments or rocks (Section 5.5.5).

Cementation is the process of excretion and crystallization of minerals in pores of the deposits. The new or authigenic minerals are called *cement* (Fig. 5.18). It leads to a decrease in porosity and to interconnection of individual grains and components in solid rock. There are other chemical diagenetic processes, other than cementation, that play an important role in solidification of deposits and their gradual transition in solid rock. The most important among them are dissolution, pressure dissolution, authigenesis, recrystallization, silicification and dolomitization (Sections 5.5.5, 5.7.1.4, and 5.7.2.1).

5.3. TEXTURE AND STRUCTURE OF SEDIMENTARY ROCKS

The sedimentary structure refers to all the features caused by their mutual relations, spatial distribution and orientation of individual components, as well as external and internal morphological forms of sedimentary rocks. The texture of rock includes the grain size, relationships, distribution and shapes of the mineral components, i.e. internal microdistribution of its constituent parts.

Primary sedimentary structural shapes (layers and laminations) are formed during deposition or shortly after, and certainly prior to compaction and lithifaction of deposits. The primary textural—structural shapes also add up the forms, the appearance and features that are in the sediment or by simultaneous deformation with deposition or shortly after deposition before covering with new sediments. All other forms that in sediments and rocks are formed after deposition, i.e. during diagenetic processes, are called secondary textural—structural forms.

In general, textural—structural shapes and structural characteristics of sedimentary rocks belong to its most important feature. The primary textural—structural sediments form under the direct result of the conditions that existed in transport and deposition of material and the resultant of all processes in the environment of deposition. The secondary textural—structural features are the result of complex diagenetic processes (recrystallization, pressure dissolution, compaction, and chemical diagenesis).

The grain size is the most important characteristic of clastic and calcareous sediments. It is closely related with physical, chemical and hydrodynamic conditions that existed during formation, transfer and deposition of debris. The investigations of grain size of clastic sediments are essentially significant for determining the conditions of weathering and breaking methods and mechanisms of transfer and deposition of material. It is also necessary for the classification and nomenclature of the clastic sediments based precisely on the grain size. The calcareous sediments originate in different conditions and present various textural—structural features, classification based on the size and shape of grains or skeletal and nonskeletal components (e.g. terminology intrasparite, intrasparrudite, grainstone, rudstone, biocalcrudite, biocalcarenites, etc.; Section 5.7.1.3). The degree of crystallinity and crystal size are the main textural features of chemical sedimentary rocks. The size and crystalline forms are microcrystalline, euhedral macrocrystalline, mosaic structure, etc. (Section 5.3.2).

The knowledge of textural—structural characteristics and layer forms of sedimentary rocks are valuable information and necessary for the reconstruction of the conditions and environment of deposition, such as, depth and water energy, transfer method of material and mechanisms of deposition, flow direction, role of organisms, shape of sedimentary bodies, facies, etc.

5.3.1. Bedding

The main structural characteristic of sediments and sedimentary rocks is bedding with wide variations that include irregular, regular or rhythmical and cyclical, gradation, sloppy, flazer, lenticular and wavy, horizontal, oblique and sinuous. The bedding is one of the first characteristic that is observed in the field as a fundamental feature of sedimentary rocks. This phenomenon is more or less clear separation of individual textural—structural, lithological or grain size distribution of unique members or "layers" in sedimentary rocks.

The layer is the geological body generally of uniform composition and internal layer forms throughout the thickness of sedimentary package. The sediments deposited below and above are separated by some discontinuity, change in particle size or mineral composition. The thickness of layer is not always the same size, but varies in wide limits, depending on the morphology of sediments below, mechanism, method and conditions of deposition and textural–structural shapes. The layer can be considered as lenticular body of different thickness and propagation, and in certain circumstances and environment of deposition and wedge-shaped body, e.g. the case for foreset of deltas and underwater dunes (Sections 7.2.2 and 7.2.3).

The separation of individual layers can be mechanically represented by the open layer or layer plane. In the absence of such mechanical separation, the bedding can be clearly identified by changes of smaller and larger components, the distribution of fossils, organic matter, change of color, porosity and methods of cementing or changes in forms, the types of rock and mineral components, changes in internal features (changing layers with oblique bedding and lamination). The layers can be separated from each other with thinner, usually soft, interlayers, like clay, silt, marl or sand, deposited between solid layers of limestone, sandstone, conglomerate and chert.

The sedimentary rocks sometimes do not include any bedding and are massive or nonbedding rocks, which is often the case in late-diagenetic dolomites and breccias. The massive rocks are often without internal organization or internal forms and not just on the rocks with no open bedding. The distinctness of two main beddings is (1) external or irregular, rhythmic or cyclical bedding, and, (2) internal bedding.

5.3.1.1. External Bedding

External bedding with the presence of separation of individual layer is the most significant structural characteristics of sedimentary rocks. The basic unit of the external beddings is the layer created as a result of sedimentation in uniform physical, chemical and/or biological conditions under constant and continued deposition. If any of these parameters changes, then there is a change of sedimentation, thus forming a new layer. The layers differ with regard to thickness by bedding (>1 cm) and laminae or lamination (<1 cm). The vertical layers are classified into two categories, (1) irregular and (2) regular, considering the grain size sorting with different or same lithological or textural–structural characteristics.

1. Irregular bedding includes a completely uneven and asymmetrical vertical sorting of layers of different types of petrographic or textural–structural forms (e.g. ACBADC), as a result of a completely irregular changes in sediment area.
2. Regular, cyclical or rhythmic bedding with the vertical sequence of alternate petrological and/or textural–structural different layers at uniform vertical periodic repetition of such changes (Fig. 5.6). The group of layers in one cycle of repetition is called a sequence, cycle, parasequence, cyclothem, megacycles or megasequence, according to periodic repetition with respect to the dimensions duration and manner of deposition origin.

5.3.1.2. Internal Bedding

Internal bedding includes textural–structural forms within a single or multiple layers. Most often, and for the interpretation of conditions and environment of deposition, the major types of internal beddings are horizontal bedding, convolute bedding, planar cross-bedding, trough cross-bedding, hummocky cross-bedding, flaser bedding, wavy bedding, lenticular bedding and graded bedding.

Horizontal bedding is a type of internal bedding in which each layer consists of many thin (0.1–10 mm) parallel laminae. Each individual lamina is characterized by unique granulometric and petrographic composition (Fig. 5.7). This

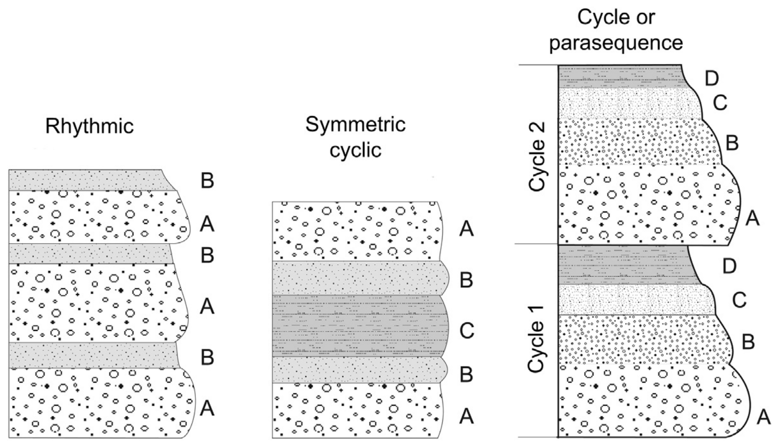

FIGURE 5.6 Regular bedding with vertical sequence of rhythmic, cycles and parasequence style of sedimentary deposition and lithification.

type of bedding typically occurs as a result of faster or slower changes in the deposition of fine-grain detritus, silt and fine sand, or changes in temperature and concentration of water.

Convolute bedding is a special type of bedding inside the layer (thickness >10 mm) or within the lamina (thickness <10 mm). It is characterized by convolute laminae within the layer that is in sequence with the top and bottom layers. The convolute bedding is generally the best and most developed in the fine sand and dust sediments. It occurs as a result of hydroplastic deformation of still unhardened sediment under the influence of strong water currents that flow over such deposits. The bedding is formed by the mutual friction between the current flow and sediment. It can also form in the postphase of sedimentation as a result of hydroplastic deformation due to the sudden displacement of water or the sudden release of gases from the sludge.

Cross-bedding is the most common and most significant layer in the form of sedimentary rocks. It consists of groups of mutually parallel lamina or layers deposited askew in relation to the outer surface layer (Fig. 5.8). The cross-bedding refers to horizontal units that are internally composed

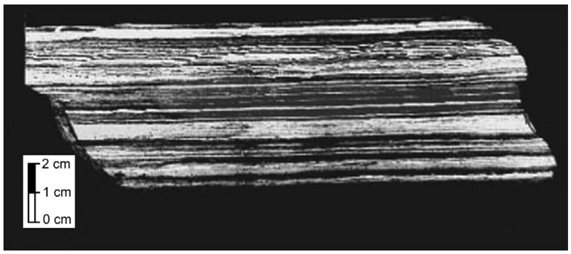

FIGURE 5.7 Horizontal bedding—vertical changes of dark clay-marly laminae and light carbonate laminae.

of inclined layers. The groups of units of the same or similar slope are called *set*. The layers and laminae within the sets that have a slope in the direction of input of materials are known as *foreset*, for example, by precipitation in the delta (Fig. 7.8(B)), large currents or underwater dunes. The cross-bedding can be designated as (1) planar cross-bedding, (2) trough cross-bedding and (3) hummocky cross-bedding according to the shape and characteristics.

Planar cross-bedding is characterized by more or less planar boundaries between sets (Figs 5.8(A) and 5.9) and is characteristic of river sediments, and the most important feature of eolian dunes and foreset underwater dunes.

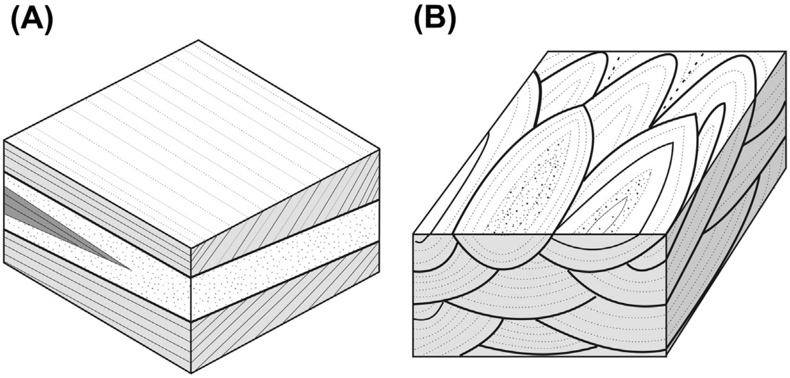

FIGURE 5.8 Conceptual diagram showing (A) planar cross-bedding and (B) trough cross-bedding.

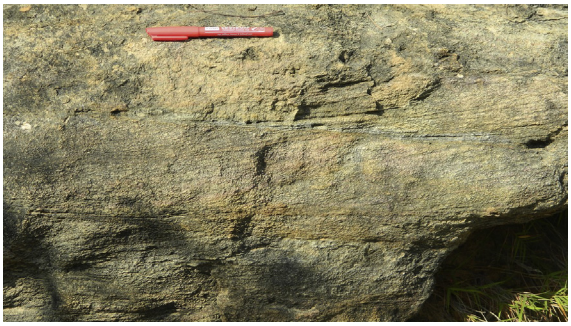

FIGURE 5.9 Field photograph of planner cross-bedding. *Source: Prof. Biplab Bhattacharya.*

FIGURE 5.10 Field photograph of trough cross-bedding. *Source: Prof. Biplab Bhattacharya.*

Trough cross-bedding have surface of sets in shape of trough (Figs 5.8(B) and 5.10). More sets and cosets of similar thickness appear regularly in between layers. This shape can be well observed in cross-section perpendicular to the axis of the trough. It is characteristic of fine-grained sandy river sediments deposited in river beds, and along with planar cross-bedding in sandy sediments of intertwined rivers.

Hummocky cross-bedding is a special form of cross-beddings, characterized by wavy or hilly sets of inclined lamina. The inclined lamina are parallel to the base, and a little wavy, and placed one above the other, alternating convex and concave curved forms, often showing erosion on older lamina. Hummocky cross-bedding is generally found in sediments of granulometric composition to coarse powder and fine sand (0.03–0.25 mm). It occurs in shallow shelf sands below fair weather wave base, which is usually located at 5–20 m depth. It is an essential feature of tempestite or storm sediments, i.e. sediments deposited in stormy waves.

Flaser, lenticular and wavy bedding are of great importance for the reconstruction and interpretation of conditions and hydrodynamic features in the environment of deposition. The gradual transition from flazer through lenticular bedding has a certain interrelationship of deposition of sand and mud (clayey-dusty detritus) and indicates decline in water energy (Fig. 5.11).

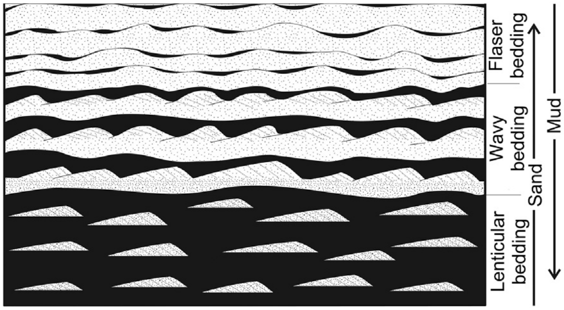

FIGURE 5.11 Conceptual diagrams depicting the flaser, lenticular and wavy bedding composed of finely granular sand (light), and clay and mud (dark).

Flaser bedding occurs in fine-sandy and weakly clayey and muddy sediments with wave and current ripple. It is characterized by cross-laminations draped with silt or clay. Flaser beds form in environments where the strengths of current flow fluctuate considerably, thus permitting the transport of sand in ripples, followed by low-energy periods when mud can drape the ripples.

Wavy bedding is genetically similar and associated with flaser bedding. It is characterized by equal amounts of sand and mud in composition. The clay—argillaceous deposits, above sands containing the wave or current ripple, precipitate in the form of continuous layers, unlike flaser beddings. The sandy wavy layers are mutually separated by a layer of clay or argillaceous material (Fig. 5.11). The sand with ripples is deposited in the period of stronger energy of water, and clay and/or pelite during weak energy of water which, in comparison to what in creation of flaser beddings last longer. Wavy bedding in modification of flaser and lenticular bedding usually occurs in the tidal plains and in the tidal environments.

Lenticular bedding is characterized by the appearance of individual, mutually laterally and vertically disconnected lenses of sand deposits within clay—silt residues (Fig. 5.11). It occurs in quiet, shallow water, usually in tidal environment of deposition. The structure is common on the foreheads of the marine delta and small lake delta, where the deposition of mud is predominant with occasional input of sandy accumulation in short periods of excessive supply of water. The sand deposits in the form of isolated unrelated wave or current ripples or lenses, specifically in stronger flow of water.

Graded bedding is characterized by a gradual decrease in grain size from the base to the top layer. The grain size ranges from gravel in the bottom, through the sand to muddy sediments at the top. The deposit usually forms in interval of T_a Boumina turbidity sequences. It follows an initial deposition of large grains and graded progressively upward finer grains with decrease in transport energy as time passes. The differences in speeds of movement control sequence of deposition of coarse and fine-grained debris (Fig. 7.10). The gradation can occur in deposition from the suspension in the final phase of severe flooding and high tides. The gradation can also occur by deposition of volcanoclastic material with volcanic eruptions. The volcano ejects large-size particles at the beginning of the eruption and followed by weakening of the eruption progressively charging smaller material.

5.3.1.3. *Upper Bedding Plane Structures*

In the upper bedding planes, most important and common forms of structures are desiccation cracks ripple marks, and occasionally even reptile footprints and imprints of rain drops.

Desiccation cracks or *mud-cracks* form when drying mud shrinks. The shape and size depend on their mineral composition, grain size, intensity of drainage, thickness and homogeneity of the layers and deposits. The cracks appear in the upper bedding planes of clay, silt, mud, clayey—sandy sediments, and muddy or micrite formed by early diagenetic limestone and dolomites. The cracks are arranged on the surface layers in more or less regular polygonal shapes (Fig. 5.12), generally V-shape in cross-section and in the lithified sediments. The cracks are

FIGURE 5.12 Desiccation cracks developed in recent sediments at Papuk, the largest mountain range in the Slavonia region in eastern Croatia.

regularly filled with sediment of upper layer rock materials. The formation of cracks are limited to the subaerial conditions in continental environments, especially alluvial flood plain, drained ponds, tidal and supratidal environments, and primarily of vast tidal plain, where water is rapidly lost from the deposits or sediments.

Ripple marks are systems of microridges and valleys, like surface of wavy sea and desert sand dunes, and often observed on the upper bedding planes of sandstone and limestone layers. The ripples (waves) are described by measuring their height or amplitude and wavelengths to ascribe the morphology, such as symmetric, asymmetric, and transverse ripples. These elements, however, provide very important information on the conditions and environment of deposition, particularly on energy and the way of the water flow. Ripples appear in groups and always on large planes (Fig. 5.13). The ripples are created by moving the unbound, mainly sandy sediments with water currents.

The wave and current ripples differ according to the origin:

- Current ripple marks occur in one-way transfer of sand with water flows or currents, i.e. currents which are moving in one direction only for long time, such as in tidal currents. The current ripples are characterized by the orientation of longitudinal axis of ripples transversely to the direction of flow and properly arranged crests and troughs. Little current ripple marks occur in muddy and fine-grain sand and limestone sediments in river environments, on the tidal plains and

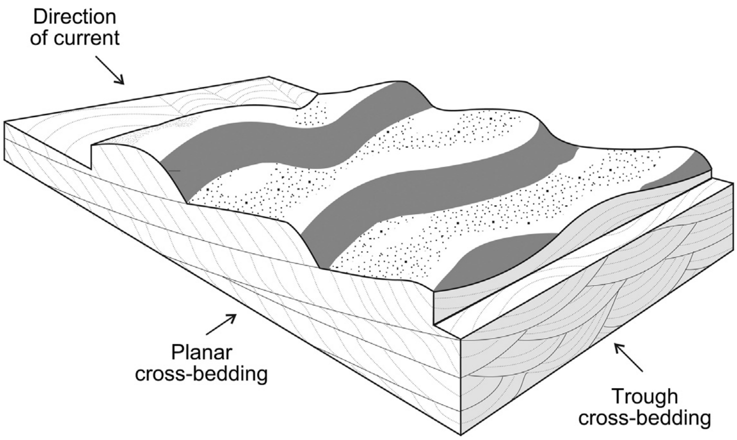

FIGURE 5.13 Conceptual diagram presenting the wave formed by ripple marks, in lateral cross-section showing the planar cross-bedding, and in longitudinal section trough cross-bedding.

sandy beaches. Large current ripple marks, known as mega-ripples, sand-waves underwater (subaqueous) dunes, occur in higher energy of water in river environments, tidal channels and backwaters. These are frequent on the tidal plains, sandy beaches and coastal shallows where the difference in the level of low tide and high tide is >1 m or shallow water exposed to strong tidal currents with waves. The current ripples are excellent indicators of energy and water depth, and if they are asymmetric also can indicate deposits transport directions (Fig. 5.14).

- Wave-formed ripple marks generally forms in weak currents because of relocating sand in oscillation motion of water with waves, i.e. in continuous circular motion of water. These types of ripples are distinguished by long, mutually parallel with arched crests. They are typically symmetrical. The most common ripples are on the tidal plains, beach front or tidal zone and lake beaches and are common in lagoons, sandy beaches below low-tide, supratidal zone and lakes.

Footprints of reptiles, particularly large Jurassic and Cretaceous reptiles, the dinosaurs, are often rare in the upper bedding plane. These marks can be preserved only in special conditions, where the reptile left footprint on the soft sediment in tidal shallows with low water supply. The high-quality and authentic prints are expected in the peritidal sediments formed under conditions of low water energy, especially those containing cyanobacteria (blue-green bacteria and blue-green algae) meadows with mud sticking property. Thereafter, gentle tidal currents bring new sediment that fills and covers the total footprints, and gradually the entire surface layer. The footprints are preserved in such environments excelled by rapid cementation of deposits. These footprints of prehistoric era are particularly significant from the sedimentary and paleontological point (Fig. 5.15).

Raindrop imprints formed during collision of large drops of rain on the soft clay, sand, and rarely on carbonate mud, which is located above the water level. The rain drops can be preserved, only if, new sediment starts to deposit quickly, while there has been no erosion or destruction of the impression. Prints of the rain drops are excellent indicators of environmental conditions and precipitation since they appear only in continental environments or muddy supratidal zone.

FIGURE 5.14 Shallow current ripple bed forms on arenitic sandstone, Kolhan Group, Chaibasa, Jharkhand, India. *Source: Prof. Joydip Mukhopadhyay.*

FIGURE 5.15 Dinosaur footprints at Istra, the largest peninsula in the Adriatic Sea, Croatia.

All these print impressions are authentic indicators of the youngling direction of stratigraphic column.

5.3.1.4. Lower Bedding Plane Structures

There will be many types of inorganic forms on the lower face of the plane surface. These will play significant role in determining the sequence of layers. These forms are found most commonly in turbidite deposits. They are divided into two genetic groups:

1. Traces of erosion resulting from the action of turbidity currents or vortex flow.
2. Traces of erosion resulting from the action of various items that are carried by water currents.

The most common signs of flow, among the traces of erosion, are flute casts, vortex casts and erosional channels, and are described.

Flute casts are triangular or spindle-shaped protrusions on the lower surface of sandstone bed. The flow of input vortex currents is more protruding on a narrow front than on the wider part of the back, which gradually disappears on the flat surface. The flutes are narrow, elongated, straight, parallel ridges generally consisting of till, sand and clay. The length of the flute casts generally ranges between 2 and 10 cm, and sometimes to 1 m. The casts occur in filling of depressions on the muddy bottom at the beginning of movement. The depressions are filled by sandy sediment and lithifaction on the lower surface of sandstone on muddy bottom. It will remain as protrusion which has greater convexity on the input than on the output of the resulting erosion and sand sediment-filled valleys. The flute casts can easily determine the direction of the paleotransport.

Vortex casts are spiral protrusions on the lower surface of sandstone. The casts have shapes similar to the spiral end of snail home. The dimensions and shapes are various. The height of protrusions generally varies from 1 to 3 cm, and their diameter between 6 and 20 cm. The casts are sand-filled depressions formed by erosion of strong vortex currents or turbulent flows. The vortex casts are good forms for determining the paleotransport directions and for reconstruction of hydrodynamic conditions in the environment of deposition.

Erosional channels are erosional forms created with the removal of sediment further into the depositional area from the portion of one or more layers. The channels have width ranging between few decimeters and tens of meters and length between few decimeters and hundreds of meters. The most common occurrences are by erosion of clay or marl bottom.

The most common traces of moving object on bottom are signs of cutting, rolling and pulling.

Groove marks are created when sharp object is dragged across the surface of muddy substrate. The length varies between few decimeters and few meters, width between one-tenth millimeter and several centimeters, and height between several millimeters. The groove marks usually appear in groups with parallel arranged linear prominence. In some places, it gradually transforms into traces of pulling. The marks occur as objects scours out a groove along the top of the bed, which is later filled by coarser sediment. The groove marks are good indicators for determining direction of paleotransport.

Impact casts are short, narrow, asymmetrical shapes embossed on the lower surface. The input end is thin and gradual, and the output end is wide with the sharp end. The lower surface looks like small wedges. The casts appear in groups, often with a different mutual orientation. The impact casts are formed by filling cavities in the muddy bottom, which has left with current carried object into the bottom (Fig. 5.16).

Bounce marks appear on the lower surface as a straight series of small bumps arranged of approximately equal, millimeter to centimeter intervals. The bounce marks occur in filling of depressions or mold, formed on the clay bottom when object is carried by vortex current. It makes contact with clay bottom and then bounces back up in the turbidity flow.

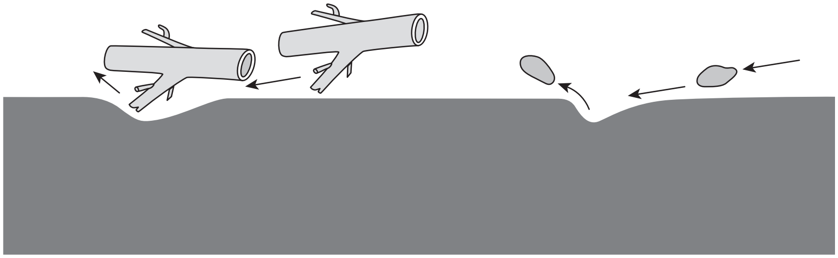

FIGURE 5.16 Conceptual diagram showing the formation of impact casts in soft sediments.

5.3.1.5. Forms Created by Underwater Slides and with the Destruction of the Layers

Slump or structure of underwater sliding is created by underwater sliding and the destruction of layers. It occurs in yet unrelated or semiplastic sediments due to the increasing angle of inclination of the bottom. The structure represents the occurrence of more or less deformed layers, often interrupted with continuity of one undeformed layer between mutually straight and parallel (concordant) arranged layers. The mechanism works in sliding of one or more layers of partially lithified or semiplastic sediments on clay substrate. The sliding takes place by gravity at an angle of inclination of the bottom of only 1–3° (Fig. 5.17). The slumps are common in sediments formed by rapid and intense accumulation of deposits, such as deltas and canyons, slopes of carbonate platform as well as upper parts of submarine slopes. The slump scars can be formed by underwater landslides of large dimensions with complex structure. In a way it is created by slip or sliding of massive sediments. The slumps occur along the low-angle inclined slopes in sedimentary rocks. Therefore, the incidence indicates the mechanism either on the synsedimentary tectonics such as subsidence of basin bottom and/or uplift of the coast and the mainland, or deposition in sedimentary body of inclined sides, e.g. the case on the front of deltas fans (Fig. 7.3; Section 7.2.2).

Bioturbation is a common name for all kinds of changes in unrelated sediments and soils, formed by the activities of organisms. It depicts the network of soils and sediments or forms as a result of the life activities (moving, digging, crawling, eating, and making dwellings) left in unbound or poorly consolidated sediments by plans and animals. The organisms itself are not preserved. The largest part of such forms occurs immediately after deposition and in the first

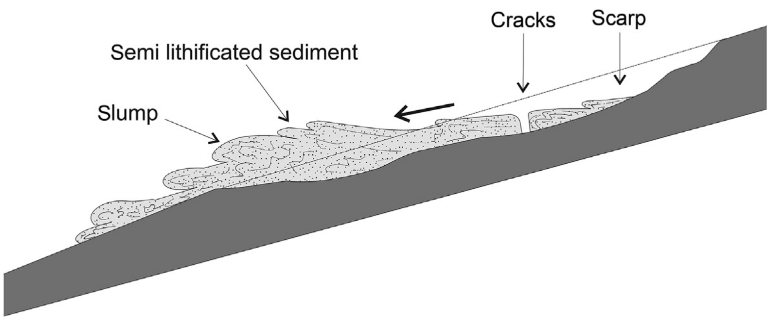

FIGURE 5.17 Conceptual diagram showing the mechanism of slump structure.

phase of consolidation of deposits. The extremely soft organisms still possess plenty of water and oxygen. The bioturbation causes destruction or transformation of primary bedding formed in sediment with inorganic material. Many of the primary internal textural and structural features may disappear by bioturbation process, e.g. horizontal, oblique or sinuous lamination, slope, flaser and wavy bedding.

Bioturbation is very common incidence under slow deposition and helps in the interpretation of conditions and environment of deposition. There is no possibility of inhabiting sediments with organisms, especially mud eaters, in rapid accumulation of deposits. The bioturbation sediments are indicators of slow sedimentation with small amounts of input and sedimentation of detritus in oxidative conditions.

5.3.2. Packing of Grains

The sedimentary rocks, especially clastic and many biochemical and chemical carbonate rocks, have grains, matrix, cement and pores. The grains in clastic sediments are clasts, i.e. solid substances remaining after the physical and chemical weathering of older rocks. The clasts are deposited after the transfer by water, ice or wind, as clastic sediments on land, in freshwater or sea. The grains (particles) in the biochemical and chemical carbonate rocks are the primary structural components formed by deposition of skeletal and nonskeletal carbonate materials within the depositional area. The grains in clastic and biochemical carbonate sediments are the basic structure of rocks or "float" within the dense mass, known as the *matrix*. If the grains or clasts are touching each other and support one another, it is called *grain-support* (Fig. 5.18).

The various matrix-support systems are the following:

1. Clast-support of unlithified deposit is characterized by grains (and clasts) in mutual contact. There is no matrix or cement in the intergranular pores.
2. Grains or clasts with grain-support cemented into solid rock, after elimination of mineral cements in intergranular pores.
3. Matrix-support or mud-support is characterized by the matrix in which the grains of clasts are not touching each other ("swim" in the matrix). Lithification of matrix is resulting in solid rock of matrix-support.
4. A general example of the structural components of a sedimentary rock with grain-support is consisting of grains and matrix.

In the mineralogical and petrological terms, the grain that built sediments and/or sedimentary rocks can be of different composition so that the grains are the following:

1. Individual mineral
2. Fragments of rock
3. The whole skeleton or shell
4. Fragments of skeletons or shells (bioclast)
5. Accumulations of carbonate minerals formed by chemical, biochemical and organic processes of abstraction from the seawater or freshwater.

The mineral grains and rock fragments of silicate composition consisting of quartz and other silicate minerals are usually covered by the common name, *siliciclastic grains* or *siliciclastic detritus*. The rock fragments of carbonate composition, i.e. fragments of older limestone and dolomites, unlike to the siliciclastic detritus, are commonly referred to as *carbonate lithic clasts* or *carbonate lithic detritus*.

The whole skeletons or shells may not be lithified on its habitat or in the location of growth. Their debris (bioclasts) are often matured as fossil detritus, or specify a skeletal detritus (for the whole skeletons or shell), and as bioclastic detritus (for fossil debris). However, the whole skeletons, shells and their debris, as the primary carbonate structural components in petrology and sedimentology of carbonate rocks, have often a common name "carbonate detritus".

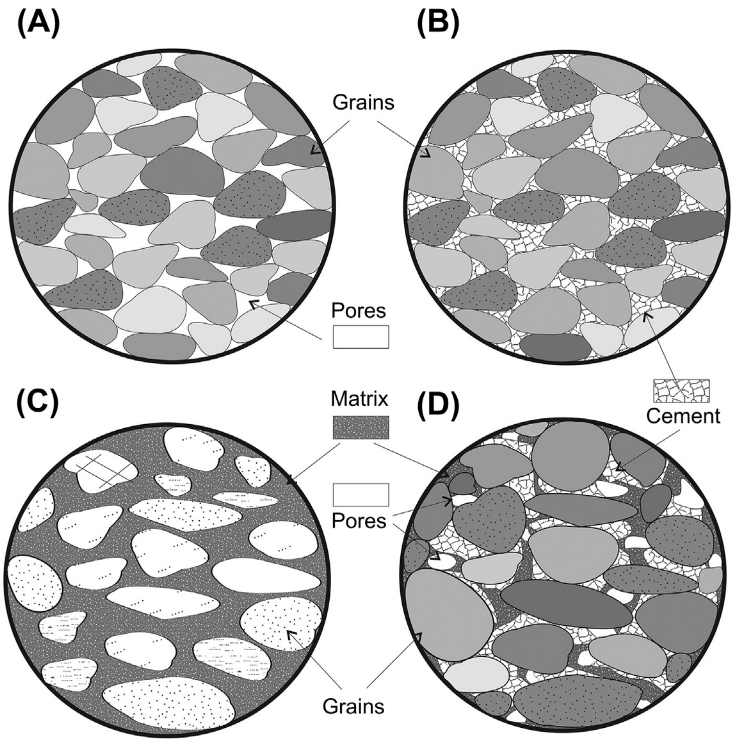

FIGURE 5.18 Conceptual models showing the packing of grains, cementation, matrix formation and lithification of clastic sediment. The various matrix-support systems are: (A) clast-support of unlithified deposit without matrix or cement in the intergranular pores, (B) grains or clasts with grain-support cemented into solid rock, (C) matrix- or mud-support with the grains "swim" in the matrix, and (D) finally, common example of sedimentary rock with grain-support of grains and matrix.

These grains usually undergo transport and deposition under the influence of ocean currents, waves or tides.

Matrix is the fine detritus, transported and deposited together with the grains (Fig. 5.18(C)). The matrix of sandstones is typically silt or clay. The same in conglomerates and breccias are fine sand, silt and clay. In limestone sediments the matrix is lime mud which is limestone lithified in micrite. The detritus with dimensions of <0.030 mm is marked as matrix. The matrix is placed in the sediment or in the interstices of grain or grains "swim" in it. In the interstices grains, the matrix is usually found with grain support. The grains or large clasts often swim in mud or muddy support (Fig. 5.18(C)).

