Chapter 5

Carbonate Sediments

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Carbonate sediments are a part of the carbon cycle (Fig. 1.14). CO_2 in the atmosphere dissolves in water and makes carbonic acid (H_2CO_3) which reacts with Ca^{2+} or Mg^{2+} to precipitate $CaCO_3$ or $MgCO_3$. This process is an important sink for CO_2. The rate of carbonate sedimentation globally is controlled by the supply of cations (mostly Ca^{2+} and Mg^{2+}) into the ocean from rivers. This again is a function of the rate of weathering of Ca-bearing silicate minerals like plagioclase.

Weathering of limestones will release CO_2 and therefore does not contribute as a sink for CO_2. During contact metamorphism when limestones are heated (to 550–600°C), $CaCO_3$ reacts with SiO_2 to form $CaSiO_3$ (wollastonite) and CO_2. Large amounts of CO_2 formed this way are released through volcanoes. When minerals like wollastonite are weathered, Ca^{2+} is released into rivers and the ocean again. Another part of the CO_2 is reduced by plants and stored as carbon or organic compounds which make up petroleum. These may also be oxidised to CO_2.

Carbonate sediments are for the most part formed (born) within sedimentary basins even if there is a clastic supply of carbonate sediments. The sedimentology of carbonates therefore differs in many respects from siliceous sand and mud. Carbonates may precipitate chemically from the seawater but most of the limestones are composed of calcareous organisms. The properties of limestones are therefore closely linked to their biological origin and the mineralogy of the carbonate skeletons. The primary composition is very important for their alteration during burial (diagenesis) and consequent reservoir properties (porosity and permeability), which to a large extent is controlled by chemical processes. Since both biologically and chemically precipitated carbonate sediments are composed of minerals we will first examine the mineralogy and geochemistry of carbonates. This is important for understanding diagenetic reactions and prediction of reservoir quality.

5.1 Geochemistry of Carbonate Minerals

Carbonate minerals consist of CO_3^{2-} and one or more cations. The most common cations in carbonate minerals together with their mineral names are listed in Table 5.1. The common rock-forming carbonate minerals are either rhombohedral (calcite) or orthorhombic (aragonite) in crystal habit. Where cations with small ionic radii are incorporated into carbonates a trigonal

Table 5.1 Mineralogy of the most common carbonate minerals

Carbonate sediments formed in normal marine environments consist of three main minerals:

Low-Mg calcite $CaCO_3$($<4\%$ $MgCO_3$) (hexagonal)
High-Mg calcite (Ca,Mg) CO_3($>4\%$ $MgCO_3$) (hexagonal)
Aragonite ($CaCO_3$) (orthorhombic)

Other common carbonate minerals are:

Siderite $FeCO_3$
Magnesite $MgCO_3$
Strontianite $SrCO_3$
Rhodochrosite $MnCO_3$
Smithsonite $ZnCO_3$
Ankerite $Ca(Mg,Fe)(CO_3)_2$
Dolomite $CaMg(CO_3)_2$

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K. Bjørlykke (ed.), *Petroleum Geoscience: From Sedimentary Environments to Rock Physics*,
DOI 10.1007/978-3-642-02332-3_5, © Springer-Verlag Berlin Heidelberg 2010

(rhombohedral) crystal lattice is formed, while larger cations result in orthorhombic unit cells. Ca^{2+} has an ionic radius close to 1 Å which is intermediate between small and large cations and near the limit of sixfold co-ordination. Thus $CaCO_3$ is dimorphous forming either rhombohedral or orthorhombic structures.

Cations smaller than 1 Å such as Fe^{2+}, Mn^{2+}, Zn^{2+} and Mg^{2+} can be incorporated in the calcite lattice. These metals all have an ionic radius of about 0.6–0.7 Å, and therefore calcite can contain considerable concentrations of these cations. The calcite group of minerals, such as siderite ($FeCO_3$), rhodochrosite ($MnCO_3$), smithsonite ($ZnCO_3$) and magnesite ($MgCO_3$), all have the same crystal structure as calcite.

