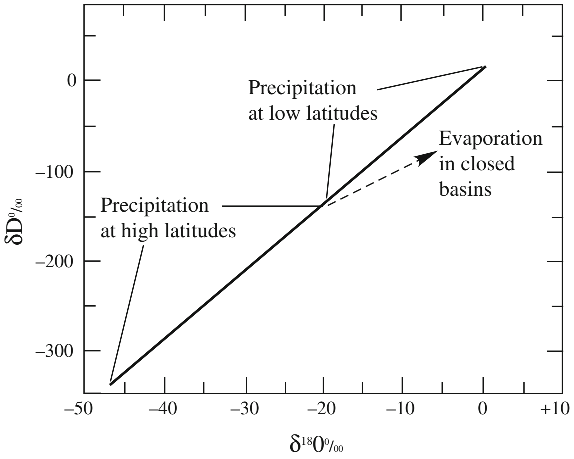

Fig. 3.4 Ratio between the isotopic composition of seawater and freshwater. Evaporites will deviate from the mixing line between these endmembers

(positive δ^{18}O). Shallow marine carbonates that are diagenically modified by freshwater, give lower δ^{18}O values than marine carbonates deposited in deeper water.

Stable oxygen isotope analyses were first used by Urey, in 1951, to demonstrate past temperature changes in seawater. By taking samples through a cross-section of a belemnite it was possible to register annual variations in seawater temperature from 150 million years ago (Fig. 3.5).

The precipitation of newly formed (authigenic) minerals gives an oxygen isotope composition which is a function of the composition of the porewater in which the mineral is precipitated, and the temperature. If the porewater isotope composition is known, the temperature (*T*) can be calculated, and vice versa.

The calcite precipitation formula is:

$$T = 16.9 - 4.38({}^{18}\mathrm{O}_{\mathrm{carb}} - {}^{18}\mathrm{O}_{\mathrm{water}}) + 0.1({}^{18}\mathrm{O}_{\mathrm{carb}} - {}^{18}\mathrm{O}_{\mathrm{water}})^2$$

Here the values for calcite are given in PDB and for water in SMOW. We see that if the δ^{18}O value for calcite is 0 (PDB) and seawater has 0 (SMOW), the temperature is 16.9°C, which may have been a typical sea temperature when the standards were precipitated.).

The above formula can be expressed graphically, enabling the temperature to be read off a curve as a function of the isotopic composition of the calcite, which is the assumed composition of the porewater during precipitation (Fig. 3.6). Similar calculations can be done for other precipitated minerals, for example for quartz using the δ^{18}O fractionation as a function of the temperature for quartz.

Carbon has two stable isotopes (^{12}C – 98.9% and ^{13}C – 1.1%). During photosynthesis a greater proportion of $^{12}CO_2$ than $^{13}CO_2$ forms organic compounds, because $^{12}CO_2$ has a smaller mass. Organic material is therefore enriched in ^{12}C relative to atmospheric CO_2 and HCO_3^- in seawater. The isotopic composition of carbon is expressed as δ^{13}C values:

$$\delta^{13}\mathrm{C} = [{}^{13}\mathrm{C}/{}^{12}\mathrm{C}(\mathrm{sample})/{}^{13}\mathrm{C}/{}^{12}\mathrm{C}(\mathrm{std}) - 1] \cdot 1000$$

All samples are compared against a standard of marine calcite, the PDB belemnite, which by definition has $\delta^{13}\mathrm{C} = 0‰$ PDB. The isotopic composition of dissolved carbon (CO_2) has been relatively constant during the last 300–400 million years, but limestones can nevertheless be dated and correlated using differences due to variation in the composition of seawater. Towards the end of the Precambrian the composition of seawater seems to have been more variable, and there this type of correlation is particularly valuable since there are no fossils. In large massive limestones the isotope composition does not change significantly during diagenesis, because the volume is so great. Atmospheric CO_2 has $\delta^{13}\mathrm{C} = –7‰$. Land plants have an average δ^{13}C value of –24 (–15 to –30‰), and marine organisms have a similar range of values. Freshwater containing CO_2 released by the breakdown of organic matter, and groundwater filtered through a soil profile, will take up CO_2 with negative δ^{13}C values from roots and organic material.