Cement is the mineral substance secreted in pores between grains after their deposition. It is postsedimentation component originated from secretion of mineral substances from pore solutions. The pores are free spaces between the grains in which there is no matrix or cement (Fig. 5.18(A) and (D)). The free spaces are usually filled with gases (carbon dioxide, methane, hydrogen sulfide, and nitrogen dioxide) and/or water or oil.

The distribution and orientation of grains in the sediment depend on the conditions during transportation, deposition and mechanical diagenesis, especially compaction or compaction due to pressure overlays. The effect of compaction is strongest in the clay sediments, and very weak in large clastic and carbonate sediments. The sediments can be distinguished into three main types with regard to the manner of packing, sorting and proportions of different grain sizes:

1. Clast-support: grains or clasts have mutual support, i.e. between the coarse grains or clasts are well sorted by finer (Fig. 5.21) or matrix (sediment consisting of pebbles and sand).
2. Clast-support: grains or clasts have mutual support, and between large grains are poorly sorted small grains or matrix (sediment has polimodal composition).
3. Matrix-support: grains or clasts are not in mutual support but they "swim" in the matrix (Fig. 5.18(C)), i.e. not to have contact matrix in which they "swim" has polimodal composition (with mud, silt and clay and contains a grain of sand).

The most important textural—structural features of sedimentary rocks are reflected by the ways of packaging, and relations between the grains, matrix and cement. The key principles of classification of sedimentary rocks are based on these features. The chemical sedimentary rocks, i.e. recrystallized limestone, dolomite, evaporites and some siliceous sediment, are composed of crystals of chemical origin and not detrite grain. These rocks have crystalline texture according to the size of the crystal and divided into the following three types:

1. Macrocrystalline texture with crystals >0.1 mm and is especially common in late-diagenetic dolomite (Fig. 5.67) and recrystallized limestone, and is a common in some types of anhydrite.
2. Microcrystalline texture with crystal in diameter between 0.01 and 0.1 mm and is common in late-diagenetic dolomite, recrystallized limestone, anhydrite, gypsum and some types of chert (Fig. 5.70), radiolarite and diatomite.
3. Cryptocrystalline texture with crystals <0.01 mm and is characteristic of early diagenetic dolomite (Fig. 5.66), cherts, radiolarite and diatoms and, also certain types evaporite rocks (Fig. 5.69).

5.4. CLASSIFICATION OF SEDIMENTS AND SEDIMENTARY ROCKS

The size of the ingredients plays an extremely important role for classification of sediments and sedimentary rocks, except sediments that are pure chemical secretions. A common terminology, based on grain size of sediments, is qualitatively indicated for sedimentary rocks in sedimentology and petrology (Table 5.1).

The grain sizes are widely used after Atterberg and Wentworth scale. The Atterberg scale covers geometric, decimal and cyclical. The Wentworth scale encompasses logarithmic and geometric based on number 2. The Wentworth and Atterberg scales are shown in Fig. 5.19. The Wentworth scale is used in sedimentology and petrology. The Atterberg scale is usually used in geotechnical, civil engineering, hydrogeology and engineering geology.

There are two major genetic groups of sediments and sedimentary rocks and there are several mixed sediments between these two main groups:

1. Clastic sediments
2. Chemical and biochemical sediments.

TABLE 5.1 Size of Grains in International Language

Greek	Latin	English
Psefit (psephos = gravel)	Rudite (rutus = gravel)	Gravel
Psamit (psamos = sand)	Arenite (arena = sand)	Sand
Alevrit (alevros = silt)	Lutite (lutum = silt)	Silt
Pelite (pelos = clay)		Clay

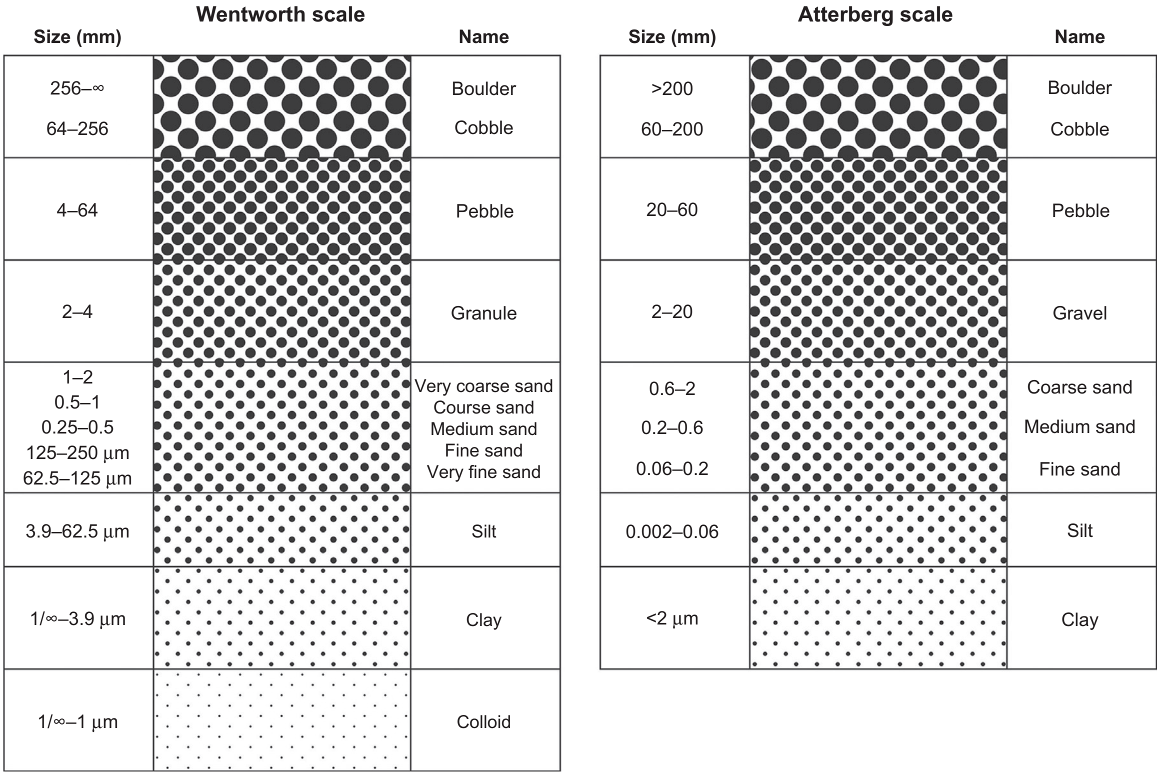

FIGURE 5.19 Comparison between Wentworth and Atterberg scale: the former is used in sedimentology and petrology, and the later for geochemical, civil engineering, hydrogeology and engineering geology.

5.5. CLASTIC SEDIMENTS AND SEDIMENTARY ROCKS

5.5.1. Genesis and Classification of Clastic Sedimentary Rocks

Clastic (detrite or mechanical) sediments and sedimentary rocks are composed of particles, grains and fragments that resulted from physical and chemical weathering. The physical breakage and destruction of older rocks are exogenous in origin and especially effective. These are solid particles, grains and fragments, i.e. individual particles composed of detrite or mineral grains or fragments of rocks, covered by a group name "clasts". Sediments and sedimentary rocks formed after shorter or longer transfer by deposition on land, in freshwater or sea are called "clastic sediments" or "clastic sedimentary rocks".

The four basic groups of clastic sediments are (Table 5.2) the following:

1. Cataclastic sediments that have been wholly or partly formed by the progressive fracturing and comminution of existing rock by a process known as *cataclasis*.
2. Rinsed residues, divided into coarse (rudite), medium (arenite) and fine (argillaceous) clastic rocks.
3. Residues are the remains of rocks that could not melt at the weathering and usually consist

TABLE 5.2 Two Main Genetic Groups of Sediments and Sedimentary Rocks

Clastic sediments
Cataclastic sediments
Rinsed residues
Residues
Pyroclastic sediments
Chemical and biochemical sediments

FIGURE 5.20 Rockfall on the Dolomite Mountain cliffs with amazing panorama at a vertical height of 2484 m from summit, Sellajoch, Val Gardena, South Tyrol, Italy.

of very resistant to chemical weathered minerals (quartz and silicate minerals) or autogenous minerals, mainly clay minerals and aluminum hydroxide.

4. Pyroclastic sediments that are formed by deposition of material of volcanic origin which is ejected by the eruption of the volcano, and that the transfer in air and/or water sediment on land, at sea or in the lake along with the smaller or larger amount of deposition of sedimentary origin, or without material sedimentary origin.

5.5.2. Coarse-Grained Sediments—Rudaceous

The coarse-grained sediments and sedimentary rocks are formed by the accumulation of grain diameter >2 mm. It can be of cataclastic origin and/or belong to the coarse-grained rinsed residue. The coarse-grained clastic sediments have following main types of sediments and sedimentary rocks:

Unbound	Debris	Pebbles	Till and diamictite
Bound	Breccia	Conglomerate	Tillite

Debris are unbound angular clastic sediments, fragments of rock of more than half have a diameter of >2 mm, and dimensions larger than grains of sands. These are the typical accumulation of debris caused by sudden and rapid rockfall under the influence of gravity down the steep slopes and cliffs (stone landslides or avalanches).

Rockfall or rock-fall or debris is accumulation of freely falling fragmented rocks (blocks) from a cliff face. The rockfalls are detached by sliding, toppling, or falling, that falls along a vertical or subvertical cliff, and proceeds down slope by bouncing and flying by rolling on talus or debris slopes. It ultimately settles on the land or steep rock slopes or at the foot of those slopes and is known as “rock-fall” (Fig. 5.20).

Gravel is an unbound accumulation of rocks, rarely minerals, well-rounded clasts, mostly in diameter >2 mm, and variable amounts of grain sizes of sand, dust, and sometimes clay, dust (mud).

Conglomerate is a firmly linked rock that mainly consists of well-rounded clasts in dimensions of gravel cemented by sand and mud component or rarely without it (Figs 5.21 and 5.22). The boundary between the breccias and conglomerates with certain types of coarse clastics may not be sharp and clear. These two types are of mutual crossings or clasts of particular

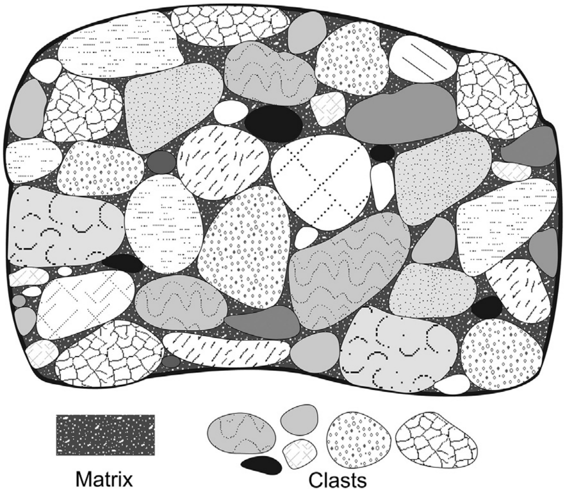

FIGURE 5.21 Conceptual diagram showing type conglomerate consisting of rounded and semirounded clasts cemented in fine-grain matrix.

FIGURE 5.22 Field photographs of conglomerate consisting of assorted grains and pebbles (rounded, semirounded and angular) of quartz (white), jasper (red) within a fine-grained matrix that have become firmly cemented together from Basal conglomerate, Kolhan Group near Jagannathpur, Jharkhand, India. *Source: Prof. Joydip Mukhopadhyay.*

petrographic composition. The conglomerate is typically of rounded and semirounded shape and the breccia is characteristically of rocks occurring in the form of angular or semirounded fragments. Some authors use the term "breccia-conglomerates" for these clastic rocks. The breccias and conglomerates are divided into intraformational and extraformational (Table 5.3) with regard to their place of origin.

Till is an accumulation of unbound and tillite of bound, poorly sorted and nonlayered moraine material dominated by fragments of >2 mm size. Such fragments often show well-preserved stretch marks and wears on one surface, as a consequence of scraping on the bottom and sides of rocks through which the glacier moved. Tillite is characterized by an abundance of fine-grained matrix, and is usually dark gray in color.

Diamictite is an extremely poorly sorted rock. It is composed of blocks of rocks and clay matrix and forms by accumulation and lithifaction of detritus derived from glacial and periglacial processes, as well as mud or detrite flows in subaerial and subaqueous conditions. Most of the diamictite clay matrix consists of different silicate minerals formed during glacial crushing (pulverization), i.e. decay and fragmentation of rocks. The share of clay matrix in relation to the proportion of rock fragments is very low. The blocks present great variability of dimensions and shapes.

5.5.2.1. *Intraformational Breccias and Conglomerates*

Intraformational breccias and conglomerates are coarse-grained clastic sediments formed by destruction and resedimentation of poorly or incompletely lithified sediment without significant transfer of fragments and clasts within the sedimentary area. Their precipitation occurs immediately after the destruction of the layer and formation of clasts, i.e. in the same stratigraphic unit. Intraformational breccias and conglomerates are usually limited to a narrow sedimentary horizon. It has no significant lateral and vertical distribution. Their origin is strictly limited to certain conditions and environments

TABLE 5.3 Genetic Classification of Breccias and Conglomerates

Intraformational Breccias			Extraformational Breccias	
Black-pebble breccias			Cataclastic breccias	
Stormy breccias			Collapse and emersion breccias	
Edgewise breccias			Postsedimentary diagenetic breccias	
Landslide and slump breccia pyroclastic breccias				
CONGLOMERATES				
Paraconglomerates <15% matrix			Orthoconglomerates >15% matrix	
Laminated matrix	Unlaminated matrix		Oligomict	Petromict
Laminated conglomeratic mudrock	Tillite	Tllioid	Oligomict orthoconglomerate <10% unstable	Petromict orthoconglomerate >10% unstable

of deposition (Table 5.3). These rocks are mostly located within the pelitic sediments and marls, often within a very shallow marine limestones and early diagenetic dolomite of carbonate platform. These rocks are excellent indicators for identifying changes in the conditions of deposition, frequent association with short emergence of deposits above the medium tide level or in tidal and supratidal environments exposed to high water energy, where they are usually deposited in stormy waves.[50,51]

Black-pebble breccias (and conglomerates) with black fragments resulting in resedimentation of erosion residues reductive black limestone deposits of coastal wetlands, marshes rich in organic matter and pyrite. It typically is located in the activity of bacteria that reduces sulfates. The rock forms by resediments depressions in tidal channels at peritidal, particularly tidal and shallow subtidal environments. The black marshes and ponds gradually change to brackish or freshwater ponds. It may result in sags and depressions on subtidal zone in areas with humid climates and reductive conditions. The carbonate sediments at the edges and bottom of the ponds and marshes are mostly all-black due to the abundance of organic matters. The storm or high tidal waves erode and break off pieces. The black pebbles wash into depression of tidal channels and deposit along with other carbonate, clay and sometimes, detritus, forming black-pebble breccia. The rocks are well isolated from the oxidation process due to the rapid covering of new sediments, so as to preserve their black color.

Stormy breccias and conglomerates or storm-tide deposits are a special kind of intraformational breccia or conglomerate. The storm breccias form in flooding and accumulation of deposits and fragments of the tidal plain and the shallowest parts of the lagoon edge or flat low coastline at storm waves and storm tides.

Edgewise breccia with flat fragments is a special type of intraformational breccia, whose origin is associated with resedimentation of flat muddy or carbonate-rich sediments. Such fragments occur in the superficial parts of the clayey and muddy sediments in their fractured desiccation cracks as a consequence of sudden drying up of deposits on river banks, flood plains and edges of lakes or ponds during low water levels. This is particularly common in the tidal and peritidal zone, and the muddy and carbonate tidal plains. The desiccation cracks can easily break down into flat fragments in high tides or storm waves that accumulate, usually far from the foundation of the depositional area.

Mudstone intraformational conglomerates are composed of spherical, ellipsoidal mud pebbles of mudstone or muddy limestone. Some pebbles may show clear traces of plastic deformation, generally within squeezing initially stronger pebbles in softer ones or kneading pebbles in the compaction. Muddy pebbles form by the destruction of incomplete lithificated muddy sediments with increasing water energy (strong tidal currents and waves, especially storm tides and storm waves) in the shallowest parts of the depositional area, i.e. the shallowest of the shallow subtidal and lower tidal zones. Their relatively frequent occurrence within the peritidal carbonate sediments is usually in connection with swallowing and/or sea-level fluctuations. A residue within the flood plain is related to the erosion action of the rivers in the rising of the water.

Land-slide and slump breccia results by accumulation of rock material with translational or rotational sliding destroying the mass of larger or smaller fragments in the form of olistostrome and slumps accumulated on land or underwater at the bottom of the slope. The slump breccias occur at the bottom of the submarine slopes of the accumulation of large amounts of sediment. It rotates during sliding down the slope and in its base accumulates in the form of deformed layers. If the deformed sediments have large dimensions, they are called "mega-slumps". Some parts of stronger lithified layers slide down the slope, break and fit into the homogenized plastic deposits making slump breccia.

5.5.2.2. *Extraformational Breccias*

Breccia is a general term for more or less tightly bound clastic rocks composed of angular to semirounded rock debris and cement or matrix (Fig. 5.23).

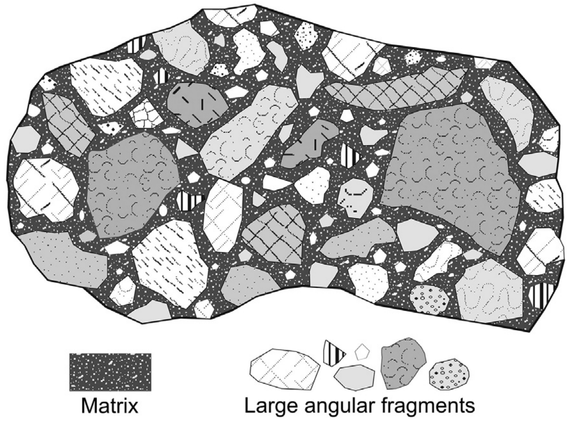

FIGURE 5.23 Matrix support breccia composed of rock debris in the form of large angular fragments of limestone and dolomite in the fine-grained matrix.

Breccias, in geological terminology, are often called by prevailing petrographic type of fragments. They can be dolomite breccia, limestone–dolomite breccia, etc. The sedimentological and petrological classification of breccias is based on the mode of their origin and is divided into the following:

1. Cataclastic breccias
2. Collapse and emersion breccias
3. Postsedimentary diagenetic breccias
4. Pyroclastic breccias.

5.5.2.2.1. EXTRAFORMATIONAL BRECCIAS

Extraformational breccias are coarse-grained clastic sediments containing clasts resulting in destruction and resedimentation of older rocks deposited in some other older geological formation. Thus, clasts originate from weathering of older rocks located outside of formation in which they are deposited. A good example for extraformational breccias is "Jelar breccias" whose clasts are deposited during the Oligocene (~33–23 million years ago) and are formed in destruction of limestones and/or dolomites deposited during the Jurassic (~200–145 million years ago), Cretaceous (~145–65 million years ago) and the Paleocene–Eocene (~65–32 million years ago). Extraformational cataclastic breccias contain clasts whose origin is related to the processes of breaking and crushing rocks with the movement of the rock mass over each other or along with each other, as well as the landslides and the collapse of the rock mass.

Tectonic is the most important factor of cataclastic, because in the tectonic movements, the largest range of rock mass moves along with enormous energy. Breaking and crushing rocks in the tectonic movements is strongest on the border between two masses that are moving, i.e. along the fault, and in the wrinkling. Small and large pieces of cataclastic rock masses break and crush during tectonic movements like landslides and rock-slip along steep cliffs. These broken rock pieces are transferred by different mechanisms, accumulated in the breccias zone and lithified. The clasts constitute special kind of cataclastic breccias.

Rockfall breccias are resulted by cementation of rock debris which pour down the steep slopes and accumulate at the base of such slopes in the form of large rockfall fans. Rockfalls are typically located at the foot of steep cliffs or ravines in between the steep rock and cliffs (Fig. 5.24). These breccias are commonly associated along with subaerial spending and strong erosion of rocks on a steep relief, along with more or less continuous tectonic uplift. The debris may move down the slope and reach in the lake, sea or river environments and/or switch to debrite flow.

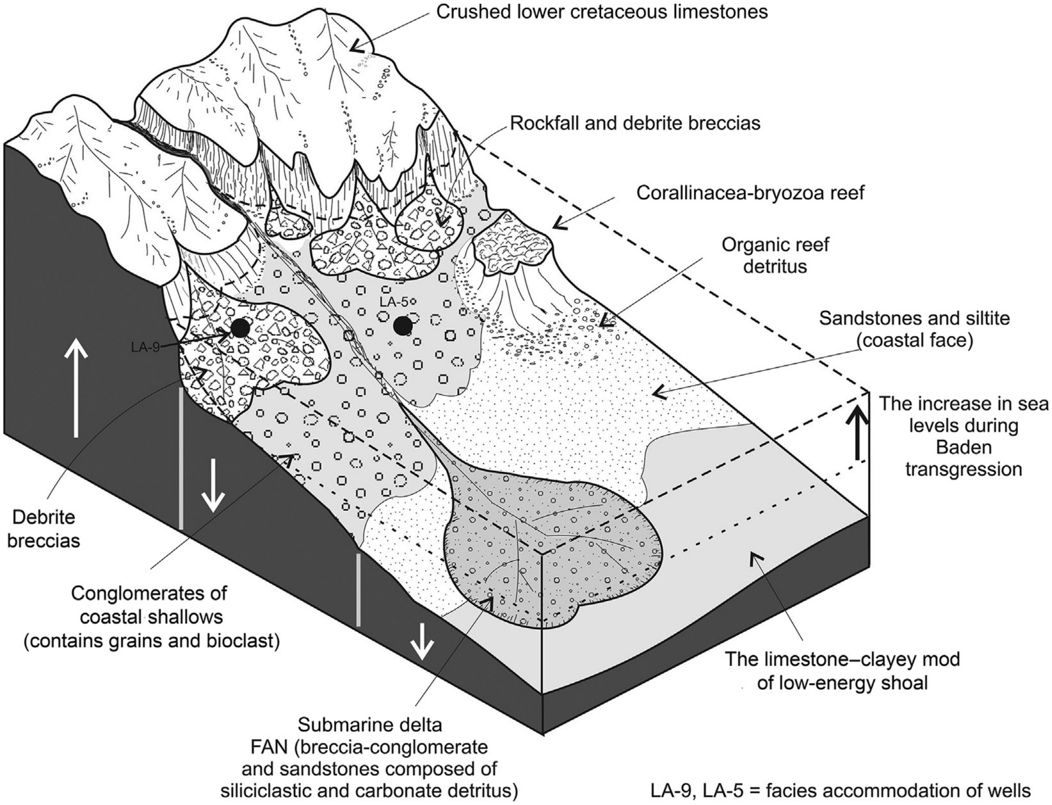

FIGURE 5.24 Idealized model of depositional facies distribution of Miocene sediments in to oil and gas field at Ladislavci, Croatia (not to scale).

Debrite breccias are formed by debrites cementation, i.e. the rock debris that has been transferred down the slope in debrite flows or in flow of the rock debris. The debrite breccias contain more matrix, usually silty material with a bit of sandy detritus, unlike rockfall. These are mainly located at the foot of submarine slopes and submarine canyons (Fig. 5.24).

The debrite breccias often include large clasts of olistolith (Fig. 5.24). An olistolith or olistostrome is a sedimentary deposit composed of a chaotic mass of heterogeneous material, such as blocks and mud. It forms by mutual enclosure relation of clasts and the abundance of finely disintegrated material or matrix of the same lithological composition. It may show similar shapes of bodies and the environment of deposition. The debrite and rockfall breccias are clearly distinguished from tectonic breccias. Rockfall and debrite breccias belong to dolomite and limestone–dolomite breccias, reservoir rocks from many oil and gas reservoirs. With the clasts of smaller or larger dimensions, such breccias occasionally contain larger blocks, even large olistolith (Fig. 5.24). The outline of sedimentary body of such breccias is wedge-shaped, fan or completely irregular, depending on the morphology of the slope or terrain at the bottom of the cliff. If debrite and/or rockfall debris plunges into a river or sea, it will be partly or completely processed into the gravel and in turn change to breccia conglomerate or conglomerate. It contains a different proportion of clasts, already in the river flow or shallow sea, as well as marine debris. The breccia conglomerate, conglomerates of coastal shallows and front beaches are formed by mixing the debrite and/or rockfall material with river sediments, coastal pebbles, shallow-sea carbonate, and fossil detritus. The coastal breccia conglomerates are suitable loci for oil field, e.g. Ladislavci oil and gas-fields, Drava depression in the south of the Pannonian basin, eastern Croatia (Fig. 5.24).

Fault and tectonic breccias are related to the tectonic zone of breaking, faulting, folding, wrinkling and pulling. These natural and mechanical phenomena crush crustal rocks into fragments and debris; dissolve the minerals later by the circulation of pore waters and finally able to be cemented in the solid rock as breccias. The solid lithified breccias is formed due precrystallizations of finely disintegrated calcareous detritus material that has emerged as a product of intense tectonic crushing, cataclastic and mylonitization. Tectonic breccias or clasts are frequently separated by only a system of tectonic cracks and not significantly moved. The tectonic breccias are characterized by clast support, and the matrix support arises in case of stronger crushing or grinding of rocks into "stone dust".

It only happens in the strongest zones of tectonic crushing or shearing during diagenesis, recrystallization and cementation of such small "stone flour".

5.5.2.2.2. EMERSION AND COLLAPSE BRECCIAS

Emersion breccias (karst breccia) are a special genetic type of carbonate breccia form in complex processes of physical and chemical weathering of limestone in subaerial conditions in the Earth's surface or in aerated zone. The emersion breccias are located in present-day karst environment in irregular shape as inserts or inlays, e.g. within the Mesozoic limestones of the Adriatic carbonate platform (AdCP). The AdCP is one of the largest Mesozoic carbonate platforms of the Perimediterranean region. The deposits comprised a major part of the entire carbonate succession of the Croatian Karst Dinarides Mountain chain with thickness up to 8 km and age between Middle Permian and Eocene.

Collapse breccias (breccias of dissolution and collapse) contain cemented clasts created by breaking of layers and rock masses during subsidence of layers after partial dissolution of fractured rock mass in the basement (melt breccia), collapse (collapse breccias) or cracking and crushing of quickly lithified surface part of sediment in mechanical diagenesis (evaporite collapse breccias). The collapse breccias are related to the processes of rock collapse, either by erosion or chemical corrosion processes. This is typically the case in karst caves, and in dissolution of layers of salt or gypsum. This is followed by collapse or subsidence of the roof clastic or carbonates rocks with their tearing into blocks and smaller or larger clasts and collapsing blocks in large corrosion cavity or cave. The collapse may occur on the steep cliffs, composed of two or more different petrographic types of rocks differently resistant to erosion or chemical weathering. It is possible, for example, the collapse of soft marls or mudstone, and firmly cemented sandstone in flysch or in turbidites.

5.5.2.2.3. POSTSEDIMENTARY DIAGENETIC (TECTOGENIC-DIAGENETIC) BRECCIAS

Postsedimentary diagenetic breccias form as a result of strong tectonic crushing of some parts of the rock mass, and followed by intensive diagenetic allochemical processes. The significant features and mechanisms are simultaneous processes including corrosion of the edges and corners of carbonate fragments, dolomitization of limestone fragments, calcitization or dedolomitization and occasional silicification of dolomite fragments. The process further continues in fine matrix disintegration and the multistep cementation of primary and secondary pore with secretion of calcite or ferrocalcite from pore solution saturated in Ca-bicarbonate.

Pyroclastic breccias are composed of coarse clasts, originate from volcanic eruptions and accumulate on the land, in freshwater or marine environments, after a short or longer transportation. These breccias are more fully discussed as part of pyroclastic sediments (Section 5.6).

5.5.2.3. Extraformation Conglomerates

Conglomerate is a solid rock formed in cementation and lithifaction of clasts with angular shape, i.e. pebble sizes of gravel (>2 mm). The mutual relations of pebbles and grains, matrix and cement distinguish between orthoconglomerates and paraconglomerates (Table 5.3).

5.5.2.3.1. ORTHOCONGLOMERATES

Orthoconglomerates are firmly cemented coarse-grained clastics which are characterized by clasts support and mainly composed of pebbles of gravel dimension and not more than 15% fine-grained matrix (argillaceous and clayey detritus), and cemented with the chemically extracted mineral cement (quartz, calcite, opal, etc.).

The oligomict and petromict conglomerates (Table 5.3) are distinguished by the mineralogical and lithological composition of pebbles resistant to wear, i.e. the amount of pebbles and grains of quartz, quartzite and chert. Oligomict conglomerates consist of >90% to wear-resistant pebbles and have simple petrographic and mineralogical composition; consist of pebbles and grains of quartzite and chert. The intergranular pores have relatively high content of chemical secreted cement. Pebbles and grains of oligomict conglomerates are the most stable remains of intensive spending of large amounts of older rocks. The rock represents the most resistant remnants of resedimentation rock debris after several cycles of transportation and deposition. Therefore, it symbolizes high degree of sedimentological maturity. The degree of sedimentological maturity is determined with content of the most resistant components as a result of several cycles of resedimentation. Pebbles of chert may be the remains of wear large masses of limestone containing lenses, nodules and concretions of chert, quartz and quartzite pebbles, remains of granite, gneiss and other metamorphic rocks that are criss-crossed with veins of quartz, zones or lenses of quartzite, or remains of quartzite inserts in phyllite, or chlorite schists.

Orthoquartzose conglomerates generally do not contain pebbles larger in diameter (8–10 cm) and do not appear in thick layers. It is characterized by a well sorting, a high degree of roundness and clasts support. The grain sizes of orthoquartzose conglomerates make a gradual transition in coarse quartz sandstone. It is typically found as thin layers within coarse-quartz sandstone of alluvial deposits or marine beaches deposited by high energy of water.

Petromict conglomerates hold more than 10% of the chemically wear unstable pebbles and grains of various petrographic and mineralogical compositions. The rocks are characterized by clasts support, and in the intergranular pores have excreted chemogenic cement: calcite, quartz, opal, and dolomite. The petromict conglomerates are mixtures of metastable pebbles (clasts) of different types of igneous, sedimentary and metamorphic rocks and grains primarily of quartz, ±feldspar and mica. The rocks are usually dominated by one petrographic type of pebbles, such as limestone (Fig. 5.25) or crystalline schist and quartzite of high degree of metamorphism. This is the most common and widespread type of conglomerate. Petromict conglomerates are characterized by relatively large pebbles, in some cases with a diameter >20 cm, as well as poor level of sorted sand grains in the interspaces between pebbles (Fig. 5.25). It mainly belongs to river sediments (alluvial fan), delta (delta head, the slope of the delta), and coarse-grained, rarely medium granular turbidites.

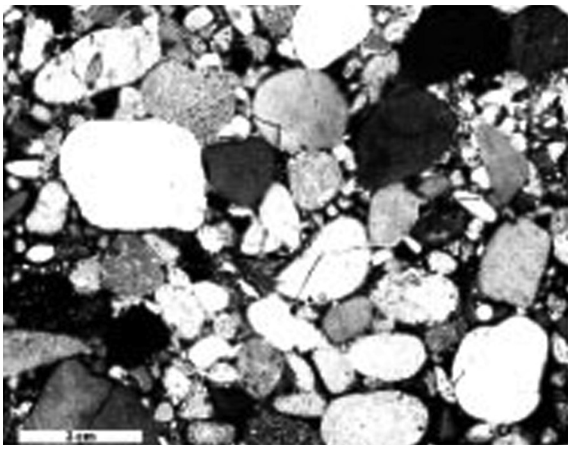

FIGURE 5.25 Petromict orthoconglomerate predominantly composed of perfectly rounded pebbles of Jurassic and Cretaceous limestone.

5.5.2.3.2. PARACONGLOMERATES

Paraconglomerates are a special type of conglomerates with a muddy or matrix support containing more than 15% clay-dusty (muddy or pelite) matrix whose share is often higher in relationship to the total volume of pebbles sizes of gravel (Table 5.3). These are in reality the sediments, which are not incurred in ordinary conditions of transportation and deposition of clastic material, but mostly a combination of iceberg transport and water floods in rapid melting of glaciers, sudden torrential flows at the foot of the mountains (piedmont zone), debrite flows or alluvial fans in sudden floods. This type of conglomerate has significantly lower distribution with respect to its other counter parts.

5.5.3. Medium Granular Clastic Sediments—Arenaceous Rocks

The arenaceous rocks include all those classic rocks with particle sizes range generally between 2 and 1/16 mm. The most common arenites are graywacke and sandstone followed by calcarenites (carbonates and limestone), oolitic iron ores and glauconite beds.