Two types of calcite are recognised, depending on the magnesium content: low-Mg calcite (<4 mol% $MgCO_3$) and high-Mg calcite (>4 mol% $MgCO_3$). Biologically secreted calcite is high-Mg calcite and typically ranges between 11 and 19 mol% $MgCO_3$. Low-Mg calcite (in most cases simply called calcite) is more stable than high-Mg calcite, and fossil fragments originally composed of high-Mg calcite are converted to low-Mg calcite during diagenesis. The alteration of high-Mg calcite to low-Mg calcite takes place by a process of leaching of Mg^{2+} ions, which leaves the microarchitecture of the grain unaffected. The exsolved Mg^{2+} may form microdolomite rhombs that are sometimes seen as inclusions in calcitised high-Mg calcites (quite common in fragments of echinoderms and calcareous red algae).

The orthorhombic lattice has an arrangement of CO_3^{2-} anions where cations larger than 1 Å (such as Sr^{2+}, Ba^{2+} and Pb^{2+}) are preferred. Analogous with this aragonite crystal structure are strontianite ($SrCO_3$), witherite ($BaCO_3$) and cerrusite ($PbCO_3$). Sr in particular is an important trace element in aragonite. Aragonite crystals forming in marine environments today contain 5,000–10,000 ppm Sr. Aragonite is unstable and after some time will be replaced by calcite which still retains relatively high concentrations of strontium. Aragonite may occasionally be preserved, particularly in dense shales, even in Mesozoic rocks.

Iron is only very weakly soluble in the oxidised state, forming hydroxides $Fe(OH)_3$ and oxides (Fe_2O_3), but in the reduced state it occurs as soluble Fe^{2+}. Reduction of iron normally takes place within the microbial sulphate reduction zone where high concentrations of sulphur will cause available Fe^{2+} to be precipitated as sulphides (pyrite, FeS_2), so that very little is available to enter the calcite structure. The principal environment in which Fe^{2+} can enter the calcite lattice to form ferroan calcite is thus in the reducing porewater below the sulphate reduction zone. The ferroan calcite may contain a few thousand ppm of iron.

Dolomite ($CaMg(CO_3)_2$) is a carbonate mineral in which layers of $CaCO_3$ alternate with layers of $MgCO_3$. Fe^{2+} is commonly found substituting for Mg^{2+} in dolomite, and a complete series extends to ankerite ($Ca(Fe,Mg)(CO_3)_2$). Dolomite formed early in diagenesis is fine-grained and can often have a magnesium deficit in relation to calcium [e.g. $Ca_{55}Mg_{45}(CO_3)_{100}$]. This is called protodolomite which during burial may be transformed into a regular dolomite.

5.2 Carbonate – CO_2 Systems in the Sea

Even if most carbonate precipitation occurs biologically it is important to understand the chemical constraints on carbonate reactions. Carbon dioxide concentration is the factor which has the greatest influence on pH and the solubility of carbonates in water. CO_2 dissolves in water to form carbonic acid (H_2CO_3), which dissociates into bicarbonate (HCO_3^-) and carbonate ions (CO_3^{2-}).

$$CO_2 + H_2O = H_2CO_3 = H^+ + HCO_3^- = CO_3^{2-} + 2H^+$$

Calcite solubility depends on the solubility product $\left[Ca^{2+}\right] \cdot \left[CO_3^{2-}\right]$. We see that when the water is relatively acid (high H^+ concentrations) the reaction is driven towards the left and the carbonate ions concentration $\left[CO_3^{2-}\right]$ will be low. With high pH (i.e. low H^+ activity), the bicarbonate $\left(HCO_3^-\right)$ concentration will be lower.

Mineral solubility is not strictly a function of the ionic concentration, but of the activity (a) which is influenced by the temperature and other ions present.