Bacterial fermentation of organic material ($2CH_2O = CH_4 + CO_2$) forms gas (methane) which is very strongly enriched in ^{12}C ($\delta^{13}\mathrm{C} = –55$ to –90‰) and CO_2 which is positive ($\delta^{13}\mathrm{C} = +15$).

Thermal breakdown (thermal decarboxylation) of organic matter produces δ^{13}C values of –10 to –25.

The strontium isotope ratio (^{87}Sr/^{86}Sr) in seawater has varied considerably through geological time (Fig. 3.7). This is because there are two radically different sources of strontium in seawater. Continental weathering supplies much ^{87}Sr to the sea since granitic rocks contains relatively high concentrations of rubidium which can decay to ^{87}Sr. Dissolution of basalt at

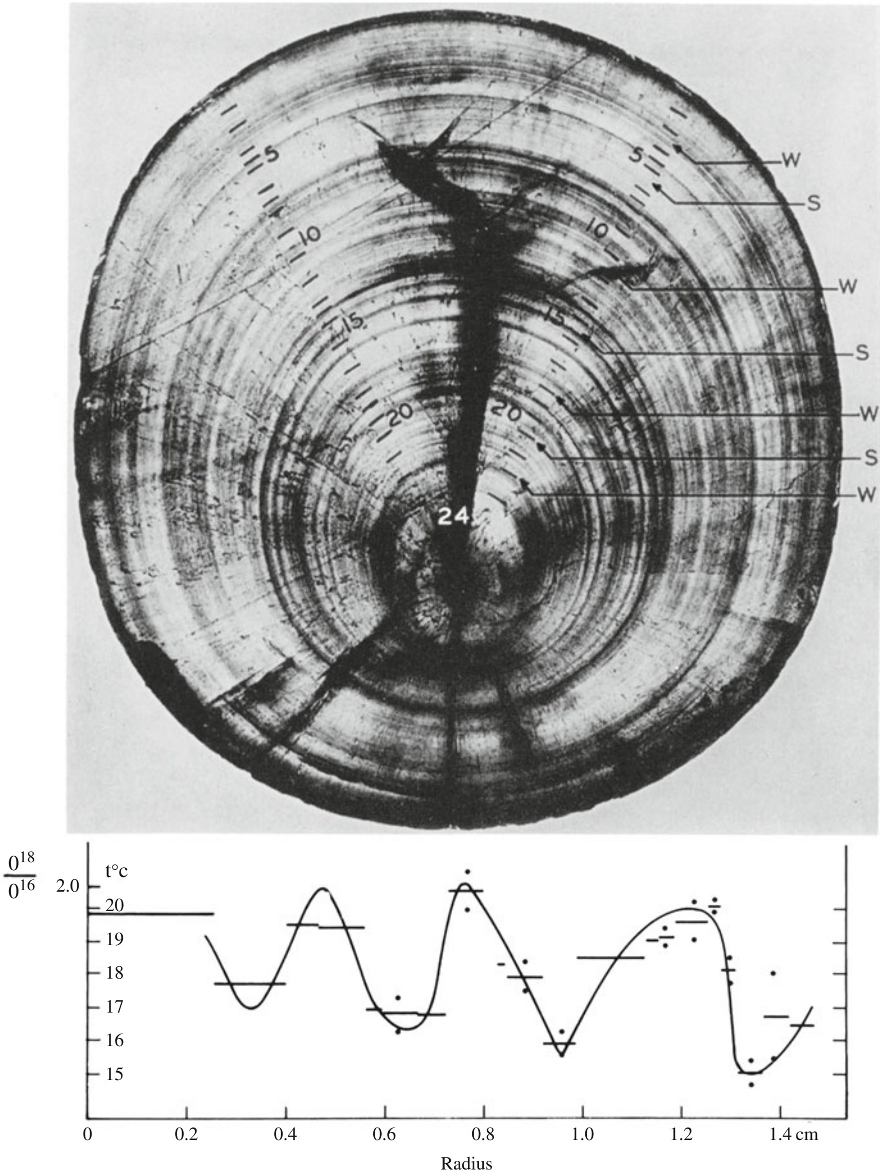

Fig. 3.5 Analyses of oxygen isotopes in a Jurassic belemnite from the centre to the outermost layer. Colder water during the winter is recorded by lower $^{18}O/^{16}O$ ratios. We can see that the belemnite lived for 4.5 years and died in the spring. (From Urey et al. 1951)

the mid-oceanic ridges will supply strontium with a relatively low $^{87}Sr/^{86}Sr$ ratio because basalt contains a little potassium and also rubidium.

When there is rapid seafloor spreading a great deal of water passes through the mid-oceanic ridges, so that the seawater receives much Sr with a low $^{87}Sr/^{86}S$ ratio. During such periods, for example in the Jurassic – Cretaceous, the creation of new warm seafloor will lead to a transgression onto the continents. This reduces the gradients and hence transporting capacity of rivers, limiting the supply of clastic material to the ocean.

Since the Jurassic, the $^{87}Sr/^{86}Sr$ ratio has risen almost continuously, and by analysing marine calcitic

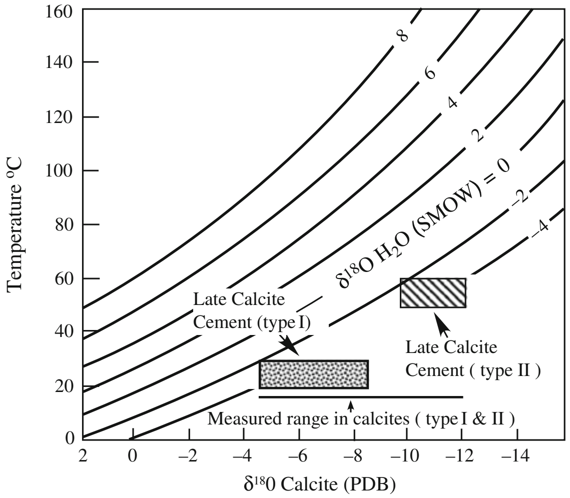

Fig. 3.6 Relation between the isotopic composition of porewater and carbonate cement, as a function of temperature (from Saigal and Bjørlykke 1987)