5.5.3.1. The Composition and Distribution of Sandy Sediments

The clastic medium granular sediments are represented by sands as unbound sediments and sandstones as solid rocks. Sands and sandstones are sediments that are predominantly composed of detrite grains sizes of sand, i.e. a grain in diameter between 0.063 and 2 mm. The rocks are characterized typically by dominance of sand-size grains with minor share of powder-size clay particles and of tiny gravel.

The primary material, grains of sand, are derived from weathering component of any rock. The mineral composition of sands and sandstone can be very different and complex depending on the parent rocks, manner of weathering, transfer and deposition. The clasts that make up sand residue or sandstone include mineral grains and rock fragments of siliciclastic and carbonate composition, as well as fossil remains of the skeleton and shells of organisms, i.e. fossil detritus. Siliciclastic components include all grains of quartz, silicate minerals and rock fragments containing quartz and silicate minerals (all clasts, muddy and clay matrix), and ingredients left after the physical and chemical weathering of silicate minerals and rocks, which are transferred to precipitation area from land (terrigenous components). Carbonate components or carbonate detritus are carbonated grains: mostly fragments of limestone, dolomite and fragments of calcite and dolomite minerals remaining from wear of carbonate rocks and minerals, primarily calcite, dolomite and siderite veins. Carbonate detritus in its origin may be either of the following:

1. Extrabasinal arises from the physical and chemical weathering of older limestone and dolomite on the mainland (terrigenous components).
2. Intrabasinal belongs to ooids, oncoids and pellets formed in the surrounding shallows or even intraclasts that originate from the destruction of carbonate rocks within the depositional area and are nearly as old as the sand in which deposited. It is often the case in Badenian sediments in Pannonian basin, east-central Europe, in which siliciclastic material derived from weathering of older crystalline and lower Miocene rocks on mainland. The intrabasinal carbonate detritus from the destruction of reef Badenian limestone from coastal shallows and underwater reefs. These are calcarenaceous sandstones (Section 5.5.3.4).

Fossil components or fossil detritus include the fossil remains of flora and fauna in the form of whole shells and/or skeletons or their fragments known as *bioclasts*. The fossil detritus in sandy sediments may originate from resedimentation from older rocks or carbonate detritus. It may be intrabasinal belong to planktonic and benthic organisms residing within the depositional area. The redeposited fossil detritus from older Baden corallinacea-bryozoa ridge rocks are often found in Sarmatian and Pannonian sandstones and intrabasinal fossil components (bioclasts of corallinacea, bryozoa, echinoderms, and molluscs) in Baden biocalcarenites sandstones of Pannonian basin.

The essential ingredients of sands and sandstones are quartz, feldspar and rocks fragments $\pm$ micas, carbonate and clay minerals, and heavy minerals (density $>2.85\ g/cm^3$). Certain types of sandstone can contain a substantial proportion of muddy matrix, fossil detritus or glauconite.

The salient features of sands and sandstones are the following:

1. Quartz is the most abundant element on the sands and sandstone derives from the wear of acid igneous rocks, crystalline schist and older sandstone.
2. Feldspars are particularly abundant ingredients of some sands and sandstone, especially molasse type, whose detritus derived from severe physical wear and rapid deposition at the foot of mountain massifs built from neutral and acidic igneous rocks and gneisses.
3. Excerpts of quartz and feldspars originate from wear of mafic intrusive and intermediate extrusive (volcanic) igneous rocks, numerous sedimentary rocks (in particular, siltstone, sandstone, chert, limestone and dolomite), as well as many metamorphic rocks (especially quartzite, phyllite, mica schist and gneiss)

are primary ingredients of many sands and sandstone.

4. Micas, especially muscovite, are regular ingredients of nearly all sands and sandstones, usually with a small share.
5. Clay minerals and chlorite in some types of sandstone (graywacke) are present in large amounts and in some types (arenaceous rocks) in minor amounts or even completely absent.

Sandstones are divided in two main groups according to relative content of grain sizes of sand and mud matrix: pure sandstone or arenites and impure sandstones or graywacke (Fig. 5.26).

5.5.3.2. Arenite Sandstones or Arenaceous Rocks

Pure sandstones or arenites are classified in to five types according to the proportion of the major components of quartz, feldspar and rock fragments:

1. Quartz arenites containing >95% quartz.
2. Lithic arenites contain <75% quartz and rock fragments has more than feldspar.
3. Arkosic arenites contain <75% quartz and feldspar has more than fragments of rock.
4. Sublithic arenites contain quartz between 75% and 95% and rock fragments have more than feldspar.

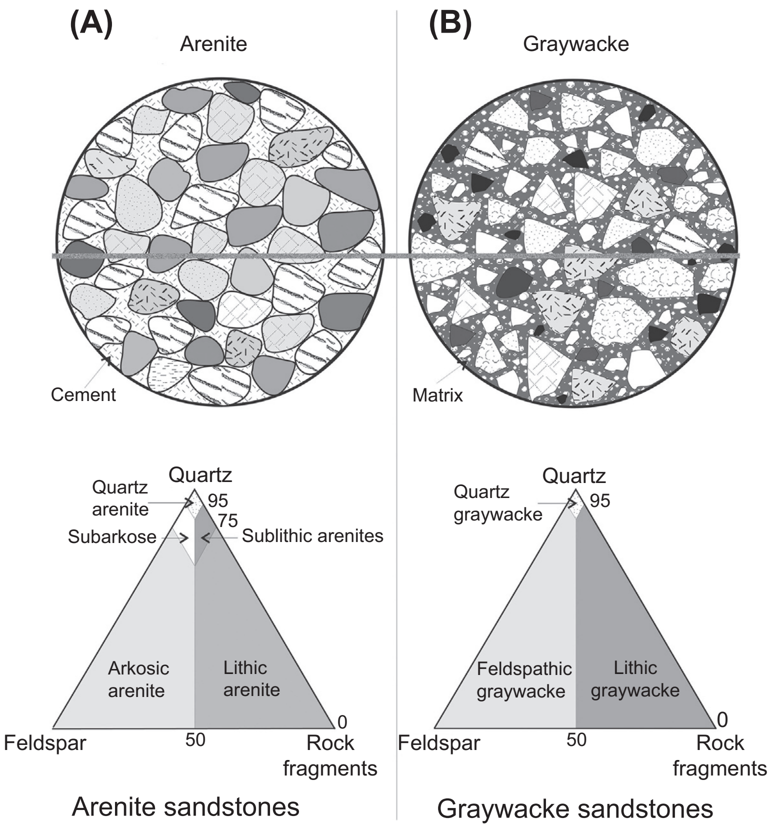

FIGURE 5.26 Conceptual diagrams showing the basic classification of sandy sandstones as (A) arenites, and (B) graywacke with further subdivisions.

5. Subarkoses contain between 75% and 95% quartz and feldspar has more than fragments of rock.

Quartz arenites contain a high proportion (>95%) of well-sorted and rounded detrite quartz grains in association with stable accessory minerals and rock fragments as well as quartz, opal or calcite cement (Figs 5.27 and 5.28). This distinct type of sandstone attains the highest degree of purity and sedimentological maturity, considering the unique mineralogical composition, and the ingredients belong to the most stable grains. Sand grains are remaining after an intense chemical weathering and the long transfer from the source rocks to the place of deposition. The final products go by strong and long-term chemical and physical weathering, abrasion and sorting of debris, often after several cycles of resedimentation. The most resistant detrite grains, mainly of quartz and rarely fragments of quartzite, remain stable even after passing more cycles of wear, transfer and deposition of sediments.

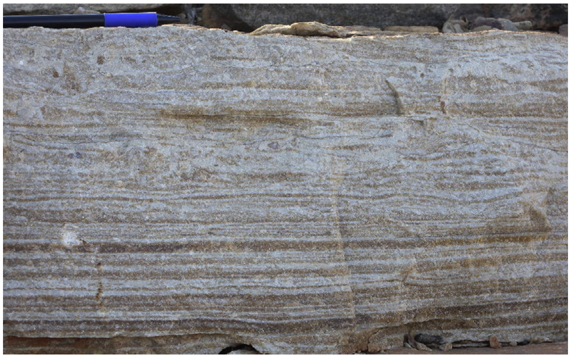

FIGURE 5.27 Laminated quartz arenite (sandstone), composed of +90% detrital quartz from Srisailam Formation, Chitrial, Andhra Pradesh, India. *Source: Prof. Joydip Mukhopadhyay.*

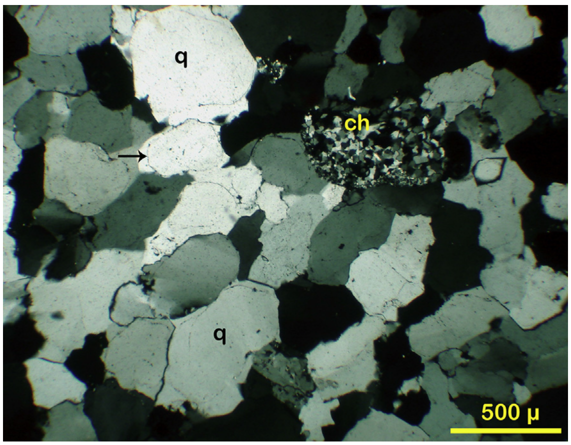

FIGURE 5.28 Photomicrograph of thin section of quartz arenite comprising of +90% quartz (q), chert (Ch) and minor accessory minerals in layered form. *Source: Prof. Sukanta De.*

Lithic arenites are the frequent and most widespread type of sandstone in the lithosphere. It contains up to 75% quartz and more rock fragments than feldspars (Fig. 5.26(A)). These are immature sandstones, which include many chemically and physically unstable rock fragments. In the lithic and sublithic arenites rock fragments, quartz and feldspars grains are generally angular or only a little rounded, and never well-rounded. The constituent minerals also contain a smaller amount of slips detrite mica, mainly muscovite and biotite. These minerals are usually cemented with calcite cement, and sometimes quartz or opal. Lithic arenites as well as lithic graywacke contain rock fragments, mostly of limestone and dolomite, and known by a special name "calclithite". They are the common type of sandstone in the tertiary.

Sublithic arenites are a transitional sandstone type between lithic arenites and quartz arenites. It is comprised 5−25% of rock fragments and 75−95% of quartz. The feldspars fraction is lower than the percentage of rock fragments (Fig. 5.26(A)).

Arkosic arenites are matrix poor sandstones mostly composed of quartz (75%), and feldspar which is more than rock fragments (Fig. 5.26(A)) and is usually cemented by fines of quartz, calcite and feldspars (Fig. 5.29). Feldspars can be completely fresh, and usually

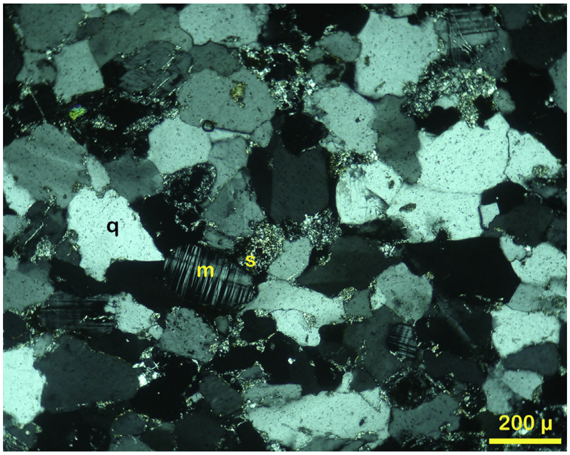

FIGURE 5.29 Arkosic arenite: medium to fine angular to subrounded grains of quartz (q) and feldspar (microcline "m"), cemented by silica and little interstitial sericitic (s) matrix with extensive sericitization of feldspar grains (s) at Proterozoic Kaladgi basin, Karnataka, India. *Source: Prof. Sukanta De.*

belong to potassium-rich alkali feldspar (microcline) and acid plagioclase (albite and oligoclase). The colors of arkosic arenites are reddish, reddish brown, pink or rarely light red. The reddish and pink colors are derived from pink microcline or hematite and limonite. In addition to quartz and feldspar arkosic arenites and subarkoses include detrite mica (muscovite and biotite), which are typically oriented parallel to the layers.

Mineral composition and structure of feldspathic arenites clearly indicate that the parent rocks from which detritus emerge are granites and/or gneisses. It also indicates that the original rocks are extensively consumed in terms of steep terrain and cold or arid climates where chemical wear of feldspars was limited or prevented by rapid transport and deposition.

Subarkoses are feldspathic sandstones with the mutual proportions of quartz and feldspars make the transition from arkosic to quartz arenites. The share of quartz varies between 75% and 95%, and contains more feldspars than rock fragments (Fig. 5.26(A)).

The arenites are comparatively of low cost depending on grain size, color, size of blocks and quality, and widely used for constructional purposes. The common uses are as building material for domestic houses, palaces, temples, cathedrals, mosque, ancient forts, monuments and minarets (Fig. 5.30), ornamental fountains, statues, roof tops, grindstone, blades and other equipments.

5.5.3.3. *Graywacke or Wackes*

Graywacke is a variety of impure sandstones and is generally characterized by its hardness, dark color, and poorly sorted angular grains of quartz, feldspar, and small rock of lithic

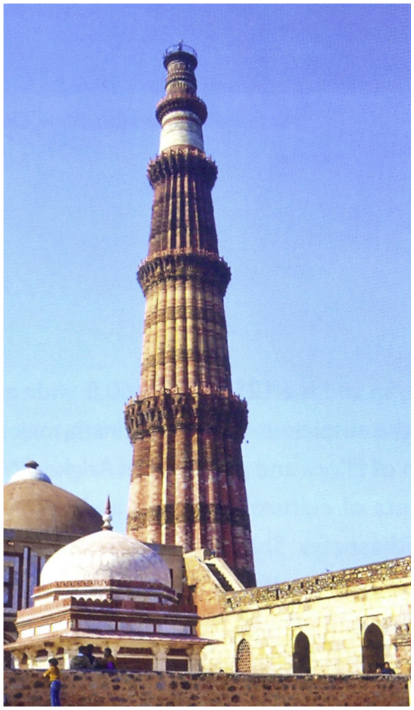

FIGURE 5.30 The Qutab Minar, a 72.5 m high, 379 stairs five story victory tower is located at UNESCO World Heritage Site, Delhi, India. It was built in 1193 AD by Qutab-Ud-Din-Aibak, the first Muslim Sultan of Delhi. It is the highest stone tower in India, made from red and buff sandstone and famous for its architectures.

FIGURE 5.31 Dark color graywacke with poorly sorted grains set in a compact fine clay/muddy matrix showing graded bedding structure at Zawar, India.

fragments set in a compact fine clay and muddy matrix (Figs 5.26(B), 5.31 and 5.32). The term *graywacke* (from the German "*graywacke*") in the geological literature was first enacted in the eighteenth century, for the dark gray, solid lithified poorly sorted sandstone in Hartz, Germany, which contain many angular fragments of rocks, grains of quartz and clay—sericite—chlorite matrix that comes from spending of unstable rock fragments. Graywacke in the Earth's rocky crust is a very widespread type of sandstone and shares 20—25% of all sandstone. Graywackes are classified in to three groups according to the proportion of main components of quartz, feldspar and rock fragments (Fig. 5.26(B)):

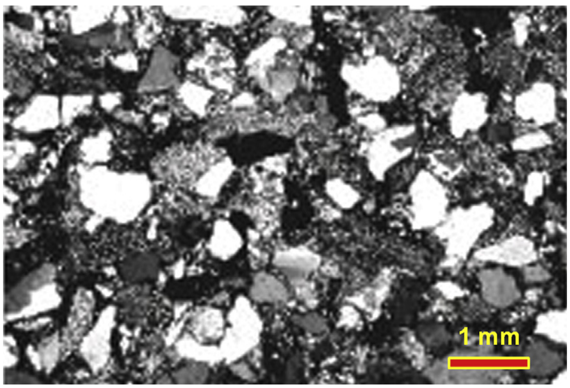

FIGURE 5.32 Photomicrograph of lithic-graywacke composed of angular quartz grains, fragments of quartzite, crystalline schist, and clay matrix.

1. Lithic graywacke containing <95% quartz and more rock fragments than feldspar.
2. Feldspathic graywacke containing <95% quartz and more feldspar than rock fragments.
3. Quartz graywacke containing >95% quartz.

Lithic graywacke are matrix-rich sandstones that with the quartz (up to 95%) contain more rock fragments than feldspars (Figs 5.26(B) and 5.31). Lithic graywacke belongs to the group of sandstones of low level of maturity due to large amounts of matrix, particularly clay minerals, illite, and metastable fragments of rock. The rocks are characterized by a poor sorting, and dark gray to dark green color due to clay—chlorite matrix and high content of dark rock fragments. The rocks may be dominated by debris of volcanic rocks (diabase, spilite, keratophyre, dacite and porphyry), followed by fragments of schist of low and intermediate level of metamorphosis (slates, phyllite, quartz—sericite, mica schist and quartzite) and sedimentary rocks (cherts, siltstone, shales and sandstones). Quartz is generally the most abundant element in the sand fraction of detritus and share is generally higher than 50%. Feldspars generally contain only acidic to neutral plagioclase with little of K-feldspars.

Lithic graywacke matrix forms by synsedimentary muddy and/or clayey detritus (protomatrix) which is converted into a dense mixture of chlorite, sericite and quartz (orthomatrix) during the diagenetic processes. This is typical of many Paleozoic and Mesozoic lithic graywacke. However, part of the chlorite—sericite matrix can come from diagenetic changes of unstable rock fragments.

Feldspathic graywacke matrix contains a considerable amount of feldspar and rock fragments in addition to quartz (up to 95%). The proportion of feldspars can vary in wide limits and is always greater than the percentage of rock fragments (Fig. 5.26(B)). In some variations of feldspathic graywacke, feldspars are even more abundant than quartz. Detrite micas (muscovite and biotite) are often present. Matrix of feldspathic graywacke is similar to that of lithic graywacke, generally thick fine-to-microcrystalline mixture of clay, chlorite, sericite, quartz and carbonate minerals (often siderite), and pyrite. Clay minerals, especially kaolinite group, originate from chemical weathering of kaolinitization of feldspar (Section 5.2.1.2). Feldspathic graywacke represent much less common type of sandstone in relation to the lithic graywacke, quartz graywacke are very rare type of sandstone.

5.5.3.4. *Mixed or Hybrid Sandstones*

Sands and sandstones which, in addition to quartz, feldspar, silicate rock fragments and mica, contain a substantial proportion of detritus chemical and/or biochemical origin or materials of other origin, are not included in the standard classification of sandstone. These rocks of new composition belong to a special group of sandstone. This particular group consists of mixed or hybrid sandstones that includes different calcarenaceous, green and phosphate sandstones.

Calcarenaceous sandstones are the genetic groups of mixed hybrid clastic and chemical and biochemical rocks. It is composed of a mixture of grain (>50% siliciclastic or quartz, feldspar, rock fragments, and mica) and limestone grain of chemical–biochemical in origin (10–50% bioclasts, fossils, intraclasts, pellets, ooids and oncoids). Calclithite that belongs to either lithic graywacke or lithic arenite contains fragments of older limestone and/or dolomite. Calcarenaceous sandstones, with siliciclasts, contain a significant proportion of fossil debris and ooids and/or oncoids and pellets. The mixed rocks gradually change to biocalcarenite limestone with the increase of limestone grains of intrabasinal origin. It will no longer remain as calcarenaceous sandstone if the share of limestone grains of intrabasinal origin exceeds 50%. The new rock is limestone biocalcarenite type.[50,51]

The fossil detritus in calcarenaceous sandstones are mostly shell of benthic foraminifers, echinoderms skeletal debris, corallinacea, bryozoa, molluscs and gastropods. In general, calcarenaceous sandstones are cemented with calcite, and occasionally may also contain fine-grained clayey–calcareous (marly) matrix.

Green sandstones contain a considerable amount, and in some places more than 50% of spherical, oval beads of glauconite accumulations of material or a mixture of glauconite, chlorite, smectite and seladonite, in addition to siliciclasts (quartz, feldspars, rock fragments, and mica). These grains are distinctly green or dark green color, and the sandstones have been named as *green sandstones*. Glauconitization is a very slow process. Green glauconitic grains forms by glauconitization processes in marine environments under low reductive conditions at normal salinity and low speed of deposition over a very long time, say several hundred thousand years. The parent materials for the origin of green glauconitic grain are biotite, pellets, wrapped grains, foraminifers, volcanic glass and volcanic ash that undergo diagenetic changes.

Phosphate sandstones are siliciclastic sandstones that include calcium phosphate (apatite) or contain a substantial proportion of phosphate detritus or phosphate ooids as cementing material.

5.5.4. Fine Granular Clastic Sediments—Pelite

Pelite is clayey fine-grained clastic sediment or sedimentary rock, i.e. mud or a mudstone.

5.5.4.1. *Classification of Pelitic Sediments*

The fine-grain clastic sediments or pelite mainly consist of silt and clay with a grain size of <0.063 mm (Table 5.1; Fig. 5.19). There are several different types of pelitic sediments

TABLE 5.4 Classification of Pelitic Sediments on the Basis of Mutual Interest of Silt and Clay

Silt		100–66%	66–33%	33–0%
Clay		0–33%	33–66%	66–100%
Unrelated		Silt	Mud	Clay
Related	Homogeneous	Siltstone	Mudstone	Claystone
	Lamination or fissility	Silt shale	Mud shale	Clay shale
Slates		Quartz slate	Slate	

according to the proportion of silt and clay, the degree of lithifaction and the features, as given in Table 5.4. Pelite sediments containing more than two-third silt components are divided according to the degree of lithifaction on the powder or as a loose silt and siltstone as related to sediments. If related or lithified rocks show lamination, therefore are not homogeneous, it is termed as *leafy siltstone*. Similarly, pelite sediments that contain more than two-third clay component, given on the degree of lithifaction, known under the name of the *clay*, as an unbound, and *claystone* as bound rocks. If their lithified version features laminated structure, it is called *clay shale*. Pelite sediments, which contain between one-third and two-third silt and clay components, are divided into the "mud" as the loose sediment and "mudstone" as a solid rock and in the case of lamination is called *mud shale*. *Loess* is a special kind of siltstone of Aeolian origin and the *marls* are mixed or hybrid rocks consisting of clay and carbonate, mainly calcite, component with variable share of powder.

5.5.4.1.1. CLAY AND CLAYSTONE

Clay and claystone generally contain predominantly one of the following three groups of minerals: illite, smectite (montmorillonite) and kaolinite group and a smaller or larger proportion of chlorite and rare glauconite. Chlorites and glauconite in claystones occur during diagenetic processes.

Illite mineral group is typical of the marine clay deposits. Illite, in the claystones, is mainly derived from the diagenesis of kaolinite by chemical weathering of feldspar. Smectite (montmorillonite) group of clay minerals contain up to 20% water and absorb Ca and Mg. Clay and claystone mainly composed of this group of clay minerals and are called *bentonites*, and form as a result of alteration of acidic tuffs and volcanic glass (Section 5.6.3). Kaolinite group of clays is typical for kaolinite rich or pure kaolinite clay known as *kaolin* (Fig. 2.16). Clays containing kaolinite group of clay minerals are characterized by a light or milky white color and in contact with water become remarkably plastic. These minerals are used as a highly valued raw material in ceramic production and with a higher proportion of powder in the manufacture of bricks and tiles. Clay and claystone rich in kaolinite group minerals precipitate in freshwater and not in marine environments because kaolinite quickly transforms into complex clay minerals in seawater. The basic characteristic of the clay with water is to become plastic, can knead and shape, after drying and firing to retain shape. This makes them perfect for pottery, porcelain, ceramic products, sculptures, tile and brick.

5.5.4.1.2. SILT AND SILTSTONE

Silt is loose pelite sediment and *siltstone* is pelite rocks, containing >66% silt grain size (particle size 0.004–0.063 mm). Siltstones are rocks, according to granulometric measurements, chemical composition and textural–structural features, that make the transition from fine-grained sandstone in the mud and clay rocks. The dominant component of siltstone is angular grains of quartz, significantly associated with the tiny grains of feldspar and mica flakes, and up to 33% clay. Some types of siltstone containing a substantial amount of carbonate, mainly calcite cement or fine-grained carbonate detritus (carbonate mud deposited along with grains of silt size), and such a rock is called *calcareous siltstone*. The calcite cement can be paved with authigenic quartz, opal or chalcedony, or sometimes mineral binder which originated from the diagenetic processes of clay minerals, i.e. sericite, chlorite and illite (Section 5.5.5.2). Siltstones are generally massive, thickly layered, strongly lithified, homogeneous, sometimes horizontally or obliquely laminated rocks. Siltstones are often represented and deposited together with the sludges, mainly in lacustrine and marine basins.

5.5.4.1.3. SHALE AND MUDSTONE

Shales are thinly laminated fine-grained pelite clastic rock composed predominantly of siliciclastic materials by granulometric composition of mixtures of clays and particles size of powder, or silt. Shales can be grouped as clay and mud shale based on the mutual shares of particles (clay and particles of powder). Shale laminations are not always just a consequence of the way of deposition. The deposition is not exclusively related to synsedimentary processes. The thin laminations of most of the shales originated during earlier geological periods are the result of mechanical diagenetic compaction processes occurring due to high pressure at greater depths of covering, which leads to the destruction of loose packed structure of particles "house of cards" in plan-parallel order (Section 5.5.5.2, Fig. 5.38).

Shales are the most common sedimentary rocks in the Earth's crust. It occurs in lithifaction and complex diagenesis of water-rich mud and powder-clay sediments (Fig. 5.38). Mineral composition of shale is diverse and variable. Shales form by combination of the composition of detritus particles and the chemical diagenetic processes. The essential ingredients are clay minerals and illite, quartz, significant amount of feldspars, chlorite and sometimes carbonates. The share of clay minerals, quartz, feldspars, chlorite, muscovite and carbonate is an important factor in the degree of lithifaction and shale laminations. The young (Tertiary) shales prevail illite, kaolinite and smectite (montmorillonite). The older shales typically contain 20–30% quartz, 5–30% detrite feldspars and 15–35% minerals of a complex group of illite–smectite–muscovite, kaolinite, chlorites, carbonates, oxides, hydroxides of iron, organic matter and sulfides. In shales of the Paleozoic age or in those at depths >3–4 km, the proportion of typical clay minerals (kaolinite and montmorillonite group) is insignificant because of their transition processes in the diagenetic chlorates and sericite or muscovite (Section 5.5.5.2).

The shales can have different colors due to the content of organic matter and oxides of some metals Black shales usually contain organic matter (carbon) and/or pyrite and are formed in reducing conditions. Red color of shale is the result of high content of ferric oxide, mainly hematite, and refers to the oxidative conditions during wear and sedimentation, which predominates in continental depositional environments. Green shales contain glauconites and chlorine and come from moderate reducing environmental conditions.

Oil shales (Fig. 5.33) contain a high proportion of kerogen (mixture of organic chemical compounds) and other naphthenes, and are carriers of potential reservoirs of raw materials or are petroleum source rocks. The term *oil shales* is used for all laminated pelite sediments, and also for laminated marls and dolomitic limestone, from which oil can be extracted by heating. Oil shales are dark gray to black color due to the high content of naphthenes and other kerogen.

Oil shales generally belong to the lake and marine sediments and occur in protected anaerobic low-energy lake, river, delta and marine

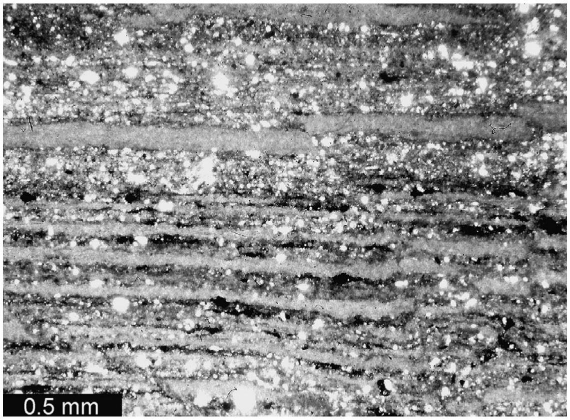

FIGURE 5.33 Oil shale composed of clayey and silty laminae saturated with kerogen and naphthenes (black), Slavonia crude oil and gas field, Croatia.

environments. Mudstones are, unlike the shale, homogeneous, solid lithified rocks that contain mixture of particles clays and powder (from one-third to two-third clay and powder, Table 5.4). The oil shales show homogeneous texture and granulometric and mineral composition is almost identical to geologic young muddy shales.

5.5.4.1.4. LOESS

Loess is a homogeneous, nonlaminated to thickly layered, poorly lithified, well sorted and extremely porous pelite-clastic sediment. The granulometric composition of loess is characterized with a high content of grain sizes of medium and coarse powder (silt). The diameter of grains is predominantly 0.015–0.05 mm. Loess usually contains small grains of powder sizes (0.004–0.015 mm) and from 10% to 20% particles sizes of clay, and sometimes even smaller share of the fine sand grain size (0.063–1 mm).

The predominant mineralogical composition of loess is detrite grains of quartz over to detrite feldspars, usually in the ratio of 4:1. The share of calcite, mainly of authigenic origin, varies in the range between 10% and 30%, and mica and clay minerals between 10% and 20%. An important feature of loess is its extremely high porosity, typically being 40–60%. The pores of loess retain water due to capillary forces, enrich with Ca hydrogen carbonate in the periods of drought and secrete calcite which cements grains of dust and clay particles. The enriched solutions typically circulate only along easily permeable parts of loess, and calcite secretes from the pores. The pores water cannot uniformly rise by capillary forces or just secreted around some of the carbonate grains. All these limitations strongly restrict loess in homogeneous cemented throughout the area. Therefore, loess undergoes irregular concretions due to uneven cementing areas and greater wear and erosion of uncemented parts resulting morphological formations known as *loess dwarfs*.

Loess forms by deposition of Aeolian powder material transferred by wind from large distances. The powder originates from the sludge left over after the flooding of vast valleys and drying of this sludge after the withdrawal of water in river beds. Wind and air currents rise and spread dry powders over long distances and deposit on land or in water. The largest amounts of loess deposited in the Quaternary, especially in the Pleistocene, in the ice ages, when the climate was dry and windy. A huge amount of sludge was deposited by melting of ice and flooding of river valleys during the interglacial periods.

5.5.4.2. Marlstone

Marls are mixed carbonate-clay rock and are composed of cryptocrystalline or microcrystalline calcite and siliciclastic detritus of pelitic dimension, primarily clay, with larger or smaller portions of powder (Fig. 5.34). Part of calcite can be of chemogenic in origin, arise from the secretion of the sea or lake water, while some may be the tiniest carbonate detritus of lime sludge. Marl is usually considered a rock that contains between 20% and 80% clay and 80% and 20% calcite.

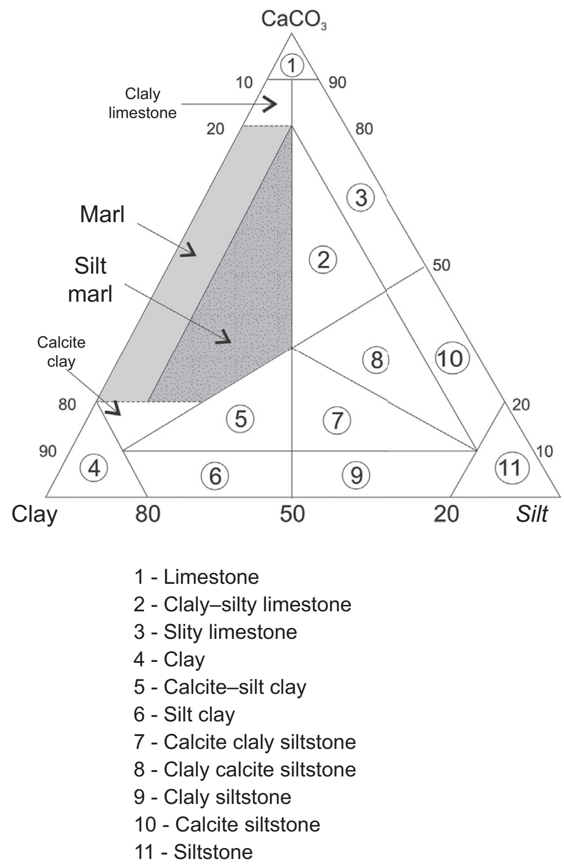

FIGURE 5.34 Detailed classification and nomenclature of the limestone–clayey–silt sediments.

Rock, originally comprised calcite and clay with mutual relationship and chemically equivalent to marl, undergoes diagenetic process in the greater depth transforming typical clay minerals in the illite, chlorite, sericite, muscovite, and designated as marl or marlite. A real "clean" marls, composed only of clay and calcite, are rare in the nature. Much more common are dusty marls containing between 10% and 33% of siliciclastic grain sizes of powder, with calcite and clay between 20% and 80% (Fig. 5.34).

