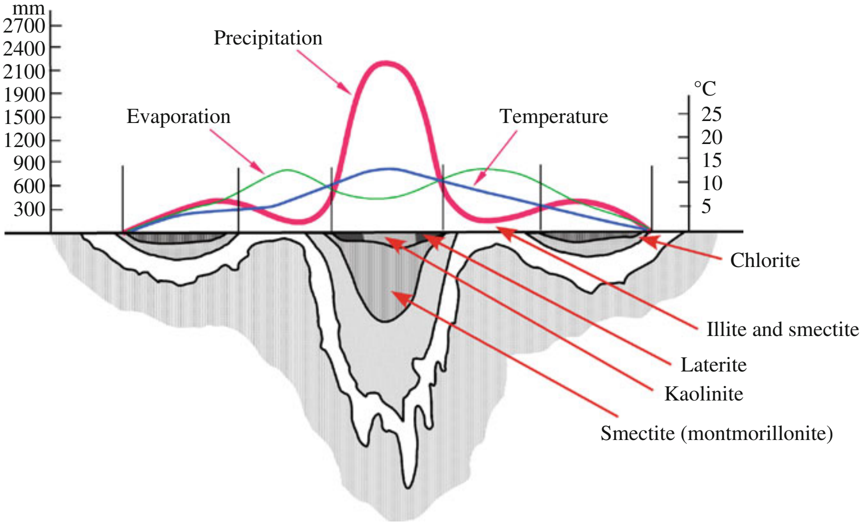

Fig. 3.14 Simplified diagram showing the distribution of weathering and common clay minerals as a function of latitude and rainfall. Cold areas and deserts are characterised by little weathering and more mechanical erosion

Smectite (montmorillonite) is thus a common clay mineral in desert areas, and its ability to swell when wet renders sediments very plastic during floods. This expansion of smectite also lowers its permeability and may be the reason why water can flow over the surface for a long time before sinking into the ground. In addition, capillary forces will prevent rapid percolation of water through dry soil. On the ocean floor near desert regions we find that illite and smectite are typical minerals, brought there by aeolian transport.

In tropical areas where precipitation is relatively high, the rate of weathering will be very rapid. This is not only because weathering processes accelerate with temperature, but also because vegetation produces large amounts of organic acids (humic acids) which are very effective in breaking down silicate minerals. Microbiological organisms such as fungi and bacteria also help in the breakdown process by producing CO_2 which forms carbonic acid, H_2CO_3.

Gibbsite ($A1_2O_3{\bullet}3H_2O$) and iron oxides (haematite, goethite, $Fe_2O_3{\bullet}3H_2O$) are constituents of the laterite which we find only in tropical areas with rapid weathering and slow erosion. Whereas iron oxides are also found at higher latitudes, gibbsite occurs almost exclusively in humid tropical areas.

Laterisation is a very slow process and takes millions of years, even in tropical regions with rapid weathering. It is therefore primarily in tropical areas that we find bauxite for the aluminum industry. Iron-rich laterites may have an iron content of over 50%, and in some areas (e.g. India) have been exploited as iron ore. Laterite forms a very hard cement-like crust over the weathering profile and is also virtually devoid of nutrients, so crop cultivation is impossible. In East Africa (especially Uganda), however, erosion has incised through a layer of Tertiary laterites. While the laterite cover remains on flat elevated surfaces, fresher, more fertile, rocks and weathering material is exposed in the valley sides. The vegetation in some tropical areas is more abundant, even if the soils are very poor in nutrients, because the vegetation recycles those nutrients which are available. If the vegetation is removed and organic material is no longer produced, oxidation and the absence of humic acids (increased pH) will lead to precipitation of oxides and hydroxides which make the soil hard and uncultivable.

Volcanic ash consisting of glass and unstable volcanic mineral assemblages may alter to smectite on land or on the seafloor. In deep sea sediments zeolites like phillipsite are common.