The dissociation constants for H_2CO_3 and HCO_3^- are:

$$K_1 = \left(aH^+ \cdot aHCO_3^-\right) / \left(aH_2CO_2^{2-}\right)$$

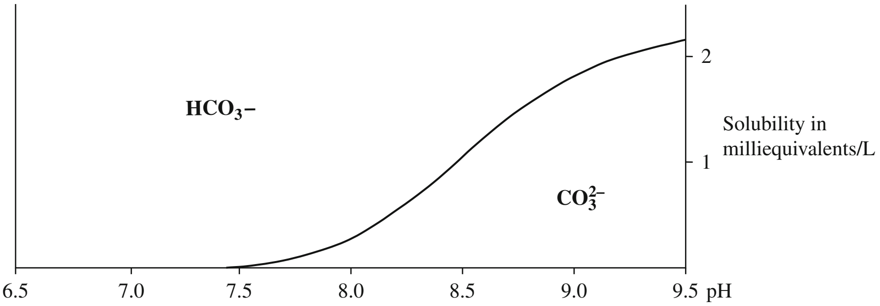

Fig. 5.1 Solubility of carbonate ions in seawater as a function of pH

and

$$K_2 = aH^+ \cdot aCO_3^{2-}/aHCO_3^-$$

This in turn requires that aCO_3^{2-} also must be higher in order to satisfy the dissociation equation. At low pH values the equilibrium will shift to the left, giving more free CO_2 and H_2CO_3 (Fig. 5.1). CO_2 is found in both water and the atmosphere, and is exchanged between them. Statistically, the residence time in the atmosphere is c. 8 years, while it is c. 600–1,000 years in the ocean. The CO_2 in the ocean is partly removed when precipitated as organic matter in the sediments, and partly by precipitation as carbonates.

The solubility of CO_2 in water is greatest at low temperatures and high pressures, decreasing as the temperature rises and pressure decreases. Since it is largely the CO_2 concentration which determines the pH of water, the pH is highest (8.0–8.5) in the warm surface layer at low latitudes, and lowest in polar areas (7.5–8.0).

Photosynthesis also contributes to the consumption of CO_2, increasing the pH of the surface water. pH decreases with water depth, not only because CO_2 is no longer removed by photosynthesis, but also because of the lower temperature and higher pressure.

Whereas photosynthesis involves the removal of CO_2 from the water, respiration adds CO_2.

$$H_2O + CO_2 = CH_2O + O_2$$

CH_2O is a general formula for sugar. During photosynthesis this reaction will go to the right. The reverse reaction is respiration. We see that while photosynthesis raises the pH, respiration will lower it. The water below the photic zone will gain CO_2 from the respiration of zooplankton, and the breakdown (i.e. oxidation) of organic matter which sinks down through the water column will also produce CO_2 and lower the pH. In shallow water, a daily variation in pH has been registered as a result of the fact that photosynthesis takes place only during the day, increasing the pH, while respiration continues at night reducing the pH. Respiration by organisms in the water below the photic zone contributes further to the pH declining downwards through the water column. The recent increase in CO_2 content in the atmosphere (from 280 to 380 ppm) will also influence the ocean water, making it slightly more acidic. Ocean water is, however, strongly buffered and the amount of carbonate that can be precipitated in the oceans is primarily dependent on the supply of cations, especially Ca^{2+} which is mostly liberated by land weathering of carbonate rocks and calcium silicates such as plagioclase.

5.3 Skeletal Components

5.3.1 Introduction

The evolution of organisms precipitating carbonate skeletons has played an important role in the accumulation of carbonate sediments and their properties. The skeletal material is widely different in size, with diameters ranging from a few micrometres in coccolithophores to more than a metre in some bivalves and sponges. The range and taxonomic diversity of major groups of skeletal organisms are shown in Fig. 5.2. However, in this text book we have limited the descriptions to those groups which are most commonly encountered in carbonate hydrocarbon reservoirs.