Marls are the most common insulator rocks in the deposits of oil and gas and are the primary raw materials for manufacturing of cement.

5.5.4.3. *Organic Matter in the Argillaceous Sediments*

Organic matter is present in small amounts in almost all the sediments, and a significant proportion is virtually located mainly in argillaceous rocks, especially mudstones, shales and marlstone. Such rocks can therefore be a source of crude oil and are named *oil source rocks*. The old name for more diagenetically tough rock is *oil shales*. *Sapropelic* is often used to name for the mudstone rich in organic matter. Organic matters in sediments are located in four basic forms: kerogen, asphalt (bitumen), crude oil and natural gas, which consist of a wide range of complex hydrocarbons.

Kerogen is a solid dark gray or black organic substance that contains hydrocarbons insoluble in the common organic solvents such as ether, acetone, benzene and chloroform. It has complex organic composition and is believed to originate mainly by wind inflicted spores and pollen of plants and very small aquatic plants (algae) that are deposited along with winds issued powder. The kerogen is necessary for their fossilization in anaerobic conditions under an anaerobic environment. Three different types of kerogen with regard to the origin of organic matter:

1. Algal kerogens (Fig. 5.33) that generate oil (characterized by high values of the ratio of hydrogen/carbon between 1.0 and 2.2 and a low ratio of oxygen/carbon, <0.1).
2. Mixed kerogens that generate oil or gas (characterized by average values ratio of hydrogen/carbon between 1.0 and 1.7 and the average values of relations oxygen/carbon between 0.0 and 0.2).
3. Humic kerogens that generate gas (a low ratio of hydrogen/carbon between 0.5 and 1.0 and a high ratio of oxygen/carbon between 0.07 and 0.25).

Asphalt or bitumen is sticky, black and highly viscous liquid or semisolid form. It is similar to kerogen in composition, but is soluble in the common organic solvents. It contains 80–85% carbon, 9–10% hydrogen, 2–8% sulfur, and negligible amount of oxygen and nitrogen. In the sediments is typically found in the pores, tectonic cracks and crushed zones.

Crude oil or *fossil fuel* is the name of the hydrocarbons that are flammable liquid at the normal pressure and temperature. It occurs in the sediments and rocks as fills in primary and secondary pores. It contains 82–87% carbon, 12–15% hydrogen and traces of sulfur, nitrogen and oxygen in the form of four types of very complex molecules of each variable: paraffin, aromatic hydrocarbons, naphthenes and asphalt. It is recovered from the parent rocks at the temperatures between 60 and 120 °C.

Natural gas is the name of naturally occurring hydrocarbon gas mixture consisting primarily of methane with other hydrocarbons, carbon dioxide, nitrogen and hydrogen sulfide. The gaseous hydrocarbons contained in pores of sediments and sedimentary rocks. It is recovered from rocks at the temperatures of about 120–220 °C because at these temperatures, kerogen is not as inert with respect to the generation of carbon.

5.5.5. Diagenesis of Clastic Sediments

Diagenetic processes convert loose, unbound, water-saturated packages of sediments to the firmly lithified sedimentary rocks by either of the system:

1. Early diagenetic processes that occur in a completely unrelated, pore-water-saturated sediments at shallow depths overlap, i.e. a small thickness of overlays.
2. Late-diagenetic processes at greater depths overlap, i.e. below the thick layers of overlays in already partially lithified rock.

In both cases, the sediment is subjected to mechanical and chemical processes arising from the depth of the overlay, composition of deposits and pore-water. This is also influenced by other physical–chemical and geological conditions of diverse intensity and importance of turning the sludge to solid lithified rock. The most significant mechanical diagenetic processes are compaction and pressure dissolution of grains, and most important chemical diagenetic processes are cementation of pores and recrystallization of unstable in stable mineral components. Diagenetic process for the different sediments can be very different and in certain types of deposits has a very uneven intensity with respect to their mineralogical and granulometric composition as well as environment and conditions of deposition.

5.5.5.1. Diagenetic Processes in Sandy Sediments

Early diagenetic processes in sandstones include all reactions between the mineral grains of sand and pore-water contained in the sand from the time of deposition to the moderate depth of the overlay. There are other reactions related to the life activity of bacteria. Early diagenetic processes in the sands are significant for the further course of diagenesis because porosity of sediment may change due to early diagenetic cementation (porosity reduction) and/or dissolution of certain mineral grains (increasing porosity). Such processes also affect significantly the late-diagenetic processes that occur when sand sediment reaches a greater depth of overlay.

The processes of compaction of sand begin almost immediately after deposition, and ending at deep covering after pressure dissolution of grain and almost complete cementation (Figs 5.36 and 5.37). The compaction processes or mechanical diagenesis of clean sandstone have significantly minor role than the chemical diagenetic process, unlike pelitic sediments, and clayey sandstone.

Comparatively loose and loosely packed sediment emerges with high porosity during the deposition of sand in the water or air. Well-sorted sand grains with high degree of sphericity have intergranular porosity of about 40% after

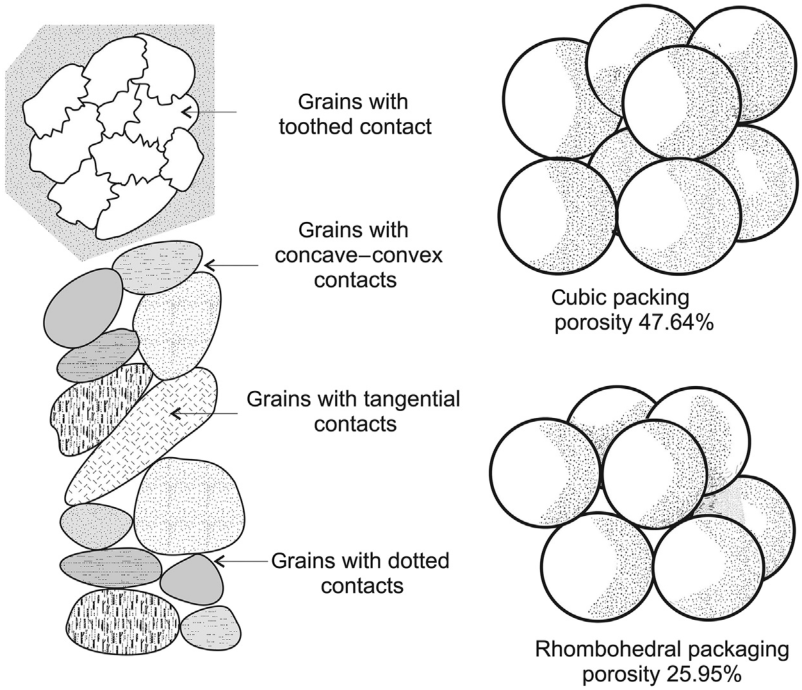

FIGURE 5.35 The main types of grain contacts in the sediment and relative packaging porosity due to compaction.

deposition. The same sands without cementing in the deeper parts of sediments possess about 15% porosity. Therefore, increasing the depth of the overlay due to compaction reduces the porosity of the sands.

Reduction of porosity due to compaction of the sand at the very beginning is substantially different for the fine-grained and coarse sand (Fig. 5.35). However, after the sands have been deposited for 1000−1500 m of thickness of new sediment, the porosity of the coarse-grained sands reduces in relation to fine-grained sands in the absence of significant amounts of clay or carbonate. Specifically, well-sorted coarse grains slide more easily during pressure, and deploy loose cubic form in denser rhombohedral packing. Compaction of fine-grain sands containing clay matrix is higher.

Chemical diagenetic processes can also start immediately after the deposition of sand, with reactions of pore water and sand grains. These are reactions of dissolution of mineral grains as well as reactions that cause the secretion of new authigenic minerals, in the form of cement and pushing one mineral with other such as feldspar with kaolinite. Chemistry of the initial pore water in sand is similar to that in water where sand is deposited. Marine pore water can circulate a few inches below the layer of sand and there in the pores of the sand cause early diagenetic cementing with carbonate or phosphate excretion. The aragonite or Mg-calcite cement (known as *beach rock cements* type) is usually secreted during early diagenesis in sea sands (siliciclastic and carbonate).

Pore water associated with deeper currents extrudes by compaction of clay deposits and moves into younger sediments at higher level. It can cause the release of mineral cement near the border of the sediment and water. In this way, carbonate cements, and hematite, limonite and Mn-oxides typically secrete in sands.

Oxidation of organic matter, particularly the life activity of aerobic bacteria, causes increase of CO_2 resulting secretion of carbonate cement. The bacteria that reduce sulfate by production of H_2S contribute to lowering the limit of redox potentials. This allows the formation of pyrite in the presence of iron and the total iron excretes in the form of sulfides. The dissolution of $CaCO_3$ excretes siderite below this zone, or in freshwater.

The sands, deposited in evaporite and sabkha environments (coastal saline), contain evaporite pore water with high content of dissolved substances that can exude carbonate calcite, aragonite, dolomite, Mg-calcite cements, and sulfate, anhydrite, and barite cements. Sandstones in the zone above the underlying water (arid environment) excrete calcite, hematite, limonite and manganese oxides as early diagenetic cements.

Late-diagenetic processes in the sandy sediments occur at greater depths overlay with two important factors.

1. General increase in pressure and direct pressure on the grain contacts, which causes severe mechanical compaction and pressure dissolution of sand grains at their points of contact to which it transmits pressure.
2. Temperature increase due to increased solubility of many mineral grains and mineral ingredients that contain constitutively water, lose water and transform it into new stable minerals under such conditions. Constitutional water is extracted from the minerals when heated, and it is in atomic state, mainly as OH-groups.

General increase in pressure at greater depth of the overlay occurs due to the weight of deposited sediment. This hydrostatic pressure causes denser packing by increasing the surface area of "grain on grain" contacts, reducing the pressure between the grains, reducing the thickness and increasing the level of lithification in sandstone (Figs 5.36 and 5.37).

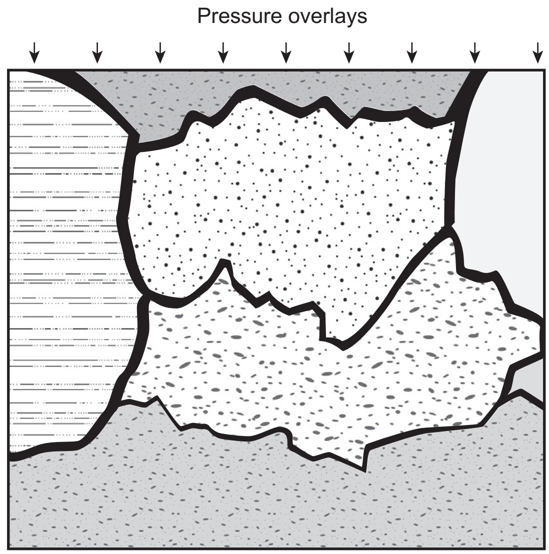

FIGURE 5.36 Pressure melting of quartz grains in contact with surrounding grains or "grain on grain" due to pressure overlays.

Pressure dissolution is partial dissolution of the sand grains, usually quartz, on the grain contacts through which pressure overlays is transmitted. This extends the melting area of grain contacts in the form of a toothed grain encroachment into the other grains (Fig. 5.36). This reduces the intergranular porosity and thickness while increasing the level of lithifaction in sandstone (Figs 5.35 and 5.37(B)). The melting points of grain to grain shape changes due to their reduction, thinning and mutual interference in one another, or grains become flatter. Pressure dissolution at greater depths covering 1000–1500 m is the most significant factor in compaction of sandstones.

Besides these effects of compaction, pressure dissolution has another important role in diagenesis as the dissolution releases silicon dioxide related to silica acid (H_4SiO_4). This mobile acid reextracts the same or neighboring sand layer in the form of quartz cement around quartz grains or "regeneration edge" or secondary growth of quartz.

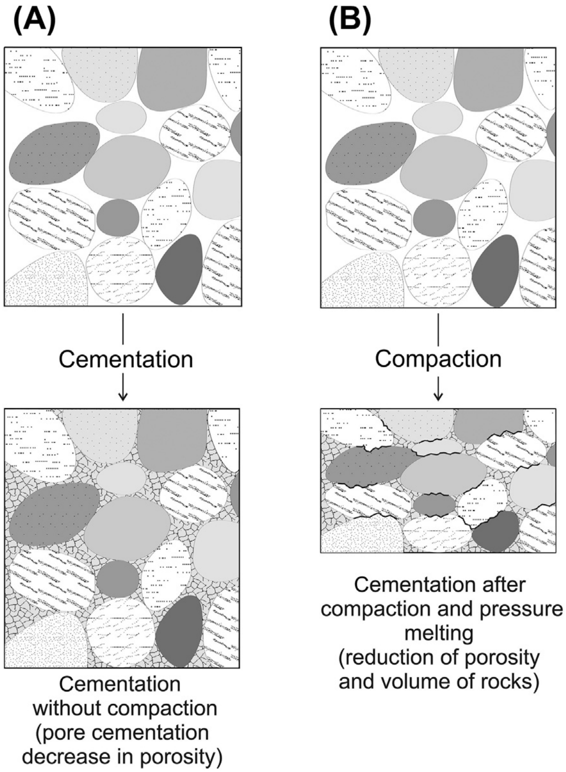

FIGURE 5.37 Conceptual diagrams showing the relationship of porosity of sandy sediments in their cementing without or stronger compaction at shallow depths covering. (A) Excretion of mineral cement in intergranular pores involving large quantity and flow of pore water for sufficient mineral cement and filling the pore spaces between sand grains. The volume of sand before and after cementing in fact remains constant with decrease only in porosity. (B) Compaction with cementation and pressure cause significant decrease in porosity and to considerable reduction in the total volume, and thus the thickness of sandstone sequence.

The rise in temperature has great influence on the chemical diagenetic process in the sandy sediments at greater depth. The effects of higher temperatures by increasing the depth of the overlay manifest the following:

1. Changes in the solubility of minerals as a function of temperature:

The solubility of mineral components of sandstone increases with increasing temperature. The pore water is enriched by ions in compaction currents that can excrete new authigenic minerals, particularly quartz cement. Cementation of sands with quartz cement is extremely slow and time-consuming diagenetic process due to relatively low concentrations of silicon in these solutions.

2. Facilitating the incorporation of highly hydrated "cations" in the lattice of carbonates:

Highly hydrated cations that at low temperatures prevalent on the surface of the Earth are in a melted state, such as Mg^{++} and Fe^{++}, cannot be in the presence of marine pore water incorporated into the carbonate lattice. However, with increasing temperature they become less hydrated and already at a temperature of 60–100 °C (the depth of coverage of 2–3 km) are excreted as Mg and Fe-carbonate ferrocalcite, and siderite cements. There are numerous examples of such rocks, such as, in deep wells of gas fields at Molve, Kalinovac, Croatia.

3. Squeezing the OH-group (constitutional water) from clay minerals and their transformation into new stable minerals (illite, muscovite, and chlorite):

A rise in temperature and pressure causes the formation of higher density minerals that contain water or constitutively contain very little. It is in sandstones with clay matrix (graywacke) in diagenetic processes at greater depths overlay manifest with transformation of clay minerals from the smectite/montmorillonite group and kaolinite in stable minerals from the group illite and chlorite, as well as muscovite, i.e. sericite matrix.

The research to establish changes in composition and stability of clay minerals with increasing temperature and pressure at increasing depth of covering shows that smectite (montmorillonite) and mixed layer of clay minerals become unstable at temperatures between 60 and 100 °C, which corresponds to the depth of the overlay of 2–3 km, and transforms to illite and chlorite. Similarly, kaolinite becomes unstable at the temperatures between 120 and 150 °C, which correspond to the depth of the overlay between 3 and 4 km, and it is transformed to illite.

Illite gradually transforms to muscovite if the pore solution containing enough K and Al. The kaolinite and illite are common ingredients of graywacke sandstone. This process typically causes sericitization of matrix, i.e. the conversion of clay minerals in fine-grained cluster of illite and muscovite, and is commonly called *sericite matrix*. Sericite is the name for the small mica flakes that are not specifically identifiable microscopically.

Cementation is the most important diagenetic process by which loose, scattered sand converts into tightly bound rock sandstone. This process occurs during the early and late diagenesis under conditions of greater depth overlay. Cement can be the authigenic mineral that has caused the reduction of intergranular porosity, therefore the mineral that separates the solution from the pores between the grains (intergranular pores) or in the pores inside the grains (intragranular pores). Sands can be cemented and transformed into sandstone in two fundamentally different ways:

1. Only by the secretion of cement in the intergranular pores of sand: this is going on with bringing of cations and anions in the melted state by circulation of pore water or diffusion of ions (Fig. 5.37(A)).
2. Pressure melting of mineral grains in the pressure points and reexcretion of minerals, usually quartz, in the form of cement.

In the first case, i.e. in excretion of mineral cement in intergranular pores of sands from the solution requires a large amount and flow of pore water to allow the extraction of sufficient quantities of mineral cement for filling the pore spaces between sand grains. The volume of sand before and after cementing in fact remains constant with decrease only in porosity (Fig. 5.37(A)). In the second case, i.e. compaction with cementation and pressure dissolution (Fig. 5.37(B)) comes with a significant reduction in porosity and to significantly reduction in the total volume, and thus the thickness of sandstone.

The diagenetic processes in sandstones and sandy sediments are due to changes in porosity, and they play an important role in the sandstone properties, i.e. the possibility of oil and gas reservoirs, aquifers of drinking and thermal water.

5.5.5.2. *Diagenetic Processes in Clayey Sediments*

Mechanical diagenetic processes or compaction in the clay sediments have a much greater role than in sandy sediments, as freshly deposited clay sediments and sludges signify loose packing components. The accumulations of clay minerals form honeycomb or "house of cards" structure (Fig. 5.38(B)) and have very high porosity, typicallybetween 70% and 85%. The pores between honeycombs aggregated clay particles are completely filled with water.

Strong compaction due to pressure overlays starts with the gradual deposition of increasing amounts of new sediment. The loose packing of particles in the honeycomb, or "house of cards" is not stable and particles began to restructure in parallel with each other schedule and significantly reducing the porosity. Primary porosity of clayey sediment and sludge is appreciably higher than the porosity of newly deposited sand. A honeycomb packed clusters of clay particles restructure or "crash" in parallel position (between 100 and 200 m, Fig. 5.38(B)). Clusters are in such a destruction of the structure oriented perpendicular to the largest surface bearing pressure, causing laminated sediment (mudstone becomes mud shale). Simultaneously with the restructuring of particles, the other important diagenetic process takes place by displacement of pore water or another fluid (e.g. oil) that filled pores in the mud. The first process causes compaction of sediment and reducing porosity. The second process causes a strong flow of water or pore fluids.

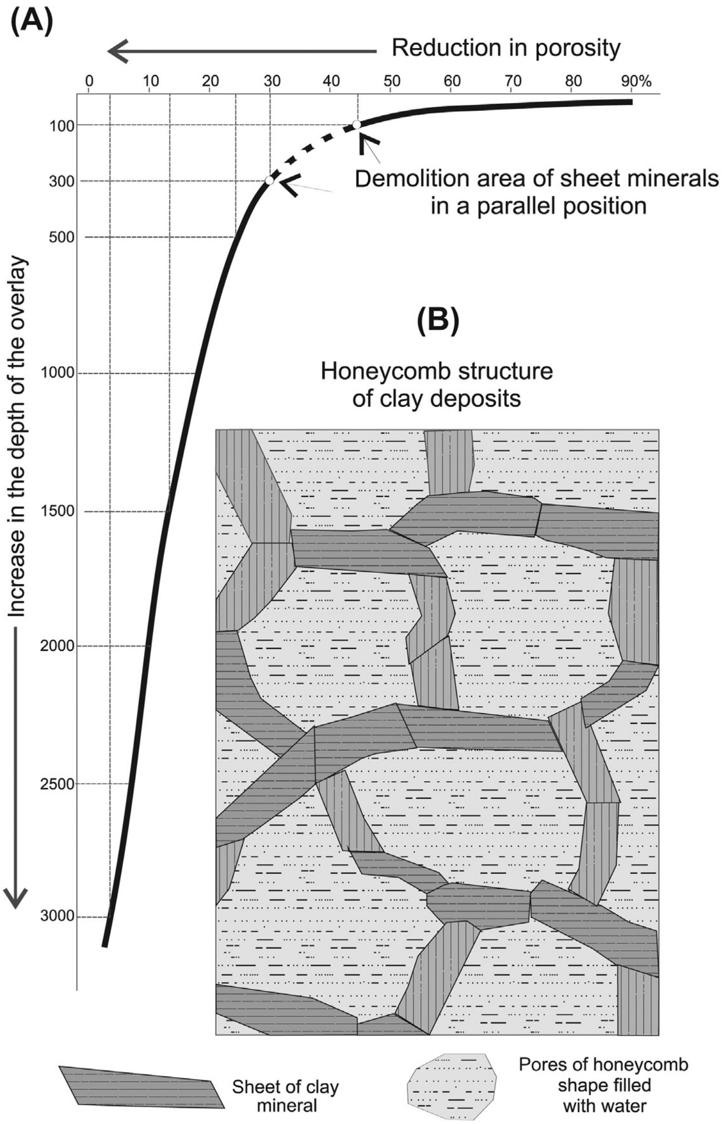

FIGURE 5.38 Schematic diagram showing honeycomb structure of the clay deposits related to increasing depth of deposition and reduction in porosity: (A) changes in porosity of clayey sediment depending on the increasing depth of the overlay as a consequence of compaction and restructuring of particles and (B) honeycomb structure.

Experimental studies show the clay compaction process to be highly compacted clay at a pressure of 50 MN/cm^2 (MN = MegaNewton) as in nature, covering equivalent of about 250 m. The curve of the general reduction in porosity of clayey sediment with increasing depth of the overlay (Fig. 5.38(A)) shows that in the beginning of the clay sediments overlay with new sediments, the porosity decreases very rapidly to a depth of 100–200 m at a small increase in depth of overlay. This is due to demolition of honeycomb or "house of cards" structure. Porosity decreases linearly with increasing depth of the overlay (Fig. 5.38(A)) from about 300 to 3000 m.

In this way, the initial porosity of about 80—85% of just precipitated sludge reduces to about 43% at a depth of 100 m covering. The porosity continues to reduce to 30% at 300 m, 13% at 1600 m, and finally 3—4% at the depth of 3000 m (Fig. 5.38(A)). Thus, the compaction of clay sediments significantly reduces the porosity, causes severe compaction flow of displaced pore water (and other fluids, e.g. oil) and significantly reduces the thickness of the sediments. In-depth coverage of about 3000-m-thick primary precipitated sludge is reduced by about three-fourth. For example, thick mud of 100 m changes to only 25—30-m-thick layer of clay shale. The geometry and shape of sedimentary bodies in the clay, shale and pelitic sediments can be visualized in this way. If turbidity or submarine fan sand or sand body occurs within such deep-seated sediments or sedimentary package, the deposits will assume a convex or lenticular shape (Fig. 5.39).

The clay deposits are compacted until the particles of clay mixed with grains of quartz, feldspar and other minerals come to closest contact with loss of water or other fluids lead to loss of plasticity. Clay is imprinted in the interspaces of quartz, feldspar and other mineral grains sizes

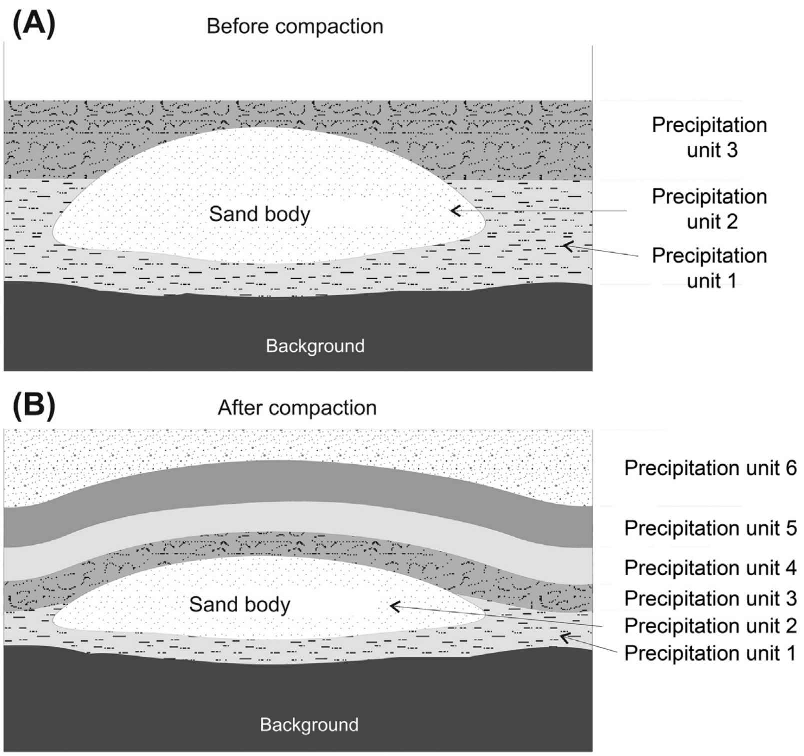

FIGURE 5.39 Experimental diagram showing the shape and thickness of (A) primary precipitated sediment and sand body and (B) changes due to the different effects of compaction on the clay and sand deposits with increasing depth of the overlay.

of silt and fine sand at high pressure. The grains are embossed on the clay and the sediment hardens mechanically. If the process of compaction by the high-pressure overlays continues, there would be deformation of certain components, pressure dissolution, and at even higher pressures resulting cracking of mineral grains.

Mechanical compaction of clay sediments has large role in their diagenesis. It is not the only important diagenetic process as it is regularly followed by chemical diagenesis. These processes are caused by changes in the chemistry of pore water when sediment comes under compaction currents. In the early stage of diagenesis, the clay sediments have high porosity with possible compaction flow of pore solution, and intense ion-exchange. The sediment is increasingly dominated by reducing conditions, and negative Eh-potential with increasing the depth of the overlay, oxygen deficiency. In the late stages of diagenesis, the porosity of clay sediments reduces and pore flow intensity. The pressure and temperature grow, and thus the speed of chemical reactions. In the final reduction of the porosity of only 0.5% at the depth of 6000−9000 m and at temperature of 220 °C, diagenetic process gradually disappears and metamorphic processes begin.

Chemical diagenetic processes in clayey sediments, due to the instability of clay minerals at high temperature and pressure, kaolinite that occurs in large quantities during the weathering process and immediately after deposition at greater depths overlay is no longer stable. The clayey sediments at greater depth covering typically do not contain kaolinite. The kaolinite completely disappears and is transformed into chlorite and illite at depths >3000−5000 m (Fig. 5.40).

Geologically old clay sediments (Paleozoic and Mesozoic) that have undergone intense diagenetic changes (mudstone and shale) usually have simpler mineral composition such as illite, muscovite and chlorite. Smectite, kaolinite and muscovite transform into more stable illite, muscovite and chlorite at higher temperatures (Fig. 5.40).

A good example of changes in clay minerals with increasing depth of the overlay is Miocene marls and marlite from deep wells and oil fields in eastern Slavonia, Croatia. Marlites (altered marl), illite and chlorite are reported as clay minerals by derivation of diagenetic processes at depth of 1300−1500 m. Chlorite occurs most intensely in the late stage of diagenesis at greater depths covering with transformation of kaolinite, montmorillonite and clay minerals. Part of the chlorite may occur in the marine spending in the early stage of diagenesis. Early diagenetic chlorites are usually rich in magnesium, and late diagenetic in iron. Chlorite is easily transformed into vermiculite and smectite, and in clay sediments often occur in disordered interstratified mixed layer minerals from a group of chlorite−vermiculite and chlorite−smectite.

Shale, formed from mud at greater depths overlay, contains with the stable quartz, the new stable minerals illite, muscovite and chlorite (Fig. 5.40).

5.5.6. Residual Sediments: Laterite, Kaolin, Bauxite and Terra Rossa

Chemical weathering of some rocks (as is more fully explained in Section 5.2.1.2) creates three groups of products of weathering:

1. Ions in the dissolved state: mainly released from rocks and hydrated alkali and alkaline earth elements (Na, K, Li, Ca, Mg, and Sr) and silicon in the form of silicic acid (H_4SiO_4).
2. Authigenic minerals: particularly clay minerals (kaolinite and seladonite or montmorillonite) and aluminum hydroxides.
3. Residues or waste of the rocks that in the spending did not dissolve (usually those containing quartz and resistant silicate minerals, especially mica).

The second and third groups are residual sediments or residues.

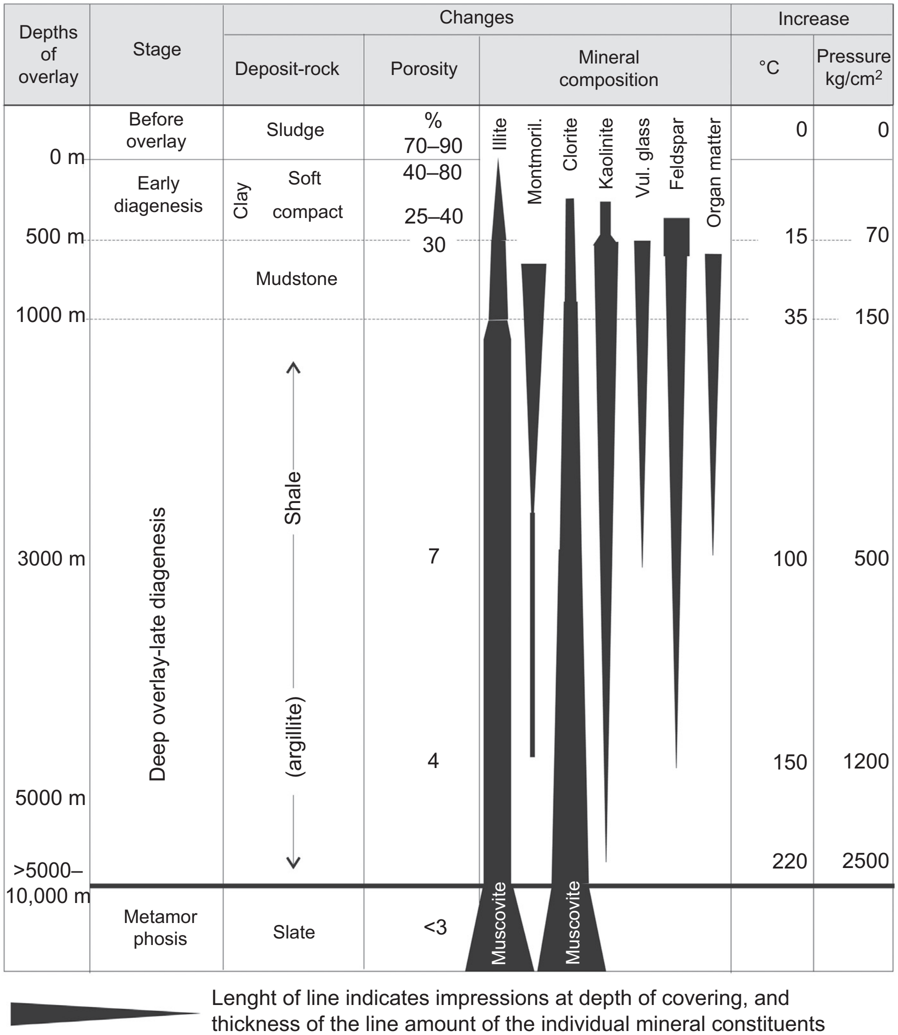

FIGURE 5.40 Diagenetic changes in mineral composition, porosity and rock types, depending on the depth of cover of clayey sediments. *Source: Revised by Füchtbauer and Müller.*[18]

In the initial stage of chemical weathering of mafic, neutral and ultramafic igneous rocks rich in olivine, pyroxene and amphibole, form authigenic minerals from group of chlorite and clay rich in iron and magnesium. Kaolinite, smectite and illite-clay are weathered products of acid igneous rocks and feldspar-rich granite-gneisses. In the advance stages of weathering, the clay is partially washed out in the form of colloidal particles, and also remains in the form of residual deposits. All magnesium and calcium minerals are leached out if the process continues uninterrupted. Quartz is the only left over or the final product or residue from primary mineral composition of rocks and newly formed authigenic minerals of the kaolinite group, boehmite,

FIGURE 5.41 Laterite soil (deep red brown color), chemical residual product from layered ultramafic complex, contains rich nickel resource from upper levels of Sukinda chromite deposits/mines, Orissa, India. *Source: Ref. 25.*

gibbsite, limonite and hematite. Strong chemical weathering, hot and humid air, and little or practically no erosion or removal of products of wear is necessary for the origin of such residue. This procedure generates residual sediments of laterite type, which are often economically significant mineral resources. The most important residual sediments petrologically include laterite, residual clay or kaolin, terra rossa (or "red soil", weathering of limestone) and bauxite.