Areas with volcanic rocks, particularly amorphous material (volcanic glass), will often form zeolites. These require a high concentration of both silica and alkaline ions in the water, which is the situation when glass dissolves. Zeolites, particularly phillipsite, are formed authigenically on the Pacific Ocean bed and are also found in lakes (e.g. in East Africa).

In summary we can say that the factors which determine which types of clay minerals are "produced" in the various areas are:

1. The rocks which are eroded/weathered (source rocks)
2. Rate of erosion
3. Temperature
4. Precipitation
5. Vegetation
6. Permeability of source rocks and sediments (percolation of water).

Typical distribution of various minerals:

1. Chlorite and biotite – high latitudes (cold climate) – rapid erosion.
2. Kaolinite – humid temperate and humid tropical regions – good drainage.
3. Smectite (montmorillonite) – low precipitation or poor drainage. Typical of desert environments, but also formed in impervious, e.g. basaltic, rocks in more humid environments. Typically formed from volcanic rocks.
4. Gibbsite – tropical humid climate – long weathering period.
5. Zeolites – formed in areas with volcanic material and restricted porewater circulation. Require a high concentration of silica and alkali ions.

3.8 Geochemical Processes in the Ocean

The ocean can be regarded as a reservoir of chemicals dissolved in water. It looks as though the composition of seawater has not altered radically throughout the geological ages from the early Palaeozoic until the present day, although there have certainly been some variations.

The supply of elements to ocean water from rivers and by water circulation at the spreading ridges must be balanced by a removal of the same elements from the ocean water (Fig. 3.15). The annual addition of salts dissolved in river water is about 2×10^9 tonnes/year. The figure was probably less in the geological past because vegetation was sparse or absent. The development of land plants that produce humic acids, which in turn produced more rapid weathering, has probably increased the supply of salts (since Devonian times). This trend was sometimes slowed by periods with higher sea level that caused widespread transgressions and converted huge tracts of coastal land areas into continental shelf (e.g. during the Upper Cretaceous) reducing the weathering and the supply of salts and nutrients to the ocean.

Some ions like potassium (K^+) are adsorbed to clay minerals supplied by rivers (B in Fig. 3.15). Sodium (Na^+) is so strongly hydrated that it has a tendency to remain in solution, while potassium will be far less hydrated and can be more easily adsorbed onto clay minerals and rapidly removed from seawater.

Most of the elements which the rivers bring to the ocean are precipitated by organic processes. Organisms can build their own internal chemical environment, and use their energy to precipitate minerals which are not normally stable in seawater. Carbonate-secreting organisms, e.g. foraminifera, molluscs etc., will precipitate aragonite or calcite even when the water is cold and undersaturated with respect to these minerals. Diatoms are so effective in precipitating silica (amorphous silicon dioxide, SiO_2), that in most places the seawater near the surface in the photic zone (photosynthetic zone) is much more depleted with respect to silica than to quartz. Organisms, when they die, will in most cases start to break down by oxidation of organic matter and by dissolution of the mineral skeletons. In reducing environments much of the organic matter will however be preserved. In shallow tropical waters, like on a carbonate bank, the seawater may be saturated with respect to carbonate (calcite), but carbonate also accumulates in cold water like the Barents Sea because the rate of dissolution is slower than the rate of precipitation.

The more efficient organisms are at building skeletons despite undersaturation, the more rapidly they will dissolve. Diatoms, for example, dissolve to the extent of 99–99.9% before they have sunk to the seabed. Only a very small proportion is therefore preserved in sediments.

Photosynthesising organisms in the surface water use up CO_2 and produce oxygen and organic matter:

$$CO_2 + H_2O + \text{nutrients} = CH_2O + O_2$$

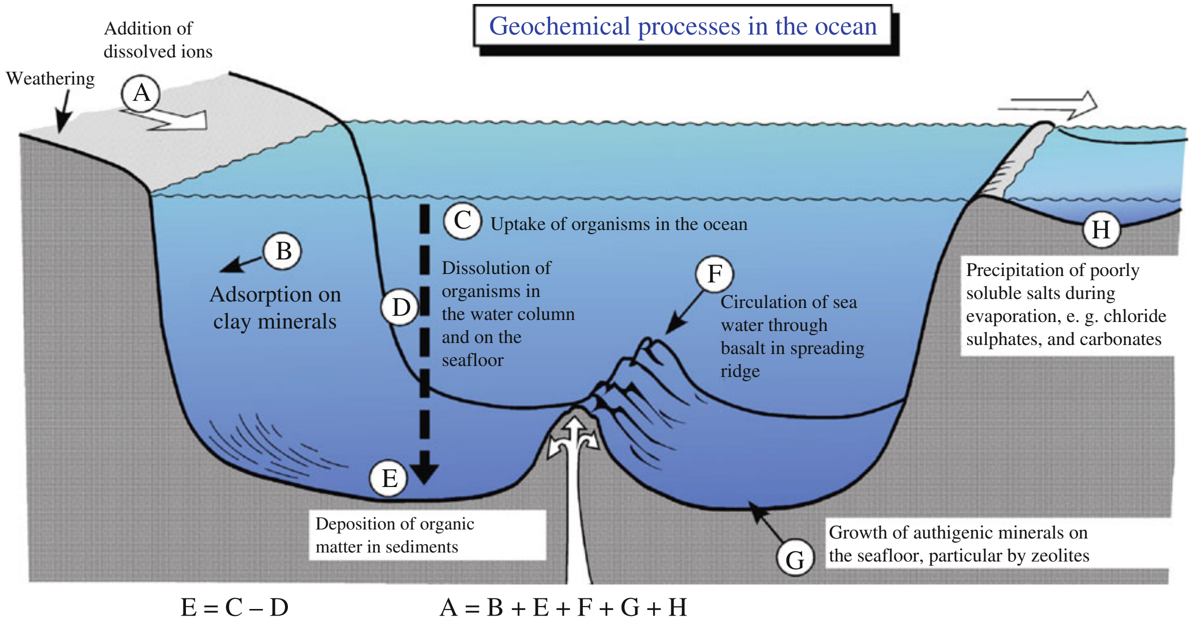

Fig. 3.15 The chemical composition of the seawater remains nearly constant over geologic time. The supply of ions in solution from rivers and from spreading ridges must therefore be equal to the removal of dissolved components by precipitation of minerals and adsorption on clay minerals. The most soluble components (Na, Cl, KCl) are only removed by evaporation

This helps to keep the pH high so that carbonates are stable or dissolve slowly. At depth in the absence of sunlight, respiration and oxidation prevail, releasing CO_2 and thus lowering the pH and increasing the solubility of carbonate.

The depth at which the solubility of carbonate increases relatively rapidly is called the *lysocline*. The depth where the rate of solution is greater than the rate of carbonate sedimentation is called the *carbonate compensation depth* (CCD). Near the equator the CCD may be at 4–5 km, becoming shallower at higher latitudes. Carbonate can therefore still accumulate on the seafloor even when the water column is undersaturated, if the rate of supply exceeds the rate of dissolution. This is analagous to snow accumulating when the temperature is above freezing so long as it falls quicker than it melts This solution of organic material liberates nutrients which can then be returned to the surface through upward flow. In this manner they are repeatedly recycled. The annual biological production in the ocean is therefore many times greater than the supply of nutrients from the land. That fraction of the organic production which has been removed from the ocean by preservation in seabed sediments must be replaced with nutrients, mostly from land. They cannot be returned to the ocean before the sediments are elevated and subjected to erosion and weathering. The amount of organic matter which is deposited in sediments is a function of the rate of production minus the rate of solution.

The growth of authigenic (newly formed) minerals on the seabed (C in Fig. 3.15) is also an important process in removing elements from seawater. The most significant are the zeolites, which can develop where sediments on the seabed have a high silicate or aluminium content, particularly from volcanic material (glass). They may remove Na^+, K^+ and Ca^{2+} from seawater, but growth can also proceed very much at the expense of elements already present in the sediment (e.g. in the Pacific Ocean). This applies particularly to phillipsite, heulandite, clinoptilite and analcite.