Fig. 3.7 $^{87}Sr/^{86}Sr$ ratio in seawater from the Cambrian to present. Based on MacArthur et al. (2001). This ratio reflects the relative contribution form weathering of continental rocks with high contents of ^{87}Sr and exchange with basaltic rocks with low contents of ^{87}Sr on the oceanic spreading ridges

fossils such as foraminifera, one can obtain rather accurate age determinations. This applies particularly to the Tertiary period, when the rise in the $^{87}Sr/^{86}Sr$ ratio was particularly rapid (Fig. 3.7).

The isotopic composition of clastic sediments can also be used for stratigraphical correlation. Then it can be more useful to employ isotopes which do not go into solution and react with water, but retain the original age of the rocks from which they were eroded. In the North Sea and on Haltenbanken the ratio between the rare earth elements samarium and neodymium ($^{147}Sm/^{143}Nd$) was used to correlate reservoir rocks both in-field and regionally.

3.5 Clay Minerals

A number of minerals are referred to as clay minerals because they predominantly occur in the finest grain-size fraction (clay fraction) of sediments and sedimentary rocks. However, this is not an accurate definition, because the clay fraction contains many other minerals than those we call clay minerals, and because the clay minerals themselves are often larger than 4 μm (0.004 mm). By "clay minerals" we usually mean sheet silicates which consist chiefly of oxygen, silicon, aluminium, magnesium, iron and water (H_2O, OH^-). Clay minerals in sedimentary basins are partly derived from sheet silicate minerals occurring in metamorphic and eruptive rocks (e.g. biotite, muscovite and chlorite), but during weathering and transport these clastic minerals are typically altered from their initial composition in the parent rock.