Laterite soils are reddish-brown color (Fig. 5.41), which are products of strong chemical weathering of mafic and ultramafic rocks rich in olivine, pyroxene and hornblende. Laterite is rich in iron hydroxides, nickel, copper, chromium, platinum–palladium and aluminum, to which also contains small amounts of humus, quartz, calcite, clay and other minerals. Laterites are widely distributed and best developed on large plains made of basalt and basic intrusive ultramafic rocks in areas with humid tropical climate and low relief (India, Africa, and South America) with weak erosion. Laterite can be a potential source of high-value metallic minerals.

Kaolin or *China clay* is residual sediment consisting of pure kaolinite (Fig. 2.16), i.e. clay minerals from a group of hydrated aluminosilicates $Al_2Si_2O_5(OH)_4$, as a residual product of chemical weathering of feldspar, mainly from granite rocks. Kaolin deposits are usually formed by deposition of kaolinite after its shorter transfer by water from the point of spending or granite gneiss, mostly in lacustrine environments. Kaolin layers are typically located along the lake sands, sludges and coal or peat. Kaolin is a valuable mineral raw material for the manufacture of ceramics, especially porcelain, and the raw material in paper production.

Red Mediterranean soil, also known as terra rossa (Italian for "red soil"), is a soil classification that has been formally superseded by the formal classifications of systems such as the FAO soil classification, but that is still in common use. FAO stands for "Food and Agriculture Organization" of the United Nations.

Red soil (terra rossa) is, in geological terms, fine-grain sediment reddish brown and yellowish-red color, which is as clay-dusty cultivable soil located on calcareous, karst terrain of the Mediterranean area. Terra rossa is the chemical weathering product of limestone under oxidizing conditions excelled by Mediterranean climate.

The distinctiveness of red soil is its red color due to soil processes peptization of amorphous iron hydroxide and the formation of tiny crystals of hematite and goethite in tiny, dense ground mass of soil. With respect to granulation of red soils belongs to the fine-grained pelite sediments, because they consist of particle size <63 mm and very small, often insignificant share of the fine sand. Mineral composition of terra rossa is usually as follows: dominant are mica minerals (mica and illite), quartz and clay minerals (kaolinite and disordered kaolinite), and the much smaller proportion of hematite and goethite as well as amorphous substances, plagioclase and K-feldspar.

Red polygenetic soils mainly derived from powder materials that cover on the limestone and dolomite surface applied by wind, and by precipitation in cavities during heavy rains. It is often mixed with a small amount of indigenous soil generated from weathering of carbonate substrates. It also results in prolonged and repeated process of resedimentation. The origin (pedogenesis or soil evolution) is essential Mediterranean climate, good permeability carbonate base for a strong drainage, pH around 7 (roughly neutral) of pore solution, strong carbonate leaching, long-term (>10,000 years) suitable conditions for the formation of hematite and goethite as well as long (>10,000 years) suitable conditions for the genesis of kaolinite and generally accumulation of clay minerals.

Bauxites are rocks that contain minerals mostly from the group of aluminum hydroxide, mainly gibbsite ($Al(OH)_3$) or aluminum oxide hydrate boehmite (AlOOH) and rarely amorphous gel ($Al(OH)_3$). In addition to aluminum and bauxite minerals regularly contain variable amounts of kaolinite and halloysite, quartz, aluminum chlorite, hematite and goethite, and as the minor ingredients rutile and anatase. Bauxites are used for obtaining aluminum ore and also as refractory bricks. Bauxites arise in two mutually substantially different geological conditions:

1. the intensive chemical consumed silicate rocks of igneous and metamorphic origin to transform so-called laterite bauxites or silicate bauxites, and
2. karst on carbonate rocks, and are known as *karst bauxites* or *carbonate bauxites*.

Laterite bauxites are typical of tropical regions of South America, West Africa, India and Australia, and the massifs of Arkansas (USA). Karst bauxites are very abundant in the Mediterranean region, the Urals, West-Indian islands and in East Asia.

The process of formation of aluminum hydroxide in bauxite is associated with the hydrolysis of clay minerals, mainly kaolinite. For such a process requires underlying material, mainly clay minerals and large amounts of water to remove the silicon in the form of silicic acid, which requires a long geological time. Previously, it was thought that the karst bauxites occur by hydration process of clay material that is exclusively insoluble left over of karst and exposed to emersion limestone and dolomite. In recent times, there is more evidence that the parent material for the origin of karst bauxite may largely derive from small material Aeolian origin, therefore, of fine-grained materials or powders were either terrigenic or volcanic origin issued by wind, and only part of the insoluble residue of limestone and dolomite.

5.6. VOLCANICLASTIC ROCK

5.6.1. Definition and Origin of Volcaniclastic Sediments and Rocks

Volcaniclastics contain more than 25% of the ingredients of volcanic origin (fragments of volcanic rock, volcanic glass, and volcanic ash); a material was ejected by volcanic eruptions, and transported by air, water or pyroclastic flows to the place where it was deposited (on land or at sea). In some places, such material can be mixed and resedimented along with greater or lesser amounts of sedimentary material detrite or biochemical in origin. In volcaniclastic ingredients, pyroclastic in origin are the following:

1. Lithoclasts, i.e. fragments of volcanic rocks ejected during volcanic eruptions.
2. Crystal clasts or crystals that are crystallized in the lava before eruption. In the pyroclastic sediments came in more or less intact, or perished condition. Most often these are sharp-edged, angular fragments of quartz crystals, feldspar, amphibole, biotite, pyroxene and olivine.
3. Vitroclasts or fragments of volcanic glass, which are generally smaller than lithoclasts and crystal clast, usually sized between 0.1 and 0.4 mm. They are angular, irregular or

angular wedge-plate sections of acid, neutral and basic volcanic glass.

Tephra is a synonym for pyroclastic materials and pyroclastic sediments and in general for reservoirs of pyroclastic material regardless of the size of the fragments and particles. Volcaniclastic sediments contain fragments and particles of volcanic origin (volcaniclasts) that termed as pyroclasts or hydroclasts considering the place and mode of origin. The pyroclasts are products of volcanic eruptions on land and hydroclast fragments and particles occur in volcanic explosions on the contact of lava and water (submarine volcanism). The rapid cooling and mechanical granulation of lava occur in the contact with water.

Scoria is the name for a dark gray and black pyroclastic accumulation takes place at eruptions of neutral and basic lava.

Pumice stones are extremely porous, vesicular and light volcaniclastic material of bright color that floats on water (Fig. 5.42). It is composed of pyroclasts of different sizes and shapes, and arises from the stronger viscous acid, silica-rich, and neutral lavas.

Volcaniclastic sediments or tephra are broadly divided into three genetic groups with respect to the origin and the primary mode of transportation and deposition of pyroclastic materials:

1. Volcaniclastic sediments originated from pyroclastic flows.
2. Volcaniclastic sediments formed by deposition of pyroclastic material from the air.
3. Volcaniclastic sediments resulting from the turbulent flow of low density and high speed.

FIGURE 5.42 Pumice stone, highly porous, vesicular and light volcaniclastic pyroclasts with low density (<1), and float on the water.

Volcaniclastic sediments originate from pyroclastic flows resulting from volcanoes hot, gas-rich pyroclastic flows and ash fragments flowing or rolling and crashing down the slope of volcanic eruption or by a similar mechanism of gravity flows. The main components of these flows are volcanic gases and primary volcanic material predominantly acidic composition. The dimensions vary from small grains to large blocks. Such flows occur from subaerial or submarine environments (Fig. 5.43). The sediments of volcaniclastic material deposited by mechanisms of one, several or more pyroclastic flows or ash flows and pumice-rich are called *ignimbrites*.

Volcaniclastic sediments formed by deposition of material falling from the air are the result of accumulation of pyroclastic material ejected by volcanic eruption high into the atmosphere. It is a fine-grain volcanic ash which after the eruption makes cloud of lapilli and volcanic ash into the atmosphere and is transferred over long distances of several hundred to several thousand kilometers away from the eruption site. The farthest reaching are the tiny particles of ash from which arise fine-grain tuff in the vicinity of the eruption precipitated by lapilli, or lapilli tuffs (Table 5.5). In this way, fine-grain tuffs usually form thin bands within the land, lake and marine sediments in connection with each eruption. The tuff settles on very large areas as the mark layers, i.e. layers formed by deposition from the same stage of volcanic eruptions, and

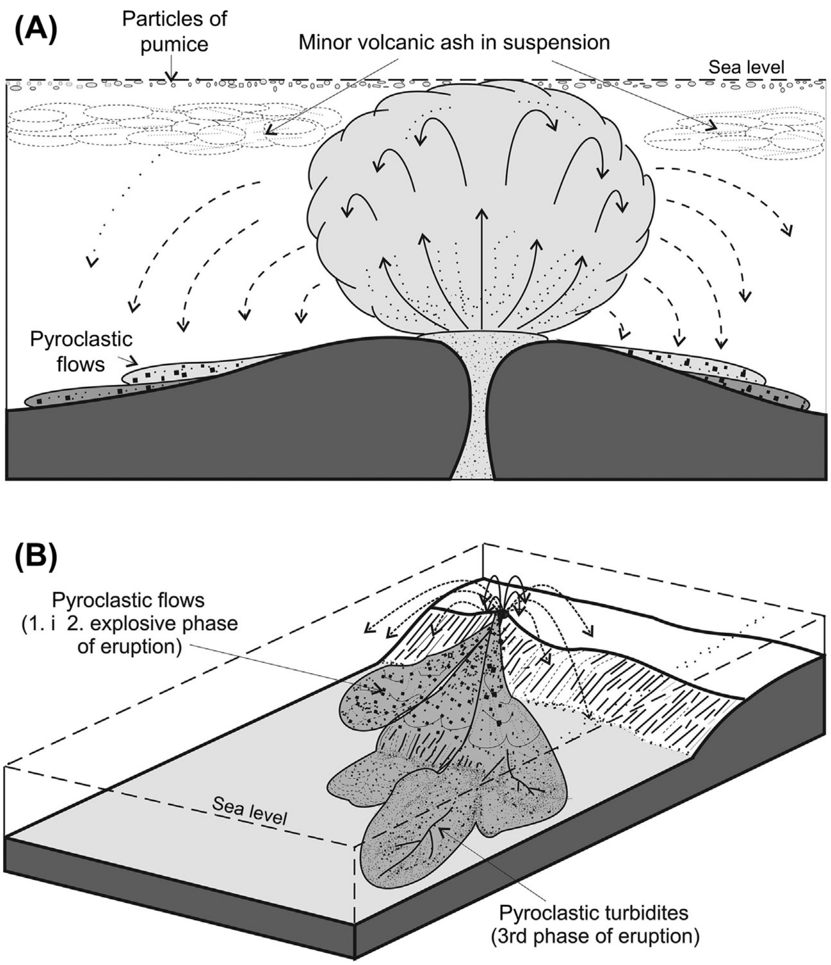

FIGURE 5.43 Deposition of volcaniclastic sediments in undersea volcanic eruptions: (A) ejection and suspension of volcaniclastic material with seawater, and (B) pyroclastic flows occurred in the first and second phases of the eruption and volcaniclastic turbidites occur in the third—low explosive—the phase of the eruption.

TABLE 5.5 Classification of Volcanoclastic Granulometry Sediment (Tephra) and Volcanoclastic Sedimentary Rocks

Particle Size	Type of Clast	Name of Sediment	Consolidated Rock
>64 mm	Volcanic bombs blocks	Agglomerate	Agglomerate
2–64 mm	Lapilli	Lapilli tephra	Lapillistone
0.063–2 mm	Large volcanic ash	Coarse-grained volcanic ash	Coarse-grained tuff
<0.063 mm	Fine volcanic ash	Fine-grained volcanic ash	Fine-grained tuff

Source: Ref. 30.

have defined the exact time of deposition of layers in which they are located.

Volcaniclastic sediments, resulting from the turbulent flow of low density and high speed, are characterized by thin and irregular layers. The sediments are precipitated from the turbulent flows generated by different mechanisms, primarily the strong interactions of submarine eruptions and the surrounding water. It mainly consists of poorly sorted sand and fine gravel (0.063–4 mm), with different composition and origin, with greater or lesser amount of pyroclasts from the last eruption, and the prevailing amount of clasts derived from older volcaniclastic and effusive from previous eruptions. The complete sedimentary cycle of volcaniclastic sediments deposited by submarine volcanic eruptions can be assumed in three different phases (Fig. 5.44).

Phase	Depositional Activities
I	Volcaniclastic precipitated from pyroclastic flow in the most intense phase of the eruption.
II	Deposition lapilli and volcanic ash from seawater during each new eruption of pyroclastic flows and no sedimentary material from turbidity flows.
III	Deposition of pelagic sediments, with brief interruptions of deposition of fine volcanic ash and/or pumice.

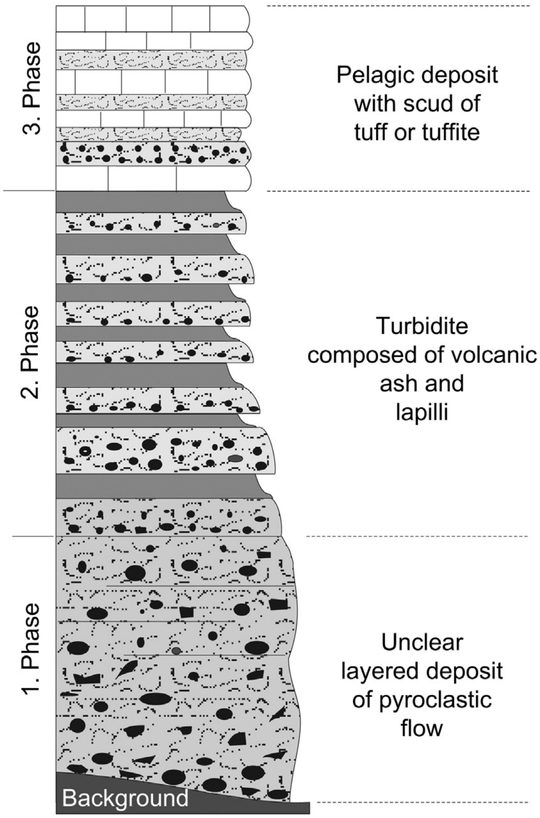

FIGURE 5.44 The complete sedimentary cycle of volcaniclastic sediments deposited in submarine volcanic eruptions. *Source: Modified and supplemented by Schmidt*[39]; *Einsele.*[13]

5.6.2. Composition of Volcaniclastic Sediments and Rocks

Volcaniclastic material or tephra is divided into volcanic bombs, lapilli and coarse and fine volcanic ash based on the grain size. Their precipitation and lithifaction make various pyroclastic rocks such as agglomerates, volcaniclastic breccias, lapilli tuffs, coarse-grained and fine-grain (pelite) tuff (Table 5.5). A mixture of clastic, biochemical and chemical material is called *tuffite*. The common types of volcaniclastic rocks are volcanic breccias, agglomerates, tuffs and tuffite.

Volcanic breccia consists of angular and semi-angular fragments and volcanic ash, i.e. the ejected material in eruption. Individual blocks and fragments of volcanic breccia are typically embedded in the matrix, i.e. lithified volcanic ash with tiny fragments of volcanic glass, which sometimes can be mixed with material of nonvolcanic origin, such as clay, silt and marl. In certain types of breccia, matrix may have vesicular (porous) structure or the structure of pumice.

Agglomerates are coarse accumulations of large blocks of volcanic material that contain at least 75% bombs. Agglomerate is volcaniclastic rock composed of pieces of lava that are in rotation and cooling in the air took on a shape, i.e. from volcanic bombs, embedded in a mass or matrix of volcanic ash or tuff. The shape and dimensions of clastic sediments consisting of pebbles of volcanic rock (volcanic bombs) are not caused by rounding and wear activity of water. It is the result of the process of rapid cooling and rotation of lava during the eruption from the volcano crater to the place of deposition. Volcanic bombs are nearly spherical or elliptical piece of lava with diameter >64 mm (or, 32 mm by some) which is erupted completely or partially in molten state, like the pyroclastic fragments. Agglomerates may contain bombs and fragments of older lava from the same crater and/or fragments of volcanic rocks that build the base of volcanic cones.

Tuff is volcaniclastic rock composed of solid volcanic ash that may contain particles of volcanic glass (vitro-clasts), small fragments of crystals formed in lava (crystal clasts) and/or fragments of volcanic rock and lava (lithoclasts). The various tuffs will be designated as rhyolite, dacite, andesite, trachyte and basaltic based on the composition of the mother volcanic eruption consisting of acid, neutral or basic lava (rhyolite, dacite, andesite, trachyte and basalt). Tuffs, which contain mostly of crystal clasts, are called *crystal tuffs*. The one predominantly composed of particles of volcanic glass (vitro-clasts) will be called *glassy* or *vitro-clastic tuffs*. The one predominantly contains lithoclasts are called *lithoclastic* or *lithic tuffs*. There would be mutual transitions members such as crystal-lithic tuff and crystal-vitroclastic tuff.

Sillar-tuffs are glassy tuffs in which lithifaction is mainly the result of crystallization in pneumatolitic activities. They consist of aggregates of angular, cuneiform, often elongated and curved shards of volcanic glass and are rich in pumice fragments in all stages of breaking. In them are also numerous small fragments of oligoclase and small amounts of biotite flakes.

Merged or *welded-tuffs* occur in lithifaction of hot ash which was hot at the time of deposition. The particles of pumice and small fragments of glass languished in soft ash in the lower parts of the mass because of its weight. Matrix of welded tuffs is porous in its top layers and easily crushed. Matrix will be less porous and harder at the bottom. Most abundant and important ingredients of welded tuffs are fragments of volcanic glass, followed by crystal clasts of quartz, sanidine, biotite and oligoclase.

Tuffite material is a mixture of volcanic and sedimentary origin, or rock that contains ingredients between 25% and 75% of the volcaniclastic origin and 75–25% ingredients of sedimentary origin. Sediments containing 10–25% material from volcaniclastic origin are called as *tuffite* or *tuffite marls* and *tuffite sandstones*.

5.6.3. Alteration of Tuff

Of all volcaniclastics, tuffs and tuffites are the least resistant to chemical weathering. The processes of chemical modification of tuffs are a direct consequence of their composition, structure and physicochemical conditions and environment of their origin and geological age. Alterations of tuffs, especially with volcanic glass, are the result of chemical reaction of glass with water so that the alternating process of dissolution of volcanic glass with the process of excretion of authigenic minerals in places where glass is melted. The most common products of such changes in tuffs are the zeolite group of minerals (Table 2.12). If temperature further increases with the depth of the overlay, they cross in to chlorates, quartz and albite.

Neutral and acidic volcanic glass gives different products of changes in relation to basic volcanic glass. These differences can be observed in the early stages of change.

Alterations of acid glassy tuffs primarily depend on the pH of pore water, seawater or freshwater. The glassy acidic tuff of $\sim$10,000 years old changes to cluster of alkali-rich zeolites (phillipsite and clinoptilolite) in the presence of basic pore solution/water with pH > 9.5. This is common in case in many lakes of arid climatic regions. Authigenic zeolites with initial high salinity are transformed to "analcime" ± quartz± or in K-feldspars ± quartz.

Acidic volcanic glass, under conditions of sea/freshwater with typical low pH, primarily changes to smectites (mainly montmorillonite group) ± opal, cristobalite and zeolite. The acid tuffs alter to bentonite due to the effects of seawater or freshwater. Bentonite (or smectite deposits) is a clay similar to montmorillonite, zeolite, cristobalite, chalcedony and opal. The process of alteration of acidic glassy tuff to bentonite takes several million years at pH 7–8.

Alteration of basic tuffs, especially basic volcanic glass of subaquatic foundation, predominantly composed of basaltic glass, occurs much faster than the changes of acid tuffs. It changes quickly to palagonite. Palagonite is a name for the brown, yellow or orange-gray resinous mixture of different minerals from the group montmorillonite, zeolites, mixed-layer clay minerals, chlorite, limonite and goethite. Palagonitization is the process of alteration of basalt glass and glassy tuffs into palagonite. This is hydration process that occurs with the addition of water and removal of alkali and alkaline earth ions, silicon and sometimes aluminum and oxidation of iron with excretion of zeolite, calcite and minerals of montmorillonite groups.

5.7. CHEMICAL AND BIOCHEMICAL SEDIMENTARY ROCKS

Chemical and biochemical sedimentary rocks belong to the endogenous sediments, i.e. sediments that occur predominantly inorganic chemical or biochemical processes. The rocks are divided into carbonate, silicon and evaporite sediment (Table 5.2) based on the chemistry of essential petrogenic minerals, organogenic components, and the system of secretion or precipitate.

1. Carbonate sedimentary rocks

Carbonate sedimentary rocks include limestone, dolomite limestone and dolomite (Table 5.2), i.e. rocks composed predominantly (>50%) of calcium carbonate minerals, calcite, Mg-calcite and aragonite, or dolomite minerals. It may also include variable proportion of siliciclastic material dimension silt, sand and clay, and authigenic noncarbonate minerals.

5.7.1. Limestone

Limestones are carbonate rocks predominantly organic, to a lesser extent, inorganic origin, in which the dominant component is the mineral calcite. They originated in lithifaction of aragonite, calcite and/or magnesium-calcite sediment. Limestones with calcite may also contain magnesium calcite, rarely aragonite and dolomite. Dolomite-limestone is composed predominantly of calcite.

5.7.1.1. Mineral Composition, Physical, Chemical and Biological Conditions for Foundation of Limestone

The limestone deposits are composed of calcite, aragonite and magnesium calcite, or only one or two of these carbonate minerals, lithified calcareous sediments (limestone) mostly contain only calcite. The other two minerals, aragonite and magnesium calcite, transform easily into stable calcite during diagenetic processes. The dolomite limestone composed of calcite and dolomite forms by late-diagenetic dolomitization. The calcite, aragonite and magnesium calcite are mainly excreted by the sea- or freshwater containing Ca-hydrogen by biochemical or organic, to a lesser extent and inorganic processes.

The secretion of calcite or aragonite depends primarily on the molar ratios of Mg/Ca. The secretion of aragonite is possible in all warm shallow seas with high molar ratio of Mg/Ca compared to the normal ratio (the world's oceans ratio is 5.26). Calcite and low-magnesium calcite secrete at a temperature of about 20 °C and at molar ratio of Mg/Ca <1, as is the case in freshwater lakes and rivers. It also excretes from the seawater with lower molar ratio of Mg/Ca at lower temperature (~10 °C) in deeper water with lower pH (but not <7.8) in the presence of SO_4^- anions. Excretion of high-magnesium calcite from seawater is mainly regulated through a tendency of organisms to build their skeletons from magnesium calcite. The percentage of isomorphic blended $MgCO_3$ in magnesium calcite depends on the temperature of seawater. The warmer water may contain high-magnesium calcite up to 28 mol.% $MgCO_3$. It can be concluded as follows:

1. Aragonite is excreted in the warm and shallow sea with at high ratio of Mg/Ca.
2. Calcite and low-magnesium calcite are excreted in cold or deep sea, where temperatures are lower, as also in lakes and rivers.

Excretion of Ca-carbonate from a solution saturated in calcium hydrogen carbonate takes place according to the following chemical reaction:

$$\underset{\substack{\text{calcium}\\\text{hydrogen-}\\\text{carbonate}}}{Ca(HCO_3)_2} \longrightarrow \underset{\substack{\text{aragonite}\\\text{or}\\\text{calcite}}}{CaCO_3} + CO_2 + H_2O$$

It is evident from this reaction that the secretions of calcite or aragonite in water containing dissolved calcium hydrogen carbonate take place, if from the hydrogen-carbonate somehow CO_2 or water is removed.

Removing CO_2 from the sea- or freshwater in nature can be caused by the following:

1. Bacteriological and photosynthetic processes of plants and cyanobacteria (blue-green bacteria and blue-green algae).
2. Heating of water.
3. Reduction of atmospheric pressure.
4. Spraying water into droplets in the waves or waterfalls.
5. Evaporation.

A good example for the extraction of carbonate by mosses and water plants which in photosynthetic processes contribute in the formation of calcareous matter on the waterfalls of rivers and lakes (e.g. Krka and Plitvice Lakes, Croatia).

The biogenic origin for most of the marine and some freshwater calcium carbonate is clearly established. The inorganic origin of many marine and surface limestone precipitations is difficult to prove. The majority of calcite creation gathers from meteor pore water under the surface of the Earth formed by inorganic processes.

5.7.1.1.1. SECRETION OF CARBONATE IN SHALLOW SEA

More than 90% of recent carbonate sediments are the result of biological or biochemical processes in marine, mostly shallow-sea environments. Their occurrence and distribution within the world's seas are directly determined by the growth and development of organisms whose life processes, especially photosynthesis and building skeletons and shells, related to the Ca-carbonate. Growth and development of such organisms are conditioned with temperature, climate, concentration and salinity of seawater. The existing seawater organisms and their preference for the construction of the skeleton or shell play an important role in the formation of the primary mineral composition of limestone deposits, especially those mainly composed of finely crushed skeletons. The favored minerals are aragonite, calcite or high-magnesium calcite. Many plant and animal species are directly or indirectly involved in the formation of carbonate sediments, or limestone. These are organisms that build their skeletons of aragonite, calcite, and thus lithified at the site of the growth form of limestone reefs. The greatest amount of diagenetic limestone deposits are caused by deposition of shell and skeleton, or their bioclasts excelled by the activity of waves, currents and bioerosion in small sections of crushed parts.

Many organisms, especially algae, cyanobacteria, mosses and grasses, to a large extent are indirectly involved in the genesis of carbonate sediments. The most significant photosynthetic processes of plants extract CO_2 and thus induce the secretion of $CaCO_3$ from sea- or freshwater containing calcium hydrogen carbonate. The photosynthetic process can source the release of 2800 g carbonate from today's tropical, warm, shallow seas, sea grass with an area of 1 m^2 in 1 year. One can get the picture of the importance of plants in limestone formations when this figure is deduce to a total area of shallow marine and counted the time of thousands and even millions of years.

5.7.1.1.2. SECRETION OF CARBONATE IN DEEPER WATER

The carbonate production is much smaller in deeper water because it depends directly on the degree of saturation of water in calcium hydrogen carbonate, which significantly reduces as the depth increase. The shallow sea is saturated, and the deeper parts of the seas and oceans in the World are poorly saturated with calcium hydrogen carbonate. Therefore, it is difficult to excrete Ca-carbonate in deeper sea.

The water depth at which the solubility of carbonates is equal to their excretion, it is called the *calcite compensation depth* (CCD). The water contains an excess of dissolved calcium hydrogen carbonate and excretion of Ca-carbonate is possible and stable above that depth (separation of calcite). Ca-carbonates are unstable below the CCD and dissolve because the water is supersaturated with calcium hydrogen carbonate, and cannot excrete. The solubility of calcite follow almost linear trend with increasing depth of the sea until just above the CCD border. Thereafter solubility of calcite sharply increases with a small increase in depth. The seawater will have no more calcite when CCD border line solubility reaches the absolute maximum (Fig. 5.45).

CCD boundary line varies depending on latitude, temperature and salinity of oceans and seas of the present day World (Fig. 5.45). In the equatorial belt of the Pacific Ocean, CCD is located at depths between 4500 and 5000 m. CCD is located between 4400 and 4900 m in the Atlantic Ocean between 40° north and 40° south latitude. CCD in the equatorial zone is at depth slightly more than 5000 m, and at diminished depth at higher latitudes up to 2000 m, and latitudes over 60° and much shallower than 1000 m.

Aragonite compensation depth (ACD) is significantly shallower than the CCD: the Atlantic

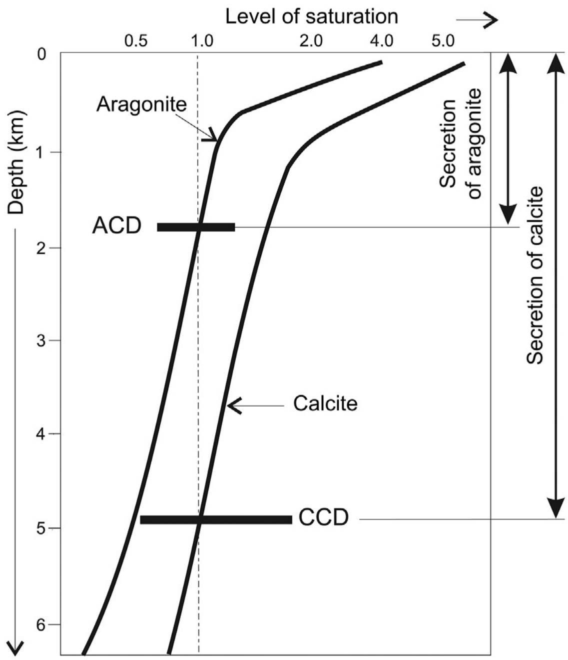

FIGURE 5.45 Position of calcium compensation depth (CCD) and aragonite compensation depth (ACD) boundary lines in deeper water.

Ocean in temperate latitudes is located at depths of 1700–1800 m (Fig. 5.45).

The positions of CCD and ACD boundary lines in the seas varied throughout Earth's geological history in rather wide limits. In the geologic past, the position of CCD has varied between 3000 and 5000 m. CCD and ACD boundary lines determine the stability fields of calcite or aragonite, in the sea from which it is clear that at deep sea (below CCD border line), there is no carbonate sedimentation (Fig. 5.45).

5.7.1.2. *The Structural Components of Limestone*

Limestones are composed of carbonate grains, limestone mud, and of subsequently extracted authigenic carbonate minerals. Carbonate grains or particles and very fine lime mud, or matrix, generally in the limestone is called "micrite" (Fig. 5.46), belonging to genetic group of primary carbonate structural components. Micrites are incurred and precipitated after a longer or shorter transfer of water in the same depositional area. These are all aragonite, calcite, magnesium calcite grains. The authigenic carbonate limestone components are subsequently, after deposition, during diagenesis extracted calcite and aragonite cements, which are commonly named as *sparite*.

FIGURE 5.46 Micrite is a compact fine-grained limestone constituent consist of calcareous particles ranging in diameter up to 4 μm formed by the recrystallization of lime mud.

Micrite is nowadays generally understood as a very small matrix limestone or lithified lime mud, which consists of carbonate crystals or particles of diameter <30 μm (Figs 5.46 and 5.56). It is dense, in the transient light of microscope slightly transparent, calcite mass composed of allotriomorphic to hipidiomorphic calcite crystals with each other straight or bent contacts. Before lithifaction, it was fine-grain lime sludge—a mixture of tiny particles of aragonite and/or magnesium calcite or calcite. After lithifaction in limestone, micrite contains only cryptocrystalline or microcrystalline calcite and low-magnesium calcite as the primary unstable aragonite and high-magnesium calcite during diagenesis transformed into the stable calcite or low-magnesium calcite.

The origin of primary structural components of limestone and Ca-minerals can be organic (biogenic), inorganic and mixed inorganic–organic. Complete sharp division of the organic and inorganic compounds is not possible because of tight intertwining ways of their foundation so that they cannot always be distinguished. Carbonate mud, which is, for example, formed by excretion of carbonates in inorganic processes, and carbonate mud originated biomineralization, i.e. secretion of aragonite and calcite in the photosynthetic processes of algae and seaweed, together are impossible to differentiate. Moreover, none of these two sludges can be distinguished with petrographic microscope, even the sludge occurs by bioerosion. Therefore, the primary carbonate structural components of limestone are divided usually into skeletal and nonskeletal.

Nonskeletal components of limestone are the primary structural components, i.e. those are of inorganic origin, often laminated (Fig. 5.47) and that clearly do not originate from skeletal material of microorganisms, animals or shells of calcareous skeletons of plants. The group of nonskeletal components that are in the form

FIGURE 5.47 Inorganic well laminated crystalline limestone composed of white calcite ($CaCO_3$) and reddish ankerite [$Ca(Fe,Mg,Mn)(CO_3)_2$].

of beads or particles belong intraclasts, pellets, peloids, grapestone grain and coated beads (ooids, pisoids, and oncoids).

The skeletal-limestone ingredients are those which consist of one or more of carbonate skeletal debris or small shells or skeletons (Fig. 5.48). The skeletal components are common named as fossil, fossil debris, biodetritus and bioclast. A special type of primary structure is the stromatolites, and the primary structural component can be both skeletal and nonskeletal origin in the matrix or micrite.

FIGURE 5.48 Skeletal-limestone, apparently laminated, with debris of small shells and skeleton, represents Devonian reef complex along the northern margin of the intracratonic Canning Basin at Lennard Shelf hosting rich zinc–lead mineralization, Australia.