Apart from this there is little direct chemical precipitation from seawater with normal salinity. This is because biological precipitation is more efficient in many cases and prevents the build-up of sufficient concentrations of the elements needed for chemical precipitation. Sulphate-reducing bacteria are active in the uppermost few centimetres of the sediment, however, removing sulphur from seawater in the form of sulphate and reducing it to sulphides which are then precipitated (e.g. iron sulphides, FeS and FeS_2).

In areas that are almost cut off from the open ocean, where evaporation exceeds the freshwater rainfall and supply by rivers, we find that even very soluble salts are being precipitated. Under these conditions, there is enrichment of elements which are otherwise precipitated only to a limited degree through biological or chemical processes, such as Na, Cl, S, Mg and trace elements such as B and Br. The amount of salt thus precipitated in evaporites has probably varied very markedly throughout the geological ages.

Biological and chemical precipitation, as described above, are not sufficient alone to account for the geochemical balance of the ocean. Important geochemical reactions are taking place in the spreading ridges in the oceans (F in Fig. 3.15). Heat from the basalt that is flowing up along the spreading ridge, drives convection cells which cause ocean water to flow through the basalts and up along the ridge. The seawater reacts with hot basalt (basic rock melt) and disolves minerals containing iron and other metals. Since seawater contains sulphur (as $S0_4^-$), this leads to precipitation of sulphides, for example iron sulphides and copper sulphides. When hot water flows up pipe-like *chimneys* in the ocean floor near spreading ridges, it mixes with the seawater and again sulphides are precipitated. When water is oxidised, iron oxides and manganese oxides are precipitated around the spreading ridges.

3.8.1 *Residence Periods for Different Elements in the Ocean*

How long does an element spend in the sea after being delivered by rivers, before it is chemically or biologically precipitated? This *residence* period is an expression of how rapidly an element is removed compared to its concentration in the ocean. For example, sodium has the longest period of residence (about 200 million years) because little sodium is removed through biological or chemical precipitation except in evaporite basins. The residence time for potassium is about 1 million years because it is more rapidly adsorbed onto clay minerals and thereby removed. Rare earths have periods of only a few 100 years.

3.9 Circulation of Water in the Oceans

Ocean currents are driven by:

1. The rotation of the earth (Coriolis effect)
2. Tidal forces
3. Differences in water density due to variations in salt content and temperature
4. Wind forces due to atmospheric circulation.

Ocean currents are extremely important for redistributing heat from low latitudes to higher latitudes. This circulation is strongly dependent on the topography of the ocean floor and the distribution of ocean and continents. Bottom currents in the ocean basins are very different from those at the surface, and often flow in opposite directions. While warm surface water flows from the equator to the poles, cold surface water sinks at the poles and flows along the ocean floor to the equator. Both currents are deflected by the Coriolis effect, towards the right in the northern hemisphere and towards the left in the southern hemisphere. While surface currents (like the Gulf Stream) will be deflected eastwards, deeper currents will be deflected towards the west of the oceans (e.g. the Atlantic Ocean). These deep-sea currents which follow the depth contours, may be strong enough to transport silt and fine sand, and the resultant deposits are called *contourites*.

The vertical circulation of seawater is highly sensitive to variations in temperature and salt concentration. In periods with glaciation at the poles, the temperature gradient in the surface water flowing from the equator to the poles is far greater than in non-glacial periods (such as the Mesozoic). Oxygen-rich cold water now flowing down from the polar regions into the ocean basins is important for maintaining oxidising conditions in the deep ocean basins.

Animals and bacteria use oxygen from seawater continuously (for respiration), and oxidation of dead organic material also requires oxygen. If we did not have this downward flow of cold surface water, the water in the ocean basins would be reducing. Some ocean basins are isolated from this circulation, and we may then have a more permanent layering of water based on temperature and salt content. Warm surface water with low density can flow over heavier, colder basal water without the water masses mixing to any major extent. The boundary between warm and cold water masses is called a *thermocline*. If the density