The first condition for obtaining relatively pure carbonate deposits is that there must be very little or no

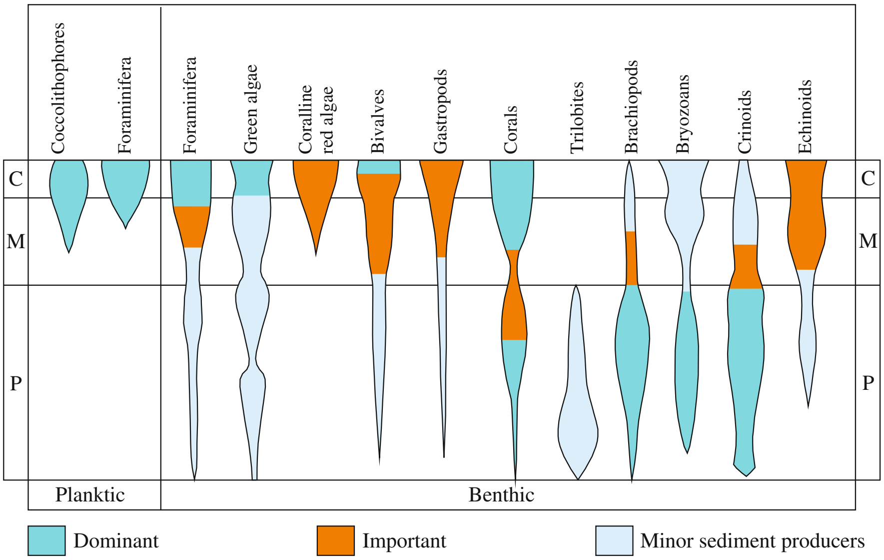

Fig. 5.2 Diversity, abundance and relative importance of various calcareous marine organisms as sediment producers. P = Palaeozoic; M = Mesozoic; C = Cenozoic (modified after Wilkinson 1979)

supply of terrigenous sediments such as sand or clay which otherwise would dilute the carbonate content. Many of the carbonate-secreting organisms require clear water because they filter out nutrients from the seawater. The presence of mud will kill organisms like corals, severely reducing carbonate production. This puts an important limitation on the occurrence of carbonate sediments in sedimentary basins.

5.4 Plants

5.4.1 Stromatolites

"Stromatolite" is the term for lamination in carbonate rocks due to the accumulation or precipitation of carbonate as a result of algal growth. Stromatolites have an intermediate status between fossils and sedimentary structures. They consist of cyanobacteria (earlier called blue–green algae) which have a growth form as unsegmented, micron-sized filaments or unicells (coccooids). The filaments occur in rows or strands within a sticky mucilaginous sheath. Only a few forms produce a biochemically precipitated skeleton, usually tubiform. Other cyanobacteria may generate organic films on the sediment surface, which trap and bind lime mud to form irregular laminae. Rhythmic variations in algal filament growth produce a laminated structure of alternating light, sediment-rich laminae and dark, organic-rich laminae (Fig. 5.3). The end result is either parallel lamination following algal mats, more complex algal growth structures (stromatolites), or a concentric type of structure (oncoids). However, there are not always algal remains to be found, and the only evidence then is the lamination in the rock.

If the laminae are flat-lying they are referred to as *algal laminated sediments*, but if they form structures with vertical relief they are called *stromatolites*. The different overall shapes of stromatolites range from:

1. Laterally linked hemispheroids
2. Discrete, vertically stacked hemispheroids
3. Discrete hemispheroids

These main types are shown in Fig. 5.4, but combinations can occur.

The lamination commonly follows the outline of the structure, or is terminated at the edge of individual heads or stacks. Individual laminae are often thickest at the centre of the structure and thin laterally towards the periphery. Laminae draping over the edge have often accumulated more steeply than the angle of repose because of the sticky surface of the cyanobacteria.