Genesis of carbonate mud, or matrix, or in the solid limestone micrite is very different. Micrite may arise by mechanical fragmentation of the skeleton, direct biogenic accumulation of small fragments of skeletal calcareous algae and coccoliths, chemical secretion of aragonite in the warm seas, excretion of small calcium carbonate crystals in the photosynthetic processes of plants, secretion of Ca-carbonate in the activity of bacteria, the accumulation of very fine detritus formed in processes of bioerosion of limestones caused by fungi, sponges, algae and other organisms that drill and destroy the foundation on which grow (bioerosion). Coccoliths are composed of thin calcite rings and discs of diameter 20–20 μm, gathered in a cluster of organisms Cocolithophridae, which are of great importance as components of many of the sea (pelagic) limestones. Carbonate mud also occurs in abrasion and mechanical crushing of limestones.

Intraclasts are carbonate grains formed within the depositional area by resedimentation lithified fragments of carbonate sediment, which occurred immediately after the destruction of sediment deposition. It can be very different in size, shape and internal structure depending on the composition, structure and texture of carbonate sediment destroyed, transferred and resedimented and deposited (Fig. 5.49). The composition, structure and lithofacies type of intraclasts are typically corresponds to the layer with activity of waves and ocean currents.

Pellets and peloids are spherical, ellipsoidal, and cylindrical or spindle-carbonate grain diameter mainly from 0.1 to 0.5 mm, rarely up to 2 mm, which is characterized by micrite internal structure. It consists of densely packed cryptocrystalline to microcrystalline carbonate containing an increased proportion of organic matter. Pellets are important and frequent primary structural carbonate components of shallow marine limestones and early diagenetic dolomites and recent carbonate sediments.

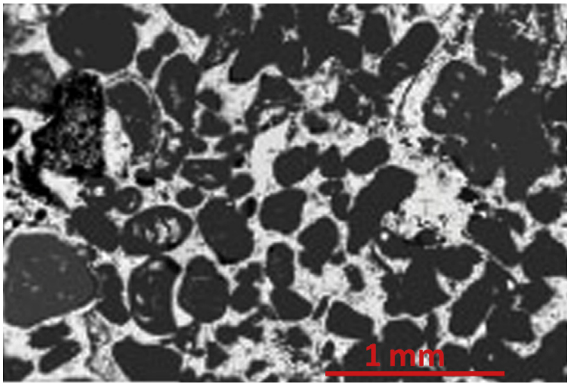

FIGURE 5.49 Intraclastic greystone: poorly sorted, rounded intraclasts with micrite structure (dark grains).

Fecal pellets are incrusted, fossilized feces of organisms that fed with sludges. They have spherical, ellipsoidal and well-rounded shapes. The shape, dimensions and internal structure are uniform in the same rock (Fig. 5.50). These are incrusted, fossilized feces and undigested remains of carbonate mud fed on sludge. They occur in all environments of deposition, in the shallow and deeper water, lived in large quantities of organisms, and preserved only under certain conditions. They are important indicators of environment and conditions of precipitation. The fossil preservation is usually possible only in the lower tidal region in the shallowest part of subtidal zone with low water energy, rapid lithifaction and cementation of deposits. The fossil preservation will be difficult in deeper and shallow water with increased strong water energy because the sediments will disintegrate/crush into loose carbonate mud before compaction, cementation and lithification. Specifically, in order to preserve fecal pellets, each pellet must move quickly from soft to the solid grain or must be cemented fast immediately after it was expelled from the organism for which optimal conditions exist in shallow water with low water energy supersaturated with calcium bicarbonate. Pellet is called only those of fecal origin and peloid are all other similar grains formed in some other way.

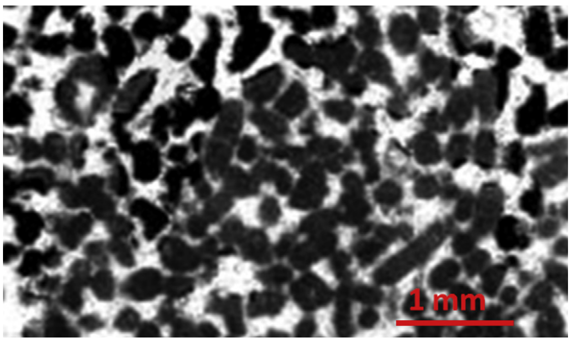

FIGURE 5.50 Pellet greystone: fecal pellets of uniform shape, dimensions and internal structure cemented in mosaic calcite cement.

Peloids are spherical and hemispherical micrite carbonate buildup in diameter usually 0.05−2 mm resulting in incrustations of blue-green algae. Unlike the fecal pellets, peloids are characterized by irregular shapes and different sizes, therefore, are not uniform in size, shape and internal structure.

Coated grains are specific type of carbonate grains of different origin and consist of clear membranes around some core. The coated grains include ooids, pisoids, oncoids or coated bioclasts. The rocks consisting mainly of them are called oolite, oncolite, pisolites. So, just rock, and not single grain, a continuation of "lite" (from the Greek "lithos" = rock).

Ooids are properly shaped, generally oval to spherical grains that consist of a core and multiple concentric membranes or laminae of different thickness (Fig. 5.51). Individual laminae can be thinner in places where the core is irregularly convex. Membranes those are located directly around the core outline the contours and shape of the nucleus, while those farther away from the core tend forming grain as close to a sphere (Fig. 5.51). The core of ooids usually is a pellet, a piece of the skeleton, foraminifera shell or some other skeleton, and grains of sand (quartz, rock fragment, and

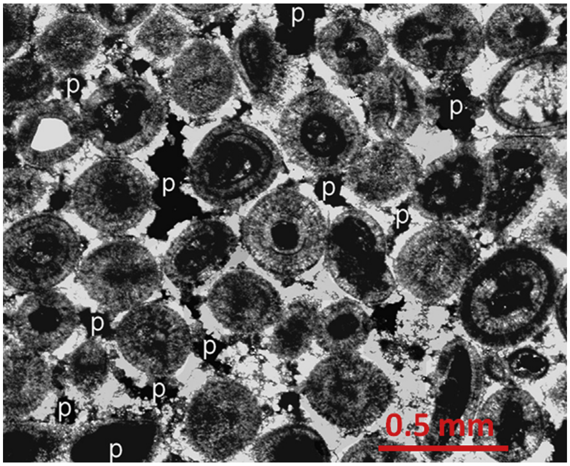

FIGURE 5.51 Ooid limestone composed of spherical ooids cemented with mosaic calcite cement (white). Part of the pore is not cemented (p).

feldspar). Ooids occur in warm, shallow seas with an average annual temperature above 18–20 °C and depths of <2 m, with a low calcium hydrogen carbonate in seawater without significantly elevated salinity. In these marine environments, it is necessary for running water with occasional changes in the intensity of its energy. The presence of granules (pellets, skeletons, skeletal fragments, and quartz grains) serves as core of ooids. The presence of organisms (bacteria and algae) removes CO_2 from the water causing the secretion of calcite or aragonite. It is believed that the growth of marine ooids need between 100 and 1000 years. The growth of ooids as shown by their concentric structure is not continuous, but in the growth of the membranes or concentric laminae, there is a relatively long time lag—no growth phase—in which the surfaces were exposed to weaker abrasion or bioerosion operation of endolith organisms.

Oolites, a sedimentary rock formed from ooids (Figs 5.51 and 5.57), play an important role in the reconstruction of the conditions and environment of deposition, particularly with regard to depth, salinity and water energy. It also serves as a significant source reservoir rocks for oil and gas due to their often extremely high primary intergranular porosity.

Pisolites (from the Greek "Pisos"—peas) are covered grains very similar to ooids, which, unlike ooids, are not primary marine structural components of limestone. Pisolite incurs during the diagenetic processes in caves, and "vadose zone" (or unsaturated water zone) under the influence and effect of freshwater on land or in marginal zones of marine, terrestrial and lake environment, as in the vadose zone around the hyper saline and in the zone of capillary lift the underlying water. These are characterized by a clearly visible regular concentric lamina material around a nucleus. The core around which there is one or more fragments of limestone. Pisolites form in caves and incur in geysers, or moving hot water, have regular spherical shape. Pisolites incur in the vadose zone and in quiet immobile water, have an irregular shape of core that resembles to the lamina, i.e. the outer shape of pisolites.

Oncoids (from the Greek "Onchos"—lumps) are grain covered with irregular shapes with carbonate jackets of micrite lamina. Lamina partially lays one over the other, usually without a clear concentric structure (Fig. 5.52), may contain remnants of organic structures as it forms with biogenic processes of algae and cyanobacteria. Many oncoids wrap beads formed by incrustation of larger number of such organisms, most of them but not all, contain a clearly discernible nucleus around which created such a small accumulation of biogenic carbonate material.

Oncoids can have very different forms of regular concentric spherical arrangement as their shape depends on whether they have nucleus or not, what is the shape of the nucleus, and the fact in which the direction fibers are faster growing. If oncoid have no nucleus or it is small, their shape is usually spherical, and construction is nearly concentric. If peloids have a large nucleus, flat or plate shape, which is often the case when the nucleus is bioclast of shell, then

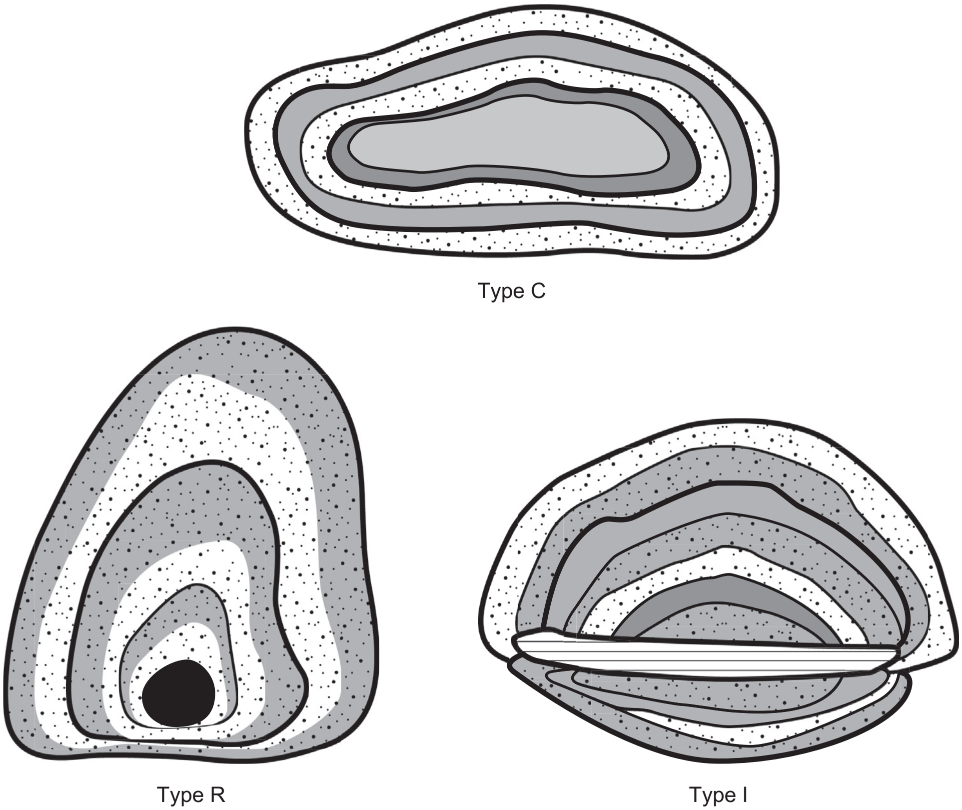

FIGURE 5.52 Structure and internal structure of oncoid type C, R and I.

oncoid is elongated (type C in Fig. 5.52). If oncoids have more irregular shape with a semicircular laminar structure, the environment was calm with only occasional tumbling of oncoid with stronger currents or storm waves (type R and I in Fig. 5.52).

Similar to ooids, oncoids are good indicators of environmental conditions and precipitation, and as a rule they occur in very shallow water, mainly in the lagoons with a low supply of water and sediment accumulation at low speed. Specifically, at the rapid sedimentation, backfilling occurs before finishing the growth of oncoids, and rapid sedimentation prevents the growth of organisms involved in the accumulation of carbonate and growth of oncoids.

Coated bioclasts are grains composed of fragments of skeleton, i.e. bioclast, and thinner or thicker micrite membrane at its surface. Membrane occurs in processes of micritization by activity of cyanobacteria, fungi that drill ground where grows. The life activity of organisms that inhabit the surface of bioclast, resulting small bore in diameter 2–30 μm of tubular shape. The holes are filled with dense fine micrite, probably the product of the secretion of carbonate through the mediation of bacteria after death of organisms. The newly formed bioclasts occur in calm, protected shallows and lagoons with depth not exceeding 15–20 m. The algae, cyanobacteria and fungi that drill the surface cannot settle on grains due to constant wear, abrasion and grind against each other in water with high energy. The coated bioclasts are often found in limestone (greystone and rudstone) deposited on tidal sandbanks and shallow water with high energy and constant activity of the waves. They arrive after the flooding and throwing with severe tidal currents and storm waves from nearby protected shallows or the lagoons environment.

Stromatolites are organic sedimentary structures (Fig. 8.17) formed by trapping, binding and/or secretion of sediment by activity of microorganisms, primarily cyanobacteria. The firmly lithified stromatolite fossils are laminated wavy, thick laminated or dome thick laminated carbonate rocks formed by binding and trapping of carbonate mud and other tiny carbonate deposits on the cyanobacterial mats. Recent stromatolites are composed of organic and inorganic laminae frequently exchanging with each other vertically. Organic laminae contain numerous genera of cyanobacteria. The inorganic laminae include carbonate mud, pellets, tiny skeletons or skeletal fragments of green algae, gastropods, ostracodes, benthic foraminifera of sediments flooded to "cyanobacterial mat" where the fibers are caught on the mucus of cyanobacteria.

Flooding of cyanobacterial mats during high tide and drying during low tide emerge organic (algal and inorganic) limestone lamina (Fig. 5.53). The carbonate sediment (mud, pellets, skeletons and fragments of skeletons) accumulates on the mat during floods. There will be no sedimentation during ebb. The moist muddy soil enables exuberant growth of blue-green algae, cyanobacteria overgrowing all the tide passed sediment. If the tide deposits large sediment on the mat (thick layer), cyanobacteria cannot outgrow, wipe out and generate fenestrations (pores of special forms) creating high fenestral porosity in limestone.

In the tidal and supratidal zone, stromatolites can easily be preserved, since the lithifaction improves with dehydration of residues and secretion of calcite, aragonite or magnesium-calcite cement in the pores by evaporation of seawater. Stromatolites also preserve in subtidal zone due to the excretion of such mineral cement from hot calcium hydrogen carbonate supersaturated seawater. The secretion of carbonate has essential role in the process of assimilation of cyanobacteria. The "cyanobacterial mats" are not preserved in the fossil stromatolites due to quick decay after being covered with sediment. The decay forms cavities or fenestrations and subsequently filled with calcite cement. Stromatolites with high fenestral porosity are characterized by high content of cement, various fenestra and modification of laminae composed of carbonate deposits (micrite, pellets, and fossils) with laminae mostly made up only of cement. Stromatolites are extremely important indicators of environment of deposition.

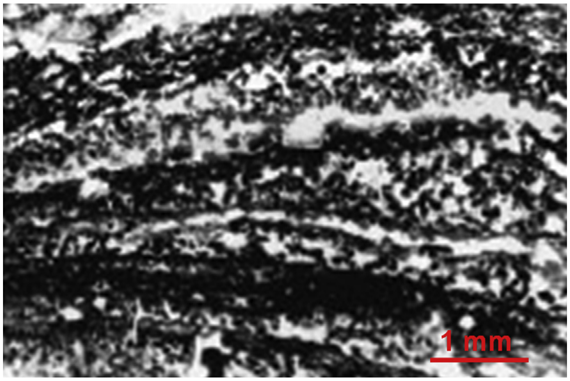

FIGURE 5.53 Stromatolites with changes of dark micrite lamina and light sparite lamina. Light laminae presents fenestrations emerged in decay of "cyanobacterial mats" that are later filled with cement and sparite represents individual fecal pellets.

Fossils, or skeletons and shells of organisms or their larger and smaller fragments in most of the limestones are important primary structural components. They are located as follows:

1. Skeleton or shells lithified on their habitat in a position of growth.

2. The whole skeleton and shell before sedimentation transferred by water currents, tides and waves.
3. Bioclasts, i.e. larger or smaller fragments of skeletons and shells.

The limestones of strict textural/structural features are direct result of ecological, sedimentological and hydrodynamic conditions of deposition environment with each of these above modes of occurrence of fossils forms. Therefore, limestones are predominantly composed of fossils, one of the three groups, and have special sedimentological–petrological names (such as rudist limestone and foraminiferal limestones). Sedimentological and petrographic labeling of limestone is based on their textural/structural and genetic features, depending on whether consists of a skeleton and of organisms lithified at the place and position of growth, of entire transported skeleton, or their fragments (bioclasts).

The well-preserved skeletons or shells of organisms lithified in position and place of growth form organogenic ridge (Fig. 7.14), mostly built of limestone (Fig. 5.55). Such sedimentary bodies are different according to morphological features:

1. Biostrome, which takes the form of layers or a large lens with more or less concordant relationship with the rocks (Fig. 5.54(A)).
2. Bioherma, irregular bulging sedimentary body shape caused by lithifaction organisms in the position and location of growth (Fig. 5.54(B)).

Reef-building organisms grow following one type of generation over another form of organogenic reefs. These carbonate sedimentary bodies can be significant reservoir rocks for oil and gas (Section 7.3.1.4), often due to high porosity and permeability over large sizes.

Limestones, which contain mostly bioclasts, are generally called bioclasts-limestone. The limestones, that contain the whole of transported skeletons, are called skeletal-limestone (Fig. 5.57(B)). The limestone, which largely contains well-sorted bioclasts and/or skeletons in diameter between 0.063 and 2 mm, is called "biocalcarenites", where "biocal" indicates biogenic calcareous components, and "arenite" for the sand size. Accordingly, in connection with the dimensions of bioclasts and the skeleton, limestones which mostly contain fossil remains of dimension >2 mm are called "biocalcrudite", and <0.063 mm as "biocalclutite" (Table 5.1).

Siliciclastic terrigenic components of limestone are detrite grains that are transferred to the depositional area by water or air. The material includes mainly quartz, clay minerals, rock fragments, particles of volcanic material and heavy minerals. Most limestones contain little terrigenic detritus, and fine size clay, silt and volcanic ash. The mineralogical and petrographic properties of these fine detritus grains can be investigated by X-ray only in the insoluble remains of limestone after dissolution in acetic, monochloracetic or diluted hydrochloric acid.

Noncarbonate authigenic minerals in the limestones include anhydrite, gypsum, quartz, chalcedony, opal, pyrite, glauconite, tourmaline, albite, K-feldspar, muscovite and zircon. Authigenic pyrite in the form of small grains or aggregates is usually a product of life activity of bacteria by sulfates reduction. Quartz, chalcedony and opal typically occur in processes of silicification or suppression of limestone mud or already hardened limestones. This is due to circulatory pore solutions containing silica acid, dissolve carbonate and secrete opal, chalcedony and quartz. Anhydrite and gypsum in the limestones may occur in the early diagenetic stage in the sabkha conditions. This happens by the secretion of calcium sulfate from highly concentrated solutions in the evaporite conditions, or during late diagenesis by suppressing of carbonates with sulfates with participation of pore solutions that contain sulfate ions.

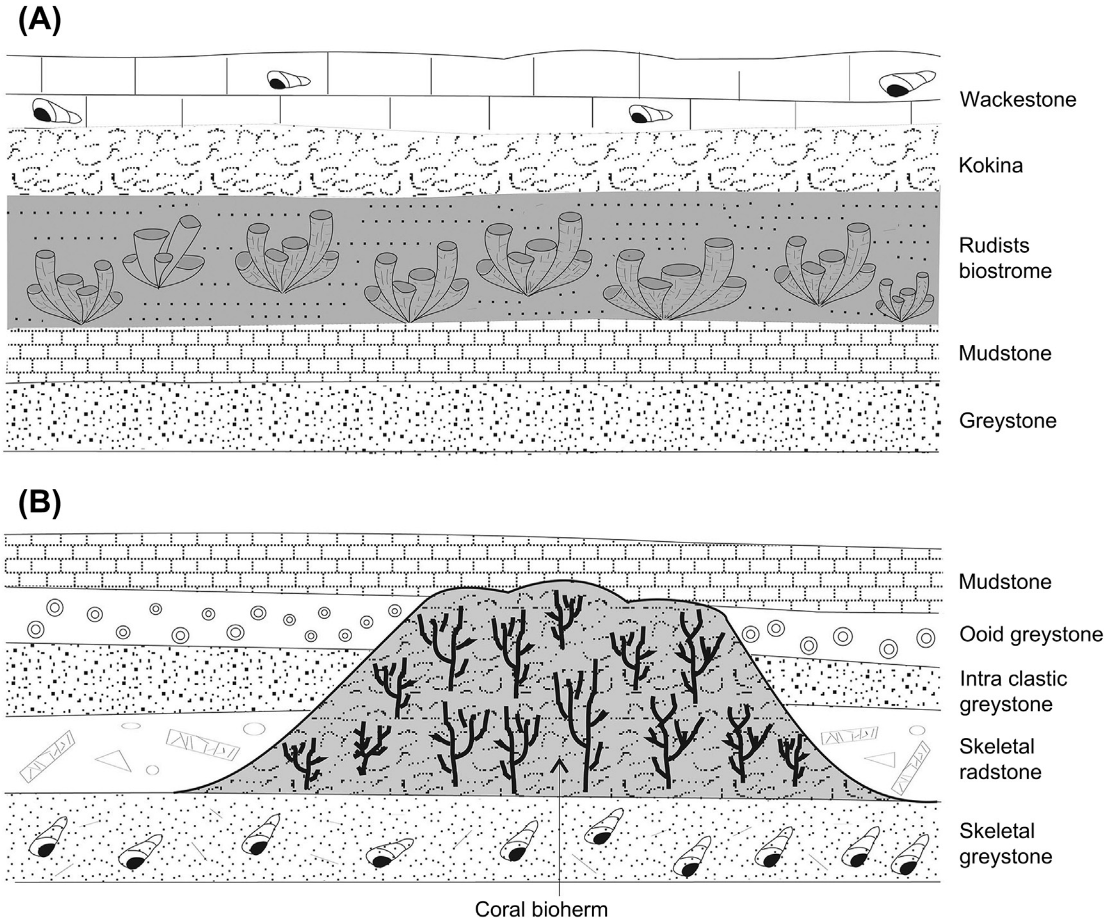

FIGURE 5.54 Morphological deposition of sediments with skeletal/shell organisms (A) regular growth layer Biostrome and (B) irregular growth discordant relation Bioherm.

5.7.1.3. Limestone Classification

Limestones are classified into three main types namely: (1) marine, (2) freshwater and (3) terrestrial with respect to the origin.

5.7.1.3.1. MARINE LIMESTONE

Marine limestones are the most common type of carbonate rocks originated from the sea. Several classifications of marine limestone in the world today exist with the broadest application by Dunham[12] and Embry and Klovan.[14] This is based on texture/structural features of limestone, the relations of primary structural components: grains (intraclasts, pellets, pelloid, wrapped grains, bioclasts, and skeleton), carbonate mud and calcite cement. Dunham classification is more applicable in describing the field and determining the limestone. Other classifications have wider application in the microscopic study of limestone, often used for early diagenetic dolomite. The classification systems are often used in field studies of limestone, as well as for the geology of oil.

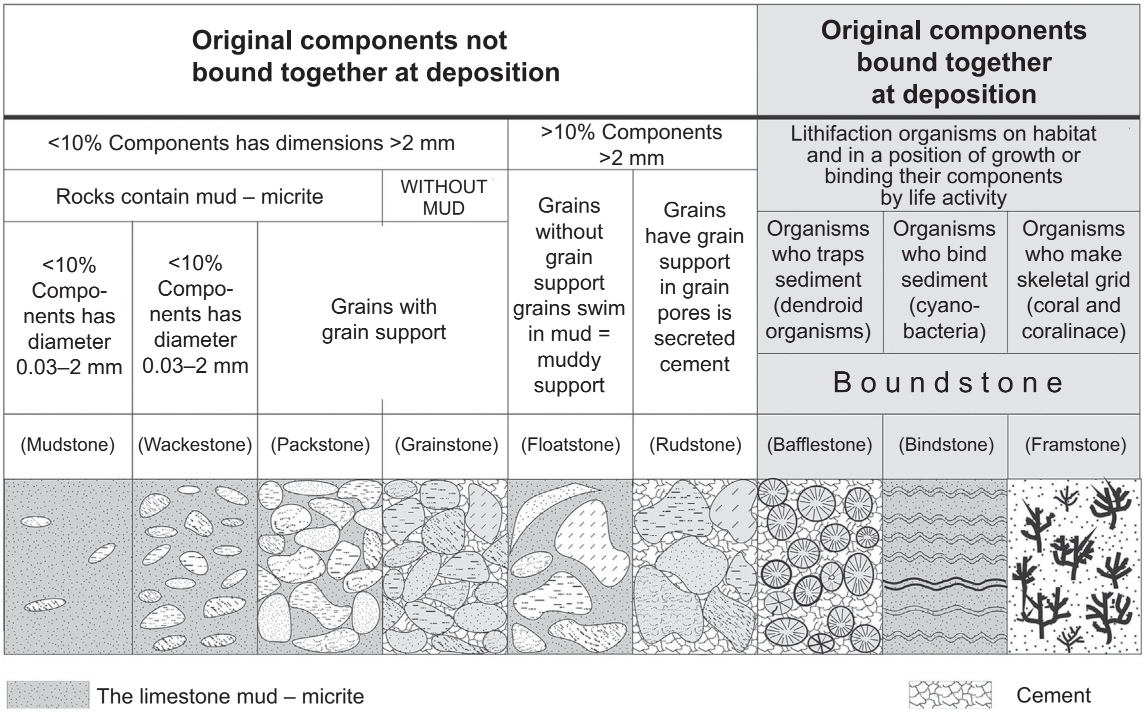

FIGURE 5.55 Limestone classification after Dunham[12] with updates of Embry and Klovan.[14]

Dunham classification of limestones (Fig. 5.55) is based on structural features, the presence or absence of carbonate mud, the relative proportion of grains and mud, signs organogenic bonding skeletal over their development, lithification on the place, and the position of growth. The system is simple and easy to apply, in the field description using limestone magnifier.

Limestone in which the primary structural components or nonskeletal and the skeletal grains/carbonate mud are recrystallized, changed and converted into calcite crystalline mass is called the *crystalline limestone*.

Besides the already mentioned crystalline, Dunham[12] distinguishes five more basic types of limestone:

1. Mudstone limestone which contain carbonate mud and <10% of the grain diameters between 0.03 and 2 mm (Fig. 5.55).
2. Wackestone limestone that contains lime sludge and 10–50% of grain, which "swim" in the mud, or a muddy, not grain support (Figs 5.46 and 5.56).
3. Packstone limestone containing grains, which have granular support, touching each other and support, and lime mud in intergranular pores (Fig. 5.55).
4. Grainstone does not contain lime sludge, but only grains that have the mutual support, and calcite cement secretes in intergranular pores (Figs 5.49–5.51 and 5.57(A)).
5. Boundstone limestone that contains primary skeletal components (fossils) tied together with sedimentation, lithificated on its habitat in the position of growth or the individual components related to organisms, with the sedimentation and formation of biostrome, bioherm (Figs 5.54 and 5.55) or stromatolite (Fig. 5.53).

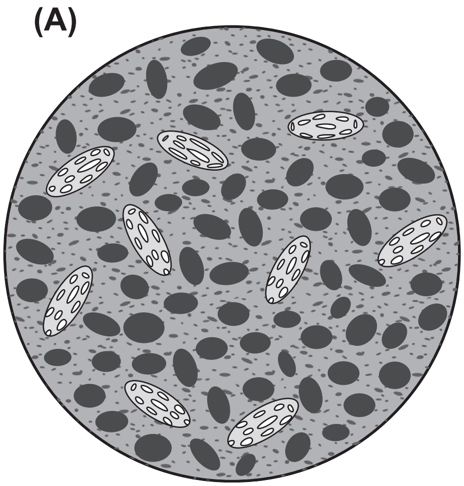

FIGURE 5.56 Micrite limestone wackestone type: (A) Pellet-wackestone is characterized by silty or matrix support of pellets, and (B) skeletal-wackestone containing lime sludge—micrite—in which there are individual skeletons and bioclasts of green algae.

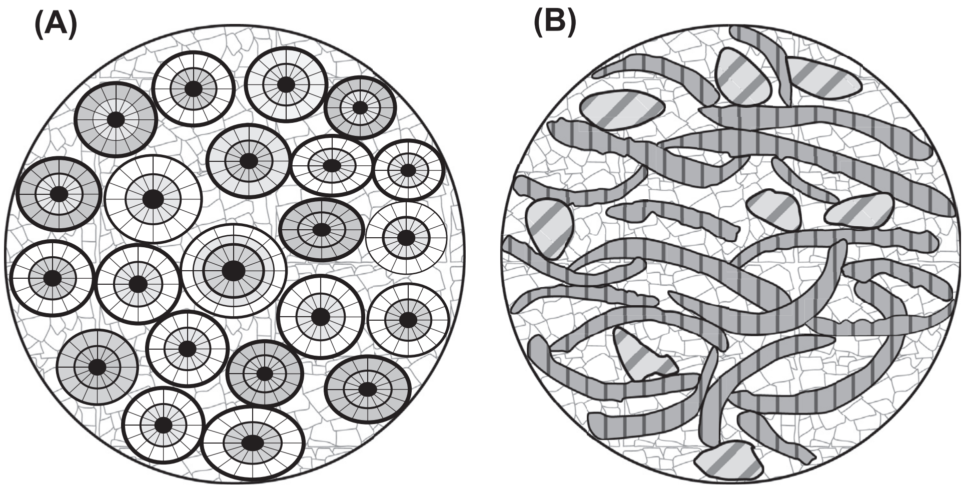

FIGURE 5.57 Greystone types of limestones are characterized by grain support and calcite cement in intergranular pores: (A) greystone-ooid composed of ooids and calcite cement excreted in the intergranular pores, and (B) Bioclastics rudstone contains fragments (bioclasts) >2 mm and cemented with calcite cement.

Dunham classification was updated by the Klovan and Embry (1972) by introducing two new types of rocks: floatstone and rudstone, containing more than 10% of grain diameter >2 mm. Baundstones are divided into three new types: bafflestone, bindstone and framestone, depending on the structure and the manner in which organisms are involved in the formation of these rocks (Fig. 5.55).

Floatstone contains more than 10% of components larger than 2 mm without grain mutual support. Floatstone is analogous to wackestone, but contains grains >2 mm by textural–structural features (Fig. 5.55).

Rudstone and floatstone differs in that the components are >2 mm with grain mutual support and between them calcite cement is extracted making rudstone analogous to greystone that contain more than 10% of grains >2 mm (Figs 5.55 and 5.57(B)).

Bafflestone, bindstone and framestone are special types of baundstone (Fig. 5.55) occur through organisms that catch sediment (bafflestone) organisms to bind themselves to carbonate mud and fine-ground sediment (bindstone or stromatolites), or organisms whose skeletons form the skeletal lattice, such as coral reefs (framestone), as shown in Figs 5.54 and 5.55.

Dunham classification is necessary to use the adjective that defines the dominant type of grain which contains limestone, for example pellet-wackestone (Fig. 5.56(A)), greystone-pellet (Fig. 5.50), skeletal-wackestone (Fig. 5.56(B)) greystone-ooid (Figs 5.51 and 5.57(A)) or bioclastic-rudstone (Fig. 5.57(B)).

5.7.1.3.2. TERRESTRIAL AND FRESHWATER LIMESTONE

Freshwater limestone forms from freshwater and limestone that occurs on land, outside the lakes and rivers, are called terrestrial limestone.

Lacustrine precipitated in lake environment is among the most important petrogenic freshwater limestone. In the lake and river environments, inorganic limestone extraction is a consequence of changes in pressure and/or temperature, and removal of CO_2 from the water due to assimilation processes of plants and/or phytoplankton (such as in Plitvice Lakes, Croatia), evaporation in arid climate areas, or mixing water with different pH, common in rivers and lakes. General textural–structural features of lake limestone are thin lamination and wrapped grain. Large amount of lake limestone of biogenous origin belongs to the freshwater stromatolites formed by capturing and binding of carbonate sediments on the fibers and mucus of cyanobacteria and mosses. Lacustrine limestone often enriched by oncoid and belongs to oncoids group arising by cyanobacteria wrapping of bioclastics or shells of gastropods and rock fragments.