Mica (muscovite and biotite) lose some potassium which is replaced by water (H_2O, H_3O^+) to form illite (hydro mica). Clay minerals are also formed through weathering reactions, for example by the breakdown of feldspar and mica. Clay minerals which are formed by the breakdown of other minerals within the sediment, are called authigenic.

Sheet silicates have a structure consisting of sheets of alternating layers of SiO_4 tetrahedra and octahedra. In the tetrahedral layers, silicon or aluminium atoms are surrounded by four oxygen atoms. In the octahedral layers the cation is surrounded by six oxygen or hydroxyl ions. Both bi and trivalent ions can act as cations in the octahedral layer. In sheet silicates with trivalent ions (e.g. Al^{3+}) only two of the three positions in the octahedral layer are occupied, and such minerals are therefore called dioctahedral. With bivalent ions (Mg^{++}, Fe^{++}) all three positions must be filled to achieve a balance between the positive and negative charges, so these minerals are called trioctohedral.

The main method of identifying clay minerals is X-ray diffraction (XRD), by which the thickness of the sheet silicates is determined using X-rays which are diffracted according to Bragg's Law: $n\lambda = 2d \sin \varphi$. Here λ is the wavelength of the X-ray, φ the angle of incidence and d the thickness of the reflecting silicate layers; d is thus a function of angle φ.

Sheet silicates may also be identified by means of differential thermal analysis (DTA), which records characteristic exothermal or endothermal reactions.

Figure 3.8 shows the structure of some of the main clay minerals. Illite consists of sheets with two layers of tetrahedra and one of octohedra, bonded together by potassium. This ionic bonding is relatively weak so the mineral cleaves easily along this plane. The bonds within the tetrahedral and octahedral layers are more covalent and stronger. The potassium content in mica corresponding to the formula of mica is about 9% K_2O, while illite has a greater or lesser deficit of potassium. Smectite (montmorillonite) has the same structure except that most of the potassium is replaced by water (H_3O^+), other cations or organic compounds (e.g. glycol). There are strong indications that smectite consists of small particles of 10 Å, plus water.

Illite is most likely comprised of several layers of these small 10 Å particles stacked on top of one another.

In an atmosphere of glycol vapour, smectite will swell from 14 to 17 Å, while illite is unable to expand because there are numerous layers bonded together with K^+ or other cations, for example NH^+. Smectite has a very high ion-exchange capacity and to some extent can exchange ions in the octahedral layer. The stability of smectite declines in aqueous solutions with high K^+/H^+ $\left(Na^+/H^+\right)$ ratio and with increasing temperature, and it converts to illite. Vermiculite has a structure reminiscent of the smectites, and also undergoes ion exchange and thus charge deficit in the tetrahedral layer, so that the bonding between each layer is too strong for much swelling to occur. Vermiculites are mostly trioctahedral, containing mostly Mg or Fe in the octahedral layer.

Glauconite is a green mineral which forms on the seabed. It is a potassium and iron bearing silicate somewhat similar to illite and contains both di - and trivalent iron. It is therefore formed right on the redox boundary, and during periods with little or no clastic sedimentation this can result in relatively pure beds of glauconite.

Kaolinite consists just of a tetrahedral layer and an octahedral layer and is very stable at low temperatures. There are no positions in the structure where exchange can precede easily, which gives kaolinite a much lower ion exchange capacity than smectite. At higher temperatures kaolinite becomes unstable and will convert to illite if K-feldspar or other sources of potassium are available (at 130°C) or pyrophyllite ($Al_3Si_4O_{10}(OH)_2$) at higher temperatures.

Kaolinite is part of the kaolin mineral group, which includes dickite which tends to form at slightly higher temperatures (100°C).

Chlorite is a mineral which consists of two tetrahedral layers and two octahedral layers, totalling 14 Å. The octahedral layer is filled with $Mg^{++}$and Fe^{++}. Magnesium-rich chlorites are typical of high