Thin lamination or microlamination of lake limestone manifests as frequent changes of two or three lithological types of very thin lamina. Most common is the two-type rhythmic changes of lamina: carbonate and fine-grained siliciclastic (silt, silt clay, clay or marl). Rhythmic change of three lamina types is often found in the lacustrine limestone: carbonate, siliciclastic and diatomaceous. Such lamination can be identified analyzing the process of formation of "varve" (annual layer of sedimentation/sedimentary rocks). The rhythmic layers are the result of seasonal changes in lake water related depositional processes or periodic changes in the amount of input of finely granulate sediment into the lake during the change of seasons. The amount of excrete carbonate in lake water is directly related to the seasonal changes of water temperature. The water surface of the lake is more heated during the warm seasons (late spring, summer and early autumn). Therefore, the phytoplankton bacteria secrete low-magnesium calcite by the photosynthetic process in the form of tiny crystals (deposition of thin light calcite micrite lamina). The chilly water of the cold seasons (late fall, winter and early spring) is not suitable to excrete carbonates other than small deposition of finely granulate siliciclastic detritus (dust, silt and clay). The lake water provides more luxuriant development of phytoplankton with the increase in the temperature. This causes increased consumption of CO_2 and thus enhances the secretion of $CaCO_3$. The rapid development of diatomaceous flourishing algae and rich diatoms during the spring and early summer can cause increased amounts of deposition of opal skeleton and formation of thin diatomite lamina.

A good example would be that thinly laminated freshwater lake limestone deposits are located in the Sarmatian Pannonian Basin leading to well drilling in many oil fields of eastern Slavonia, Croatia. These rocks record changes in carbonate and clayey lamina bands of thickness between 0.2 and 1.5 mm. Among the grains of biogenous foundation in lake limestone are the most important oncoids incurred through cyanobacteria and green algae in the shallow waves and weak lake water.

Terrestrial limestone includes limestone cover (sinter), travertine, crust limestone and cave limestone or speleothems. Limestone sinters are highly porous, typically soft and form on the waterfalls of rivers and lake by secretion of calcite on moss, cyanobacteria and aquatic plants (Fig. 5.58). This process is particularly intense in the splash of waterfalls. The extraction of $CaCO_3$ due to release of CO_2 from water containing Ca-hydrogen as photosynthetic processes of plants and due to changes in pressure/temperature conditions in the spraying of water or its warming. The famous travertine barriers on waterfalls were formed in this way. The other example is the case of the Plitvice lakes and waterfalls and river Krka and Una, Croatia. These barriers consist of calcite or low-magnesium calcite in the form of irregular masses of limestone mud, micrite cover or shell, secreted on the remains of aquatic plants (moss, grass, fibers of cyanobacteria and branches of trees), as well as in form of sparite crystals that fill the pores of different origin. It also contains small amount of detrite material, mostly quartz grains in size of powder, fine sand, muscovite and clay minerals. It is very common events that thin films or fine carbonate mud (micrite) quickly envelop water plants growing in the river or lake, trees in the water or its branches, fragments of limestone and dolomite, and fragments of destroyed travertine barriers. Micrite shell and irregular masses make irregularly built skeleton or grid barriers, and rapid incrustation occur more or less solid mass from which "grow" travertine barriers.

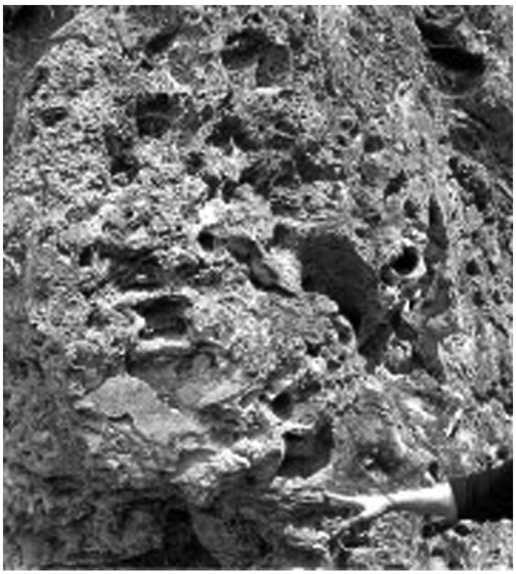

FIGURE 5.58 The limestone travertine: calcite clusters with numerous small and large holes (molds) of now rotten plant remains, Plitvice Lakes, Croatia.

Large porosity of travertine is partly a result of rotting organic tissues of water plants and/or cyanobacteria, and partly they are dissolution cavity or cavities in which there was CO_2 and/or other gases formed by oxidation of organic matter. It is known that limestone barriers on the waterfalls of rivers and lakes occur mainly at temperatures between 10 and 30 °C with the annual accumulation of carbonates by 1–3 cm "growth" of travertine barriers, thus increasing the level of the lake. However, most of the secretion occurs in hot water during the summer months.

Travertine is lithified firm, spongy, cell built, irregularly laminated or layered limestone formed mainly by inorganic calcite secretion from the warm water around thermal springs, geysers, mineral water rich in carbonate and CO_2 or from hot sulfate springs. With high porosity and relatively high hardness, travertine is characterized by different textural–structural features: a thin and irregular lamination, and cell-like material (Fig. 5.59). Travertine deposition is a consequence of secretion of $CaCO_3$ due to inorganic and organic release of CO_2 at raised temperature in relation to the environment at the time of its outbreak to the surface of the Earth in hot springs. Travertine may be of origin in participation of both inorganic also organic processes related to the activity of bacteria that live in a "meadow" and/or bacterial coating on surfaces repeatedly or continuously covered by hot water. Temperatures of thermal water sources from which travertine arises are ranging between 20 and 95 °C. The annual accumulation (portion of "growth" of travertine in hot spring) is quite uneven and varies from a few millimeters to 20 cm. In many cases there is a connection between the deposition of travertine from hot water and volcanic activity, as testified by the frequent association of travertine and volcanites.

Carbonate components occur by inorganic processes are consist of large rhombohedral calcite crystals in the form of sparite cement or

FIGURE 5.59 Firmly lithified spongy, cell-like built travertine originated by calcite secretion from the warm waters around the thermal springs.

calcite crust with thickness up to several centimeters. It also forms pisoids, partially formed biogenic cryptocrystalline lumps and bacterial pisoids composed of calcite crystals in diameter of 0.5–20 μm.

Crusty limestone includes terrestrial limestone rocks known as "caliche" or "calcrete" which occur in semiarid and arid areas with dry climate and annual rainfall between 200 and 600 mm. The evaporation of water from soil is greater than the total annual rainfall. The pore water is saturated in Ca hydrogen, rises to the surface due to strong evaporation and forms calcite in the form of secreted crust clusters, caliche or calcrete. Crusty limestones usually have small thickness of the crust. This is an important indicator of paleoclimatic conditions, interpretation of environment and carbonate deposition and indicator of fine marine sedimentation, or vadose diagenesis or subaerial spending of limestone.

Cave limestone or dripstone is "stalactites" formed around water dripping, saturated in Ca-bicarbonate in the limestone caves and cavern. Cave limestones that grow from the floor upward are called *stalagmites*. Stalactites often join stalagmites to create "stalagmate" (Fig. 5.60). Stalactites grow due to the secretion of

FIGURE 5.60 Stalactite–stalagmite. *Source: University of Missouri.*

calcite from the evaporation of water droplets hanging from the ceiling of a thin film of water that drenched the rock, and the sudden release of CO_2 from the water saturated in Ca-bicarbonate in the moment of impact of water droplets that cap in a cave.

5.7.1.4. Limestone Diagenesis

5.7.1.4.1. DIAGENETIC ZONES AND PROCESSES OF CEMENTIZATION

The solid limestone rock of present day occur by early and late-diagenetic processes/conversion of water saturated primary hard and soft bulk of limestone sludge and grains under specific zones (location) and environmental condition such as the following:

1. Diagenetic processes in marine zone (1 in Fig. 5.61)
2. Diagenetic processes evaporation zone (2 in Fig. 5.61),
3. Diagenetic processes in condition of mixed zone with meteoric and seawater (3 in Fig. 5.61)
4. Diagenetic processes in condition of meteoric and vadose zone (4a and 4b in Fig. 5.61)
5. Diagenetic processes in greater depth overlay (5 in Fig. 5.61).

Diagenetic processes in marine zone occur in sediments that are soaked with seawater at the bottom of the shallow or deeper sea, the tidal flats and shores. In open marine environments or in the marine area, diagenetic processes strongly depend on water depth and, geographical location, and on tidal flats, shores, the most important factor is climate. The temperature and pressure of seawater has great role in the diagenetic process of limestone sediments due to lowering of the warm water from the surface to deeper/cooler parts of the sea/ocean depth. This further modified by photosynthetic processes with the role of marine plants and animals in the content of CO_2 dissolved in water in the form of hydrogen carbonate. The large differences in physical and chemical conditions prevailing in marine diagenetic zone in shallower areas and at depths usually distinguish between two main marine diagenetic zones: shallow-sea diagenetic zone and deep sea diagenetic zone.

Shallow-sea diagenetic zone is the area significant for diagenetic processes of cementization or secretion of fibrous aragonite and Mg-calcite cement in the pores of carbonate deposits.

Deep-sea diagenetic zone is characterized by pore water unsaturated with aragonite. Only the mosaic (blocky) calcite cement secretes with

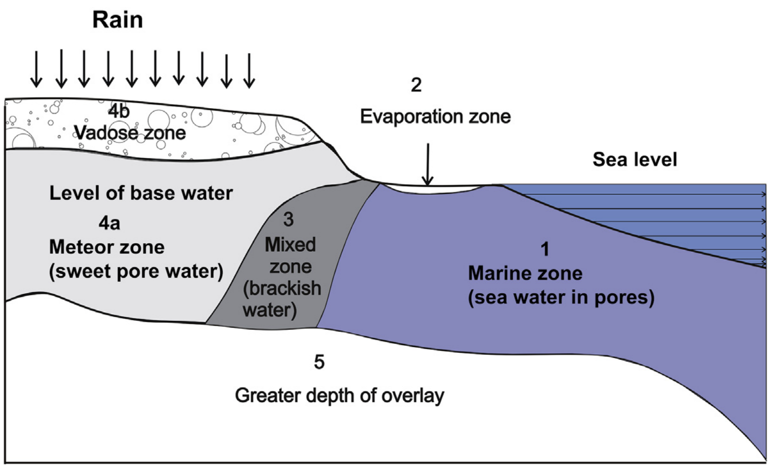

FIGURE 5.61 Schematic diagram of diagenetic zones of carbonate sediments.

the dissolution of aragonite above CCD boundary line. There is no secretion or calcite cement below this line with the dissolution of calcite ingredients. Kohout convection is the circulation of saline groundwater deep within carbonate platforms. In the deep-sea diagenetic zone, very slow process of dolomitization occurs due to thermal convection and saturation of seawater with respect to dolomite (Section 5.7.2.3).

Diagenetic processes occur in evaporation zone when strong evaporation of seawater from the saline or sabkha, and the pores of limestone deposits around in areas with dry, arid climate. In addition to the secretion of aragonite, there is early diagenetic dolomitization (Section 5.7.2.2) and secretions of evaporites minerals say gypsum, anhydrite and halite (Section 5.8.1).

Diagenetic processes in condition of mixed meteoric and marine (brackish) water occur in underground mixed zone where mixing meteoric (rain) sweet and salty seawater. This zone is very variable in shape, spread and geometry in depth and laterally. Depending on the oscillation of sea level, underground mixed zone moves farther from the sea towards the land (relative upper sea level), or from the mainland, extending from the coast towards the sea (relatively lower sea level), which is especially important for dolomitization processes (Section 5.7.2.2 and Fig. 5.67).

Diagenetic processes in meteoric zone (sweet water pore) taking place or in meteoric zone or vadose zone (Fig. 5.61).

Meteoric zone is the region below the basal levels of freshwater, in which deposits are continuously soaked with fresh basic water (Fig. 5.61). There is sweet pore water poor in Mg^{2+} and Na^{+} ions, and generally oversaturated with Ca^{2+} ions, and so is excreted calcite mosaic and "blocky" cements.

Vadose zone is the area above the permanent level of basic freshwater in which the pores in the rock filled with water occasionally during the rainfall and the residual rainwater (Fig. 5.61). Most of the time sediments are in subair conditions, i.e. the pores are either filled with air in the summer and with freshwater in the rainy period. All meteoric (rain) water flow to the sea through the vadose region play key role in the diagenetic process in met-stable carbonate sediments. In areas with heavy rainfall and porous deposit, meteoric water is quickly moving through the surface of the sediment and thereby powerfully dissolves limestone sediments. This process leads to increased concentrations of Ca-hydrogen carbonate, so that evaporation of rainwater in dry periods during the porous carbonate deposits, leads to secretion of calcite in the form of microstalactite calcite, or mosaic cement as well as secretion of vadose ooids.

5.7.1.4.2. DIAGENETIC PROCESSES AT GREATER DEPTHS OF COVERING

Diagenetic processes in deposit located at greater depth are covered with new thicker sediments (Fig. 5.61) and no longer operate diagenetic processes appropriate for surface and subsurface conditions. The depth of the overlay is not yet enough to act metamorphic processes (depth $>5500-6600$ m). This diagenetic area is interrupted by free exchange of fluid and chemically active atmospheric gases, particularly oxygen and CO_2, and progressively increasing the temperature and pressure. The porosity decreases drastically by compaction processes and significantly reduces the ability to change fluids. Pore fluids have already suffered changes in the composition because of the interaction and mixing of ions contained in the original pore water and fluids originating from the surrounding sediments, particularly those related to compaction flow. The water squeezes in the compaction of deposit. Porosity reducing of limestone deposits is the most significant result of diagenesis at greater depths of covering, and as a result of mechanical and chemical compaction (pressure melting) and cementization as a result of drainage sparite Druze calcite cement.

Compaction includes processes of mechanical compaction, squeezing water and chemical compaction related to pressure dissolution and formation of "stilolite" (serrated surface). Mechanical compaction and squeezing of water have a significant impact only in the mud, deep water carbonate deposit, especially pelagic mud and chalky deposit (Fig. 5.62).

Pelagic mud and chalky deposit i.e. deposits which contain scaffolding of the sea or planktonic organisms, have high primary total porosity (~80%) of which intergranular porosity accounts for ~35% after deposition. The porosity is reduced to ~65% and less, due to the rapid redeployment of squeezing water, reduction of isometric keletal grain size, mechanical reorganization of grains and change of the structure of deposits, at a depth 50 m of covering. At depths between 50 and 200 m began breaking the grain, and at depths >300 m pressure melting processes. The porosity of pelagic mud gradually further reduces (Fig. 5.62).

Shelf carbonate mud (Fig. 5.62) has significantly different compaction in pelagic mud. It mainly consists of elongated particles and needle-like, not isometric, shape, whereby the needles of aragonite act bipolar bind water molecules. The structure of carbonate mud looks like "honeycomb" or "structure of the house of cards" clay deposits. The effects of squeezing the water reduce considerably higher than those at pelagic mud. The primary total porosity of ~70% reduces to ~40% after restructuring of needle particles in the horizontal position at a depth of 100 m and then do not change until the beginning of the process of pressure melting at ~300 m depth (Fig. 5.62).

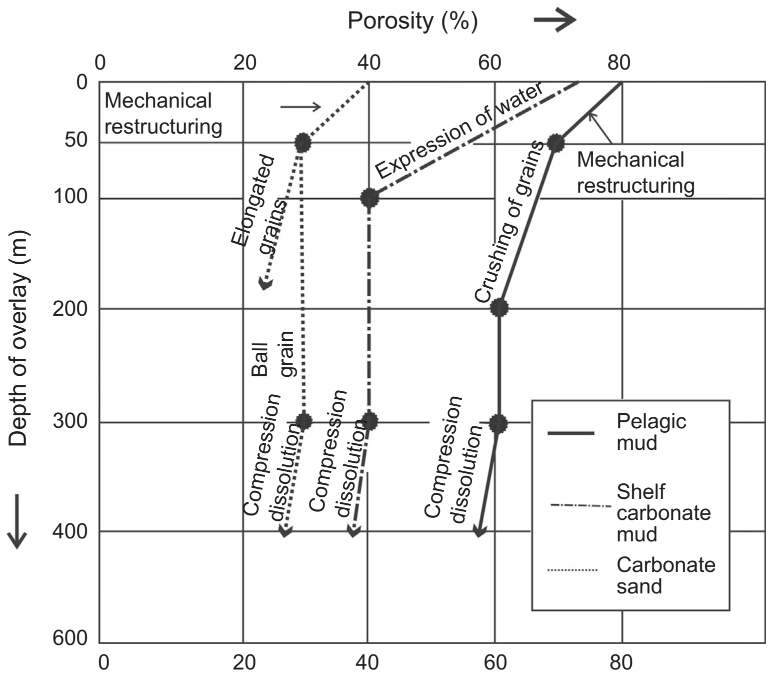

FIGURE 5.62 Diagrams of changes in porosity with increasing depth of the overlay with schematic representation of the main processes that lead to changes in the pelagic chalky mud and deposit, shelf carbonate mud and ooid, peloid and bioclastics limestone sands. *Source: Modified after Scholle*[40]*; Enoch and Sawatsky.*[16]

Carbonate sands have grain support. After cementization greystone types of limestone, characterized by significantly different effects of mechanical compaction and squeezing of water from pelagic mud and shelf carbonate mud (Fig. 5.62). Primary intergranular porosity of ooid or peloid sands is less than previously stated mud and chalky sludge due to sphere grain shape. There will be stronger decrease of porosity in the first 50 m depth of the overlay. The original 40% will reduce to 30% (Fig. 5.62) due to redeployment of spherical grains of unstable rhombohedral, more porous in stable, less porous cubic grain packing. The pressure melting starts at the grain contacts to about 300 m depth (Fig. 5.62).

Chemical compaction includes processes of pressure melting on contact with the formation of stilolite at depths of covering of few hundreds to a thousand or more meters. Stilolitization significantly reduce the porosity and the total thickness of limestone deposits.

Cementization at greater depths of covering in the limestone sediments are mainly down to the secretion of coarse crystal calcite cement and/or iron dolomite (baroque dolomite). Baroque iron dolomite typically contains 15 or more molar percent $FeCO_3$, and occurs with the participation of hydrocarbons at greater depths of covering at temperatures between 60 and 150 °C or fills voids or mineral substance that suppresses the surrounding carbonates in the rock.

5.7.1.4.3. ISOCHEMICAL AND ALLOCHEMICAL DIAGENETIC PROCESSES

Isochemical diagenetic processes in limestone do not lead to changes in chemical composition of limestone, but change only their porosity and structure. The most critical multifunctional mechanisms are dissolution of some mineral substances (halite and aragonite), transformation of aragonite and magnesium calcite in calcite, secretion of aragonite or calcite cement in the pores (cementization summarized in Sections 5.7.1.4.1 and 5.7.1.4.2), bioerosion, micritization of carbonate grains and activity organisms (endolithic) that drill foundation on which they grow and recrystallization of limestone sludge (micrite) and microcrystalline calcite in microcrystalline and/or macrocrystalline calcite or conversion of limestone type mudstone, wackestone and floatstone in crystalline limestone (Section 5.7.1.3; Fig. 5.55).

Allochemical diagenetic processes in limestone lead to changes in chemical composition of limestone and limestone deposits by circulation of pores solutions that bring into some other chemical compounds and anions (such as Mg^{2+} and Si^{4+} cations and SO_4^{2-} anion, and borrowing Ca^{2+} and CO_3^{2-}). Most significant allochemical diagenetic processes in limestone are silicification, anhydratization and dolomitization.

Silicification is an allochemical diagenetic process in which solution enriched with Si-ions, usually in the form of silicic acid (H_4SiO_4) in carbonate rocks suppress calcite, aragonite and dolomite with opal, chalcedony or low-temperature quartz, meaning, silicon hydroxides or oxides, and dissolved carbonates taking in the form of Ca-hydrogen carbonate. Like other allochemical diagenetic processes, silicification may induce another untied and unlithified deposit at the early diagenetic stage, or already rigid and solid rock is replaced during late-diagenetic silicification. Silicification processes in limestone generates autogenous quartz, opal or chalcedony in the form of single crystals or crystal aggregates, and nodule, lump, lenticular or implants of hornfels.

Anhydratization in carbonate rocks may be the process or forcing early diagenetic carbonate or anhydrite deposits, suppression of carbonate minerals in the solid limestone or dolomite anhydrite during late-diagenetic process, and secretion of anhydrite in the pores, cavities and veins of limestone, dolomite and other rocks in the circulation of pores solution containing sulfate. Sulfate ions-rich solutions usually originate from tidal saline (sabkha), or salt ponds or lakes left in the recesses by tidal environment after the withdrawal of the sea. Early diagenetic anhydratization in such environments requires strong evaporation with increasing temperature and a permanent increase in salinity ("sabkha-conditions"). Late-diagenetic anhydratization occurs during circulation of pores water containing SO_4^{2-}-ions through the rigid carbonate rocks, with the suppression of carbon compounds anhydrite. Such suppression will be of unequal intensity, irregular, and often in the rock selectively anhydratizationed only some components, while others remain largely fully preserved. In late-diagenetic anhydratization with large anhydrite crystals in limestone are usually found numerous tectonic venation, cavities and pores filled with anhydrite crystal aggregates as a result of secretion of anhydrite from solution that are circulated in these rocks.

Dolomitization is the most important and common allochemical diagenetic process that engages the limestone deposits and limestone, and turning them into dolomitic limestone or dolostone or simply dolomite. Dolomitization is a process by which dolomite is formed when magnesium ions replace calcium ions in calcite. It involves substantial amount of recrystallization.

Limestone enjoys major shares of sedimentary rocks in the Earth's crust. It is easily identifiable due to softness, color, texture and instant effervescences with hydrochloric acid (HCl). The natural landscape of limestone gives an excellent panorama in the country sides (Fig. 5.63).

Limestone is readily available, relatively easy to cut into blocks/carving and long lasting. Limestone is very common in architecture and sculpture across the World (to name a few Great Pyramid, Egypt, Courthouse building, Manhattan, USA, Golden Fort, India), historical monuments and buildings. It is the primary raw material for the manufacture of quicklime (calcium oxide), slaked like (calcium hydroxide), cement and mortar, as flux in the blast furnace in iron industry, soil conditioner, aggregate, glass making, paper, plastics, paint, tooth paste, medicines and cosmetics. The fossil bearing (cyanobacteria algae, skeletons and shells) limestones are potential sources of phosphate, petroleum and gas.

5.7.2. Dolomites

Dolomite is a carbonate mineral composed of calcium magnesium carbonate [$CaMg(CO_3)_2$]

FIGURE 5.63 High N–S trending low-dip hills at the east bank of river Nile stands for an vast resource of commercial quality limestone (top of the picture). The river cruse near Esna town, Egypt, presents a typical landscape with luxuriant growth of date palm trees in the middle and the flowing Nile water in the foreground.

FIGURE 5.64 Massive dolomites, sedimentary carbonate rock hosting zinc–lead mineralization from Zawar Mine, Rajasthan, India. The brownish yellow color in the top right hand of the specimen indicates sphalerite (ZnS) minerals.

(Fig. 5.64). The term is also used to describe the sedimentary carbonate rock "dolostone/dolomite rock" predominantly composed of the mineral dolomite ≥50% magnesium.

5.7.2.1. *The Origin of Dolomite*

Dolomites are carbonate rocks mainly composed of the mineral dolomite. The mineral is stable in seawater in nature and not known examples of its direct extraction from seawater in large quantities required for origin of dolomite rocks. Dolomite occurs by suppression of aragonite or calcite, i.e. dolomitization process. Dolomitization occurs in nature or even in untied limestone deposit or in already solid limestone rocks. Dolomites that occur in the untied deposit are called early diagenetic or sin-sedimentary. It also forms by dolomitization of limestone as late-diagenetic or postsedimentary events.

The origin of large amounts of dolomite is by suppression of calcite or aragonite through direct secretion from the seawater as consequence of the strong hydration of Mg-ions. The tendency Mg-ions is to be dissolved in seawater, and not in the crystallized state. Mineral dolomite is a two salt of Ca-carbonate and Mg-carbonate with a crystal lattice in which the properly sorted layers of $CaCO_3$ of calcite structure and layers of $MgCO_3$. The main obstacle for producing minerals dolomite from seawater requires complex arrangement of its crystal lattice with respect to calcite crystal lattice, aragonite and high-magnesium calcite due to much easier excretion from seawater than dolomite. The dolomitization in normal seawater may occur as special cases (Section 5.7.2.3).

The process of transforming calcite or aragonite to dolomite by bringing in Mg-ions can be shown by the following chemical reaction. The calcite (or limestone) joins Mg-ion in solution and removes free Ca-ion:

$$\underset{\text{calcite}}{2CaCO_3} + Mg^{2+} \longrightarrow \underset{\text{dolomite}}{CaMg(CO_3)_2} + Ca^{2+}$$

The process of dolomitization by this reaction can be achieved only in the presence of solvent, that adds Mg-ions to the new formed rock, and excludes free-Ca ions. In nature, dolomitization is actually happening by the following:

1. Bringing in Mg-ion
2. Releasing of carbonate anions CO_3^{2-}
3. Consumption of all available Ca-ions and not needed thereafter to remove Ca-ions from calcite or aragonite.

It is a process of dolomitization according to the following reaction and equation:

$$\underset{\text{calcite}}{CaCO_3} + Mg^{2+} + CO_3{}^{2-} \longrightarrow \underset{\text{dolomite}}{CaMg(CO_3)_2}$$

Sea, as freshwater, may be saturated with respect to dolomite and calcite. Mixed marine and freshwater (5–50% seawater) is unsaturated with respect to calcite and saturated with respect to dolomite. Dolomitization is suitable with pore solution of mixed groundwater zone, if they include a mixture of freshwater with 5–50% seawater. Dolomitization is particularly intense in the sabkha conditions, if the molar ratio of Mg/Ca compared to that in normal seawater that amounts to 5.26, strongly increased at ~10−30 (Section 5.7.2.2).

5.7.2.2. *Early Diagenetic Dolomites*

Early diagenetic dolomitization or singenetic/sin-sedimentary origin of dolomite occurs, as shown by numerous studies of recent examples, in untied deposit in the following:

1. Supratidal zone, the coastal saline (sabkha conditions) and salt lakes
2. In the zone of mixed marine and freshwater.

Early diagenetic dolomitization in supratidal zone is possible, in case, the limestone deposit is drenched with seawater during high tidal waves and in coastal saline (sabkha) and salt lakes with strong evaporation of residual sea/salt water. Early diagenetic dolomitization also occur at annual temperature of >30 °C, as well as an increase of molar Mg/Ca ratio in pore water or saline water between 15 and 30, as opposed to 5.26 in normal seawater. There is no early diagenetic dolomitization of only sedimented carbonate deposits on the bottom of the sea at normal or slightly elevated salinity and normal temperature of seawater.

In cases of early diagenetic dolomitization in sabkha conditions key factor is the evaporation of seawater at high tides and storm waves soaking carbonate deposit or evaporation of water that is lost in the recesses of high-tide zone in the form of salt lakes, saline and sabkha.

Dolomitization in the zone of mixed marine and freshwater may occur in early diagenetic or transitional stage from early to late stage diagenetic and even in late-diagenetic stage. This process of dolomitization is based on the fact that dolomite easily takes place from a mixture of marine and meteoric freshwater than from the sea or freshwater. Dolomitization in the mixed zone of marine and freshwater (brackish) will particularly be intense when the mixture contains between 5% and 50% seawater. The water mixed with a ratio of 5−50% seawater and 95−50% of meteoric water is oversaturated with dolomite, and unsaturated compared to calcite, which allows the formation of dolomite at the expense of calcite.

Dolomitization in the zone of mixed marine and freshwater begins in early diagenetic phase and the deposition lasts for a few hundred thousand years (>200,000 years), as the process is very slow. The mixed zone of seawater and freshwater, during an extensive period of time, moves simultaneously with the lowering or rising of sea level. Dolomitization will be weaker or stronger be affected large parts of coastal limestone deposits in the case of lowering of sea level (Fig. 5.65).

Early diagenetic dolomites are characterized by all the textural−structural features and layer forms as of original deposit. There are pellet, oncoid, micrite and intraclastic dolomite often with desiccation cracks or traces of erosion on the upper surfaces caused by storm tides and waves. The early diagenetic process will dolomitize all existing soft limestone sediment to a certain depth. These are, in general, pure dolomite rock without undolomitized remains, relics of limestone and contain small dolomite crystals, typically <0.01 mm. The early diagenetic dolomitization occurs specifically at a relatively high concentration of solutions that are near saturation or saturated with respect to dolomite. The process also begins to crystallize many crystals covering all the ingredients of limestone deposits, regardless of the primary mineral composition, crystal size and primary structural components (Fig. 5.66). Early diagenetic dolomitization completely transforms all the ingredients of limestone deposits to cryptocrystalline dolomite.

5.7.2.3. *Late-Diagenetic Dolomite*

Late-diagenetic or postsedimentary dolomite occurs by dolomitization of limestone with circulation of pore water and cold seawater, the source of Mg-ions, through the permeable limestone, at greater depths in groundwater zone of mixed freshwater and seawater. In late-diagenetic

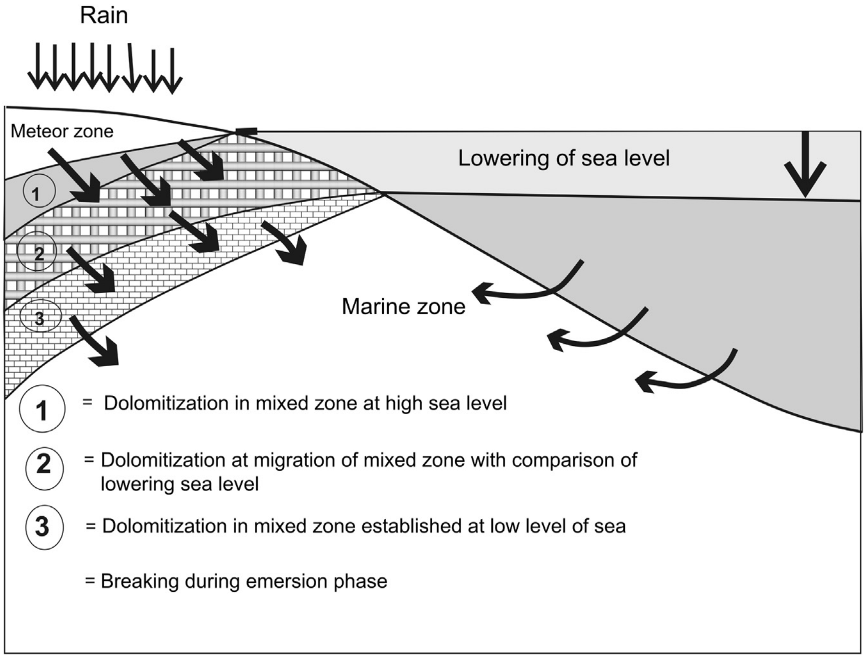

FIGURE 5.65 Dolomitization in a mixed zone of marine and freshwater in wet conditions (humid) climate with migration of mixed zone in the direction of the sea due to the relative lowering of sea level.

dolomitization at greater depth of covering the main problem is insufficient flow or circulation of pore water and bringing of Mg-ions from large distances. In late-diagenetic conditions, 35,000 m^3 of pore water at 80 °C temperature with the usual medium composition (molar ratio Mg/Ca = 0.25 and magnesium concentrations of 0.1−1000 mol of water) is required to fully dolomitize 1 m^3 of limestone. Such circulation of pore water in limestone can be achieved only through a very long time, during the whole geological periods. Dolomitization at greater depth of overlay occurs with the presence of fluid pores at relatively high temperatures (ranging between 60 and 160 °C) and very variable chemical properties during the entire process of dolomitization.

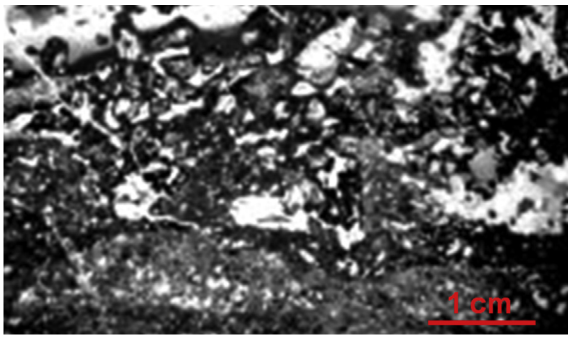

FIGURE 5.66 Microscopic glass slide of early diagenetic stromatolite dolomite, characterized by cryptocrystalline structure—dolomite crystals <0.004 mm (dark), and fenestra filled with microcrystalline dolomite cement (white) from Upper Triassic formation, Medvednica Mountain, central Croatia.

As the concentration of Mg-ions in the pore water is very low, full dolomitization of limestone will require large amounts of pores water flowing over long time. Growth of dolomite crystals is slow and starts start with small number of crystallization embryos followed by large

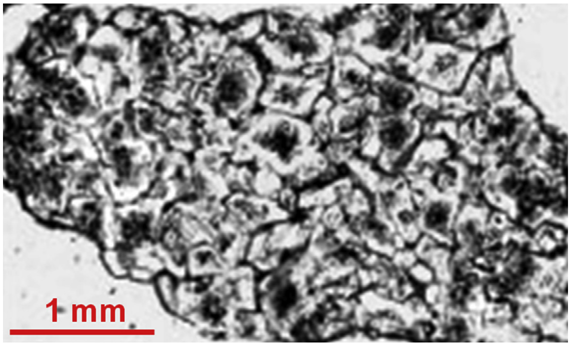

FIGURE 5.67 Late-diagenetic dolomites with macrocrystalline mosaic structure hypidiotype to idiotype dolomite crystals which in the center contains zonic distributed impurities of kerogen, from Wells Jaddua-1, Syria between depth of 450 and 460 m.

crystals (0.1–0.4 mm) with idiomorphic contours (Fig. 5.67). The result of such dolomitization is a complete change of texture–structural features of limestones and origin of dolomite rocks with macrocrystalline or microcrystalline idiotype or hypidiotype mosaic dolomite structure. Late-diagenetic dolomite texture and structure are significantly different from early diagenetic dolomite.

Limestones are dolomitized with different intensity, from place to place, due to different permeability, capillary force and the degree of tectonic cracks of certain parts of limestone layers affected by late-diagenetic dolomitization level of pore waters with variable intensity of circulation. The proportion of dolomite usually decreases from the center toward the edges of dolomite body with undolomitized remains of limestone.

Kohout (thermal) convection model flow of seawater is probably the most significant factor in late-diagenetic dolomitization of limestone at greater depths of overlay in the area of marine carbonate slopes. It is known that water in the special physical and chemical conditions can circulate through the limestone slopes of subsea carbonate by mechanism called by the author as "Kohout thermal convection". Kohout (1967) found that cold seawater from large depth may, due to convection or transfer of heat, flow and penetrate in the limestone on the outskirts of carbonate slopes containing basic water of higher temperature than the water temperature from the depths of the sea. Cold seawater is unsaturated with high magnesium calcite and aragonite, but oversaturated with dolomite, and secretion is possible from dolomite. Dolomitization by Kohout convection model is very slow and geologic time-consuming process.

2. Evaporite sediment and sedimentary rocks

5.7.3. Evaporites

Evaporite sediments or evaporites are sediments and rocks created by chemical secretion from extremely concentrated natural solution (saline) by strong evaporation of water. Evaporite deposits start forming from the edges of salt lakes in the coastal saline (sabkha), enclosed lagoons and bays in areas with arid, i.e. dry and hot climate. It is necessary to boost faster rate of evaporation of water flow in order to constantly increase the concentration of salt in water. The common examples of evaporites deposition are gypsum, anhydrite, halite and K–Mg salts (polyhalite, silvine, kizerite and karnalite).

5.7.3.1. Mineral Composition, Origin and Classification of Evaporites Rocks

In the initial stages of evaporation and concentration of seawater, that allows the secretion of Ca-carbonate in the form of aragonite, high-magnesium calcite or calcite and ends with dolomite. The dolomite then suppresses the Ca-carbonates, as explained in Section 5.7.2.2. The salt concentration increases to about 3.5 times with the succeeding evaporation of water and the salinity of seawater rises to approximately 120%. The mineral gypsum begins to crystallize at this stage at a temperature of 30 °C and continues until the concentration of salt in water does not grow to 4.8 times higher than in normal seawater salinity (Table 5.6). The secretion of

TABLE 5.6 Limit Values Necessary to Increase the Concentration of Seawater at 30 °C for Extraction of Minerals Evaporites

Mineral Excreted	Increase in the Concentration of Seawater
Calcite, aragonite, dolomite	To 3.5 times
Gypsum	3.5–4.8 times
Anhydrite	4.8–9.5 times
Halite	9.5–11 times
K–Mg salt	>60 times

Source: Ref. 16.

anhydrite commences above this concentration at temperature of 30 °C. Necessary increase of concentration in relation to the normal concentration of seawater and the sequence of secretion of singular evaporite minerals at a temperature of 30 °C displays in Table 5.6.

The secretion of Ca-sulfates (gypsum and anhydrite) can take place from solutions of small concentration at temperatures much higher than 30 °C. Gypsum, for example, is excreted at a temperature of 58 °C from the water with normal salinity, and anhydrite secretes much above that temperature. On the other hand, gypsum and anhydrite can secrete at lower temperatures, if solutions have a high salinity. For example, anhydrite begins to exude at a temperature of 60 °C from seawater with normal concentration. The same secretion begins at 20 °C from the water with 7 times higher concentrations at arid saline or sabkha. The secretion of anhydrite, gypsum, halite and K–Mg salt is directly dependent on temperature and salinity of water. Normal salinity requires high temperature, and with increasing salinity the secretion of evaporites is possible at lower temperatures, especially in saline or sabkha and salt lakes.

Gypsum, anhydrite and halite evaporite sedimentary rocks can be found much more likely than evaporites rocks containing K–Mg salt.

Gypsum is excreted in the closed shallow seawater and salt lakes in the initial stages of drying sabkha. The initial salinity might not reach the concentration suitable for the secretion of anhydrite (Table 5.6). The extract of gypsum or anhydrite depends primarily on the concentration (salinity) of water and environments in shallow-sea water or protected shallow or salt lake, and evaporites sabkha conditions.

Anhydrite (sabkha anhydrite) is excreted in large amounts in association with early diagenetic dolomite in coastal saline or sabkha at temperatures of about 25–35 °C in conditions of dry climate and strong evaporation of water, which significantly increased the concentration of Ca-sulfate and salinity at approximately 4–7 times higher than normal salinity of seawater.

Halite (rock salt, Fig. 1.9) is excreted mostly in close marine shallow waters, saline (sabkha) and occasional salt lakes which during dry periods left without water in the form of layered cyclic sequence. Such sequences often destroyed completely by diapirism, which are very prone to salt deposits. In diapirism, by plastic injection in roof sediments a significant part of the salts can dissolve. In subaquatic conditions, i.e. the closed shallow sea and salt lakes, salt crystals in evaporation grow, at the surface of water, particularly intense at the contact water-sediment and within the sediment due to the relatively slow growth of crystals and slightly elevated salinity, resulting in large crystals of halite.

Diapirism is an anticlinal fold or sedimentary layers in which a mobile core, such as, salt or gypsum, has pierced through the more brittle overlying rocks.

The primary porosity in the salt sediments is directly dependent on the dimensions of the crystal and place of their origin. Mechanical compaction can be very different compared to the thickness of salt deposits as it depends on the pore waters and the waters in surrounding sediments outside evaporite deposits. Migration of highly concentrated fluid from the salt deposits in the water layer or from the water in the residue can cause dolomitization of limestone deposits, and cementing early diagenetic salt and other deposits in the form of extraction of gypsum, anhydrite and calcite. In such cementation primary textural–structural features of evaporites deposits may preserved very well, such as lamination, nodule, stratification, and so on.

From the standpoint of geology and petroleum the evaporite complexes, especially halite and gypsum deposits, are excellent insulator rocks beneath which often found significant amount of oil and gas accumulation.

5.7.3.2. Petrology and Diagenesis of Evaporite Sediments

The common textural and structural feature of the sabkha anhydrite is nodular configuration or nodular anhydrite, thicker and/or thinner concentric layers, lamina, or just thin layers of dolomite. Anhydrite within nodule consists of different oriented, elongated to needle crystals (acicular anhydrite). Relationship of anhydrite and dolomite in nodular anhydrite depends on salinity, temperature and strength of water evaporation in saline, as well as the duration of sabkha conditions and the content of sulfate in saline water. Extraordinary examples of sabkha cycles with nodular sabkha anhydrite are found in deep exploratory oil wells anhydrite–carbonate complexes in the Long Island district, Croatia. Upper Permian evaporites and associated carbonates and the fine-ground clasts of central part of the Dinarides (central and northern Dalmatia, Croatia and north-western Bosnia) belong to the regressive sedimentary system with evaporation conditions of coastal sabkha and peritidal environment.

Playa are the coastal salt lakes that remain with very little water or without during dry periods in the peritidal environment zone. The tides and ebb, and coastal sabkha salt water are lost in the recesses of high-tide zone (Fig. 5.70). Such environments are found along border parts of the sea in younger Perm (geological period of <265–251 million years). The level of sea gradually declines with regressive tendency, and the continental environments of clastic Playa and evaporite coastal environment progress in shallow-sea sedimentary area. While the clastic rocks (Fig. 5.68) precipitate in the environment of front beach and/or playa to the salt lakes, the community of carbonate and evaporites (anhydrite, which on the surface is hydrated in early diagenetic gypsum and dolomite) is created in the coastal sabkha and supratidal zones in condition of permanent relative lowering of the sea levels and shrinking of the sea area (Fig. 5.68).

Most of the anhydrite arises directly in the sabkha conditions and part of the anhydrite can come from dehydration of gypsum in sabkha cycles that originated in the tidal zones (intertidal) or in the initial stages of drying sabkha. Large amount of gypsum arising in underwater conditions could be dehydrated in anhydrite. These anhydrites have pseudomorph based on gypsum, and often preserve beautiful contours of gypsum crystals. Dehydration of gypsum to anhydrite is reversible process that can be shown by the following reversible reaction:

$$\underset{\text{gypsum}}{CaSO_4 \cdot 2H_2O} \leftrightarrow \underset{\text{anhydrite}}{CaSO_4} + \underset{\text{water}}{2H_2O}$$

$$\xrightarrow[\text{increase in temperature and salinity}]{}$$

Gypsum dehydration takes place at increase of salinity and temperature, and hydration of anhydrite at reduced salinity and temperature. Anhydrite occurs on the surface of Earth in arid hypersalted, and gypsum in the colder and less salty environments. If the gypsum came under the influence of hypersalted fluid its

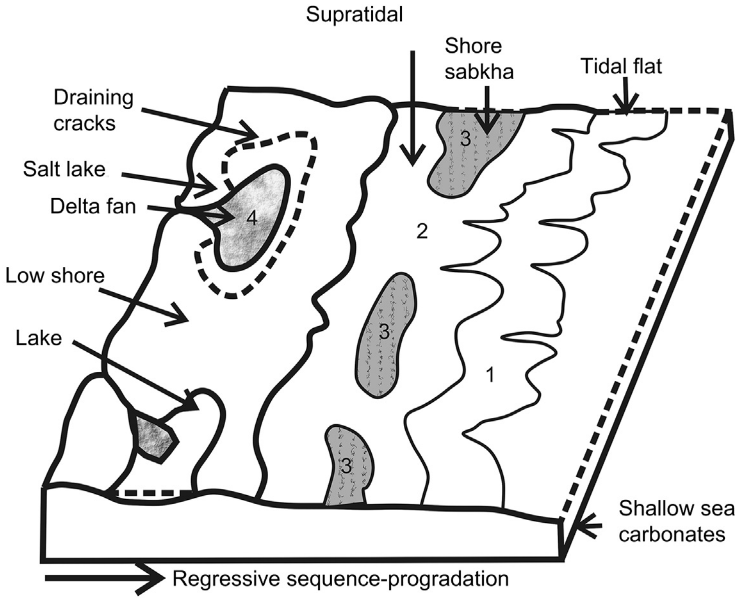

FIGURE 5.68 Environment of deposition of calcareous–evaporite complex in central Dalmatia: (1) tidal zone or intertidal environment with the deposition of limestone, (2) supratidal zones or supratidal environment with coastal sabkha, (3) early diagenetic dolomites and evaporites (evaporite-dolomite facies) and (4) salt lake in which deposit fine-ground and gypsum crystals.

conversion into anhydrite occurs at temperatures between 25 and 45 °C and the depths of the overlay of 1–2 m. The pore or meteor water, under the influence of average salinity of pore fluid and the geothermic gradient of 1 °C in each 33 m depth and if the temperature rises from ~20 °C on the surface to ~50–60 °C at depth of the overlay of >1 km, gypsum goes into anhydrite by dehydration. The relics of gypsum crystals are often preserved in the newly created anhydrite. On the other hand, under the action of pore and meteor water at normal salinity at depths cover of <1 km the anhydrite hydrates to gypsum increasing its volume by about 38%.

The conversion of gypsum to anhydrite causes other diagenetic effects at greater depths, especially melting, cementing, dolomitization and anhydratization, secretion of secondary anhydrite in cracks, tectonic cracks, cavern and melt holes in limestones and dolomites. These anhydrites and rocks in which they appear do not belong to evaporates, or be considered evaporite deposits.

Hydration of anhydrite into gypsum usually begins along cracks of cleavage anhydrite crystals and along tectonic crushed and fissured zones in the form of veins microcrystalline and macrocrystalline aggregate of gypsum or fibrous gypsum cluster.

At a higher degree of hydration of anhydrite to gypsum, larger crystals of newly created gypsum fit relic anhydrite or centripetal push anhydrite crystals. Homogeneous, fibrous gypsum occurs at complete hydration of anhydrite, which contains the remains of a rare anhydrite. Hydration of anhydrite to gypsum depends on the reduction of temperature and salinity of pore water contained in evaporates, especially by long effect of fresh rainwater on anhydrite surface. This process is particularly intense in tectonically fissured and crushed anhydrite, as

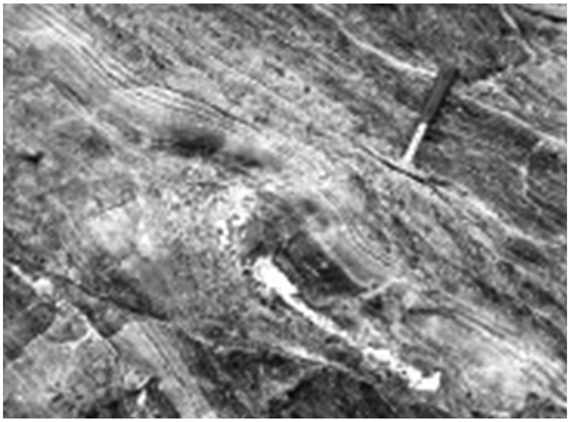

FIGURE 5.69 Gypsum with laminae and layers of early diagenetic dolomite rich in organic matter (black). Gypsum appears only in the surface of the evaporite complex, where it is originated by hydration from anhydrite.

it is the case of the upper Permian evaporites surrounding of Sinj and Knin, Croatia (Fig. 5.69).

Hydration process of anhydrite to gypsum and dehydration of gypsum in the anhydrite can be in the same rocks frequently repeated. While the thin lamina of early diagenetic dolomite, and organic matter in evaporites, due to repeated expansion and contraction, forming terminates or pleated lamina, nests and bent strips (Fig. 5.51). That is so-called enterolithic folding like tectonic folding, which are often interpreted like it. Although it is similar to tectonic deformation, it is not due to tectonics, but recrystallization and chemical changes in the volume of Ca-sulfate for shrinkage and expansion during hydration and dehydration, reversible transitions anhydrite in gypsum and gypsum in anhydrite.

The volume of evaporite rocks increases during hydration of anhydrite to gypsum by about 38%, which is accompanied by strong stresses and diapirism, injecting gypsum into the surrounding rocks, usually in the roof of evaporites. In the process enterolithic folding occurs on account of significant differences in the degree of plasticity of gypsum or lamina in dolomite which contain sabkha anhydrite, and typically leads to cracking or complete destruction of thick dolomitic lamina. In this way, along with actual tectonic crushing, result in dolomitic-gypsum breccias composed of fragments of dolomite and gypsum binder or matrix. The share of dolomite in the sabkha anhydrite is considerably smaller than the share of what was originally, because it is suppressed by early diagenetic anhydratization processes already in sabkha, and also in the hydration and dehydration processes in enterolithic folding and diapirism. Diapirism is mainly moving plastic gypsum and dolomite remains.

3. Silicon sediment and sedimentary rocks

5.7.4. Siliceous Sediments and Rocks

Silicon sediment and sedimentary rocks are composed of autogenous non-detrite silicon oxides or oxides with water. Siliceous rocks are composed of opal-A, cristobalite or opal-CT, chalcedony, quartzite and cryptocrystalline or microcrystalline quartz, which are in biochemical or inorganic chemical processes extracted from aqueous solutions enriched in silicic acid, H_4SiO_4. They can occur by deposition of opal skeletons and inorganic secretion of these minerals in solution containing silica acid. In chemical secretion silicon minerals suppress the original minerals in deposits and rocks in the process of silicification. This leads to silicified limestones, dolomites and tuffs, as well as nodule, lenses and lumps of chert in carbonate rocks.

5.7.4.1. Mineral Composition, Origin and Classification of Silicon Sediments and Sedimentary Rocks

Opal-A and opal-CT are primary constituent of the silicon sediments, and the silicon rocks have in addition of quartzite, quartz and chalcedony.

Opal ($SiO_2 \cdot nH_2O$) is an amorphous mineral flint, mixture of amorphous SiO_2 and opal-CT, i.e. cryptocrystalline cristobalite with 8−10% of water. In silicon sediments occurs or as an ingredient of opal skeletal diatoms, radiolaria and spiculae sponges diatom (biogenic opal or opal-A) or its origin is related to processes of surface-silicification as well as processes of early diagenetic and late-diagenetic silicification of deposits or solid rocks, with the participation of solutions enriched in silicic acid (H_4SiO_4).

Besides biogenous origin (opal-A of which are built houses of radiolaria and diatoms or needles of diatom sponge) and diagenetic origin (as a product of secretion of aqueous solutions of the normal temperature), opal may be hydrothermal in origin (as a product of secretion from the hot solution), as for example, in the case for geyserite.

Low-temperature cristobalite or opal-CT is a low temperature tetragonal modification of SiO_2, stable below 270 °C which is generated in silicon sediments during diagenesis by transformation from opal-A, i.e. opal skeleton. This transformation occurs in a mild increase of temperature at depths of covering a few hundred meters. Thus, opal-CT is a transitional structural form between biogenous opal (opal-A) and quartz.

Quartzite is cryptocrystalline short-fiber variety of incompletely recrystallized of chalcedony into quartz whose fibers are elongated in direction of crystallographic axis c. It occurs by recrystallization in diagenetic processes from opal-A, mainly in the recrystallization of radiolarian shells, in the presence of pore fluid saturated with quartz and rich in magnesium and sulfate. It also occurs in association with elongated fibrous chalcedony which is difficult to distinguish in micrographic thin section.

Quartz in silicon sediments, especially in layered and striped chert, appears in the form of microcrystalline and cryptocrystalline isometric clusters, and in flint in the form of dense cryptocrystalline clusters. Quartz is found in the silicon sediments made by silicification of carbonate sediments and rocks (chert concretions, nodules, bumps and lenticulares):

1. As microquartz in the form of isometric idiomorphic, mosaic crystals of diameter <35 μm, which intrude into each other, and often contain many small impurities.
2. As megaquartz in the form of mosaic equidimensional crystals of diameter from 50 to 300 μm.

Chalcedony is microcrystalline fibrous variety of quartz with small shares of water (1−2% H_2O probably built in the form of SiOH layers). Chalcedony fibers occur in parallel with each other or radially arranged ball, kidney or irregular clusters. Chalcedony is found also in the form of veins, and botryoidal mass within cherts.

The criteria for the classification of silicon sediments and silicon rocks are based on organic or inorganic origin, degree of lithification, diagenetic change and the textural and structural characteristics (Table 5.7).

5.7.4.2. Siliceous Sediments and Siliceous Rocks of Biogenic Foundation

The most important organisms and its opal skeletons that participate in the formation of siliceous sediments are diatoms, radiolarians, spicule of sponge and silicoflagellate. In the group of biogenic silicon sedimentary rocks (Table 5.7) of petrographic important sediments are diatomaceous, radiolarian and spicule muds as loose deposits, and diatomaceous and radiolarian earth and porous spiculite as weak lithificated and porous rocks, and as firmly lithificated, thick rocks without porosity: diatomite, radiolarite and spiculite.

Diatomaceous mud, diatomaceous earth and diatomite are silicon sediments mostly built of skeleton of diatomaceous algae, and with them often and skeletons of silicoflagellate, radiolaria, clay minerals, Fe oxides and Fe hydroxides. Recent diatoms are widespread in the cold sea around the South Pole and the northern Pacific

TABLE 5.7 Distribution of Silicon and Silicon Rock Sediments by Way of Origin, Structure and Mineral Composition

A—Silicon Sediment of Biogenic Origin			
Prevailing Silicon Ingredient	**Untied Sediment**	**Poor Lithified and High Porosity**	**Solid Rock without Porosity**
Diatoms skeletons	Diatoms mud	Diatomaceous earth	Diatomite
Radiolaria skeletons	Radiolaria mud	Radiometric earth	Radiolarite
Spicule sponge	Spicule mud	Porous spiculite	Spiculite
B—Silicon Sediment of Diagenetic or Other Origin			
Authigenic quartz chalcedony and/or opal		Geyserite porcellanite	Layered cornea flint, novaculite jasper nodular cornea

Ocean. There is also the largest deposit amount of recent deposition—diatomaceous mud—with predominant ingredient of diatoms skeletons. With the marine environment diatoms were and still today, adapted for life in marine and lacustrine sweetened water, so that within lake sediments often form a lamina or layers exclusively composed of opal skeleton, (diatomite lamina). The lake water poor in earth-alkalic ions (lake with "soft water"), and rich in dissolved silica, nitrates and phosphates, ecologically are favorable environment for the development of diatomaceous which deposit diatomaceous mud after dying and gradually turns in diatomite in lakes with areas of cold climate.

Diatomite, unlike diatomaceous mud and diatomaceous earth, is very hard, dense low-porosity rock, of light gray or white color, composed opal skeletons of diatomaceous, amorphous opal-A, cemented together with opal or in older rocks, microcrystalline or cryptocrystalline quartz or fibrous chalcedony cement. Chalcedony fills the pores of the largest dimension.

Radiolarian muds, radiolarian earths and radiolarites are predominantly composed of radiolaria skeletons built of opal-A, diagenetic transformed chalcedony and quartz. Radiolarian belongs to protozoa—marine plankton (zooplankton) organisms that float near the sea surface. These are single-celled organisms whose homes consist of $SrSO_4$, some organic silicate, or opal-A. The only preserved fossils are opal homes (opal-A) of spherical shapes, diameters between 50 and 250 μm, usually about 150 μm. The rocks consist of fungous glassy membranes with many regular radially spaced thorns.

Radiolarites are thick rocks of glassy shine, have microgranular structure, mainly composed of radiolaria skeleton and fibrous chalcedony aggregates. Black radiolarites are rich in organic matter and are called *touchstone*.

Spicule muds and spiculites are mainly composed of spicule silica sponge, built of opal-A. Opal-A in spiculites, during diagenetic processes, as one of the skeletons built and the one excreted as cement, recrystallized in opal-CT and cryptocrystalline quartz, and chalcedony. Spiculites also contain carbonate, clayey and powder matrix as essential ingredients and glauconite. Spicule of sponges is constructed from opal or chalcedony, and an elongated central channel of spicule filled with opal cement.

Biogenic silicon deposits occur in areas with high primary production of opal and radiolarian skeletons or spicule with low influence of terrigenous material and low carbonate, or the CCD boundary line is located at short depth. All or most of the carbonate in such environment is dissolved in water column before it sediments at the bottom, or melting occurs within sediment located below the CCD boundary line. The solubility of opal in seawater is relatively good and enhanced with increasing temperature and depth, and therefore deep sea silicon sediments are good indicators of diagenetic processes. Silicon muds have high porosity (75−90%) and remain diagenetic unchanged near the seabed, up to several hundred meters of deposits.

5.7.4.3. Siliceous Sediments and Siliceous Rocks of Diagenesis Origin

The silicon rocks are divided into two groups based on appearance, texture characteristics, form of occurrence and origin: inorganic and/or diagenetic origin (Table 5.7).

1. Weak lithificated and high porous rocks; geyserite, porcelanite, tripoli.
2. Firm lithificated, dense rocks with no porosity: layered cherts, flint, novaculite, jasper, nodular and lenticular cherts.

Geyserite is a siliceous sedimentary rock which occurs by secretion of opal from hot water in geysers and hot springs at its outbreak to the surface of the Earth. Geyserite and rocks of similar origin are known as *silicon sinter*. Geyserites are incrustation of fibers and pearls (silicon sinter) resulting in the secretion of opal in evaporation of silica-rich hot springs fiorite, according to the locality of Santa Fiora from Tuscany in Italy where the "sintered silicon" is extracted as stone for making ornaments.

Porcelanite is a chert variety cryptocrystalline in structure, blurry shine of white color very similar to unglazed porcelain. It consists of opal-A, opal-CT (cryptocrystalline cristobalite) and sometimes tridymite. It is more porous and softer than chert. It occurs by diagenetic processes of recrystallization of opal-A into opal-CT from radiolarian muds and secretion of tridymite from pore solution in a greater depth of the overlay.

Tripoli is white or light gray, porous silicon sediment composed of microcrystalline quartz. It occurs by partial silicification of carbonate rocks, where the quartz component stays after the weathering, while the carbonate component almost entirely secreted from the rock.

Cherts appear in two ways:

1. As layered rocks.
2. As nodules, lenses and irregular clumps.

These rocks are known under the general name of chert, and some call it hornfels. Cherts include all solid-silicon rocks, regardless of origin of silicon mineral, consisting of cryptocrystalline or microcrystalline quartz of non-detrite origin and/or chalcedony (Fig. 5.70), and opal-CT. These are dense, very hard rocks, sharp fracture silicon minerals contain Fe-oxides or hydroxides and organic matter (Fig. 5.70). The silicon minerals within cryptocrystalline to microcrystalline mass composed clearly preserved skeletons, or their unclear remains, "ghosts" due to intensive recrystallization. It applies to radiolarians that from the entire silicon skeleton most resistant to recrystallization.

The dimensions of quartz crystals in the cherts rarely exceed 10 μm (Fig. 5.70), and for further research of cherts structure needs electronic microscope.

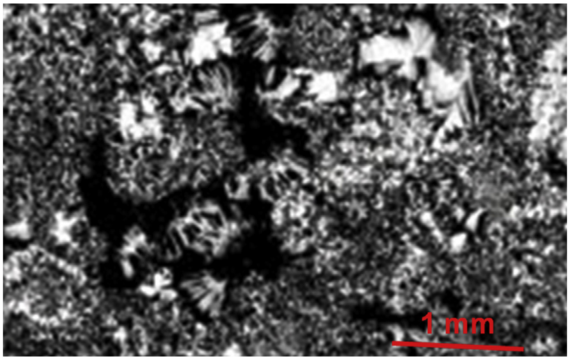

FIGURE 5.70 Microscopic recording of chert composed of microcrystalline quartz cluster and fiber chalcedony.

Bedded cherts (layered hornfels) appear in the form of thin layered (3–8 cm) or tens of meters thick chert deposits within dark gray to black shale or fine-grained graywacke sandstone, layered iron sediments, and striped cherts. Bedded cherts are common in preCambrian, Paleozoic and Mesozoic. The Jurassic and Cretaceous deposits occur almost everywhere in the World. The chert family can be described as the following:

1. *Cherts*, in the wider sense, are known as flint, novaculite and jasper, porcelanite and tripoli.
2. *Flint* is the chert with cryptocrystalline texture used as artifacts, weapons and tools of prehistoric man.
3. *Novaculite* is a variety of light or white, dense and solid chert, laminated, Devonian age, characterized by homogeneous cryptocrystalline to microcrystalline anhedral texture, isometric tiny quartz crystals and over fibrous chalcedony.
4. *Jasper* is a dense, opaque variety of cryptocrystalline chalcedony, contain significant proportion of Fe-oxides and hydroxides namely hematite, limonite and goethite so that reddish characteristic come from hematite and brownish color from goethite.
5. *Tripoli* is a naturally-occurringfine-grained microcrystalline mineral from chert family. It has special application abrasive mineral used in a variety of industries for sharpening, buffing and polishing end uses.
6. *Novaculite* is a form of microcrystalline or cryptocrystalline quartz of chert family. The color varies from white to gray-black and the specific gravity shows an increase from 2.2 to 2.5. The very hard dense rock is used as abrasive machining for steel tools, sharpening and grinding blocks or whetstone.

Nodular and lenticular cherts occur within limestones and dolomites, and significantly less within pelite and sandy sediments. It consists of microcrystalline and/or cryptocrystalline quartz, equidimensional quartz crystals, with smaller/larger amount of quartzite and chalcedony, and opal-CT. Microcrystalline quartz in limestone suppresses micrite mass, typically contains numerous small impurities of calcite, evaporite minerals and/or the primary structural components (micrite, pellets, ooids, and fossils), chert concretions in limestone of southern Istria (Croatia). In general, nodular and lenticular cherts are egg or spherical shapes regardless of whether they appear inside layer or between two layers (Fig. 5.71).

Most bedded cherts occur mainly by processes of recrystallization of diatomite, radiolarites and spiculite or acid tuffs and volcanic glasses. Nodular and lenticular cherts generally occur in the processes of suppression of carbonate sediments or some other rock with opal, chalcedony or quartz, with the participation of silicon acid, i.e. processes of silicification (Section 5.7.1.4.3).

Sediments and sedimentary rocks that originate from igneous, metamorphic and older sedimentary rocks, is ever forming new sedimentary deposits through the millions of geologic age. Erosion of preexisting rocks is the primary source of natural embryo-grains, that move, deposit, lithify and form the sedimentary rocks. The process continues for eternity (Fig. 5.72).

FIGURE 5.71 Egg-like chert nodule and spherical impression in limestone from which was removed chert nodule. Southern Istria, Croatia.

FIGURE 5.72 Erosion continues to sculpt the extremely water saturated sandstone accelerated by flash flood of Virgin River at Zion Canyon, Utah State, USA. The natural erosional caves and holes at about 4600 feet (1400 meter) above the Mean Sea Level fascinate scientists and nature lovers, like these kids (Srishti-Srishta) to rest for a while. The erosional fines and coarse materials move near and far distances to form new sedimentary rocks over geological time. *Source: Soumi, September 1, 2013.*

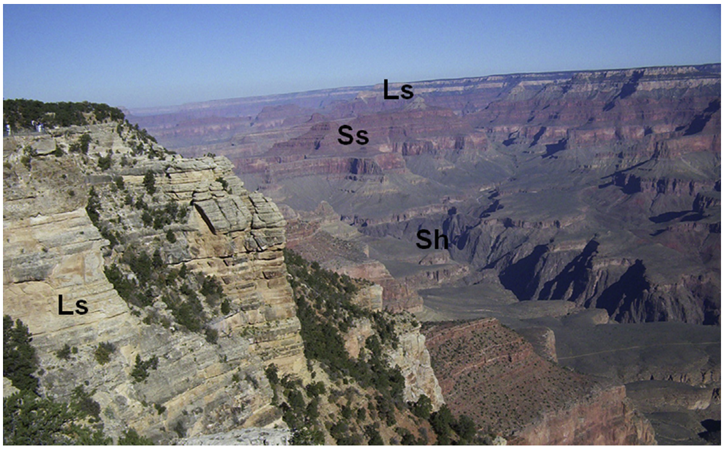

FIGURE 5.73 Visit to awesome Grand Canyon, a steep-sided gorge in Arizona State, is a dream for any geologists, trackers and nature lovers. The Canyon is 446 km long, up to 29 km wide and attains a depth of over 1800 m. It is carved by the Colorado River exposing over 600 million years of Earth's geological history through layer after layer of igneous, sedimentary and metamorphic package of limestone (Ls), sandstone (Ss), shale (Sh), conglomerate, schist over granite basement. The South Rim limestone mined for rich lead ore. Photograph: September 30, 2005 from the South Rim at ∼2,100 m above mean sea level.

The sedimentary depositional system preserves its own history for the students of mineralogy, stratigraphy and exploration geology (Fig. 5.73).

FURTHER READING

Tucker et al.,[54] Tucker,[55] Bathurs,[1] Engelhardt,[15] Füchtbauer,[19] Flügel,[20] Pettijohn et al.,[32] Potter, et al.,[35] Slovenec,[43] Slovenec et al.[42] and Sam Boggs[10] provide a detailed description on sedimentary rocks and their origin. Moore[31] and Boggs (Jr)[3] will be an interesting reading on the subject. Academicians and students knowing Croatian language will be benefited reading Tišljar[47–51] on sedimentary rocks.