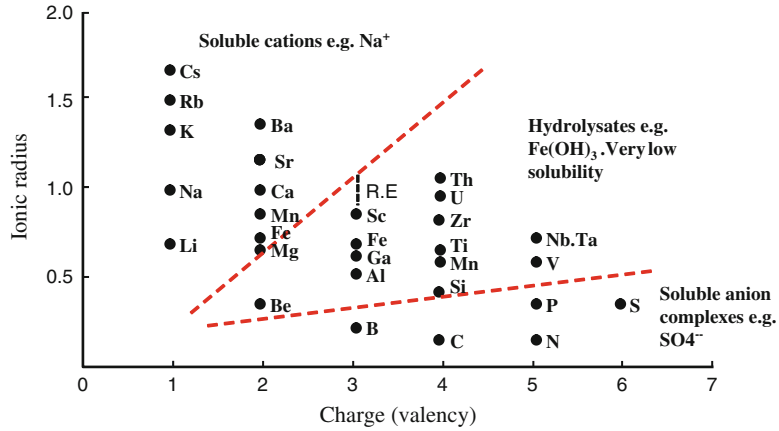

Fig. 3.2 Ionic radius and charge (valence) for some geochemically important elements. Ions with low ionic potential are soluble as cations (e.g Na^+, K^+) while ions with intermediate ionic potentials will bond with OH^- groups and have very low solubility, forming hydrolysates (e.g $Al(OH)_3$), Fe $(OH)_3$). High ionic potentials make soluble cation complexes like CO_3^{--} and SO_4^{--}. The ratio between these parameters - the ionic potential - can be used to explain their behaviour in nature

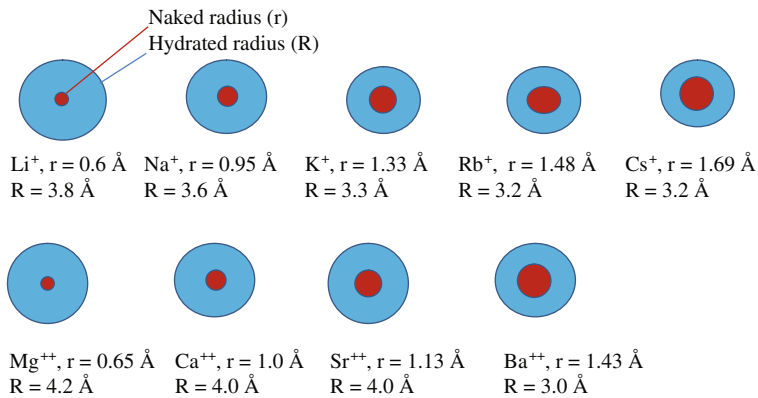

Fig. 3.3 Ionic radius (in Ångstrom units) of hydrated and non-hydrated ("naked") ions of alkali metals and alkaline-earth metals. The smaller ions have higher ionic potentials and form stronger bonds with water molecules so that they become hydrated. This hydration effect is reduced with increasing temperature

strength of the M-O bond is not merely a function of the valency and radius, and the picture becomes far more complex. The concept of ionic potential is nevertheless still useful; we see that during weathering, elements with low ionic potential remain in solution along with the anionic complexes of metals and non-metals with high ionic potential. This is reflected in the composition of seawater. The hydrolysates, on the other hand, become enriched on land as insoluble residues or through weathering (Al^{3+}, Fe^{3+}, Mn^{4+}, Ti^{4+}, etc.). Note also that Fe^{++} and Mn^{++} which occur in reducing environments have lower ionic potential and are much more soluble that Fe^{3+} and Mn^{4+}.

The most soluble ions remain in the seawater until they are precipitated as salt when seawater is concentrated during evaporation. In addition to the chlorides (i.e. NaCl, KCl), these are mainly salts of cations with low ionic potential, and of anions with high ionic potential, e.g. $CaSO_4{\cdot}2H_2O$, Na_2CO_3 and carbonates such as $CaCO_3$ (calcite), $CaMg(CO_3)_2$ (dolomite) and $MgCO_3$(magnesite).

The principle of ionic hydration and the size of the ionic radius are capable of explaining a whole range of geochemical phenomena. Among the Group I elements of the Periodic Table, we know that Li^+ and Na^+ are enriched in seawater. This because the strong hydration prevents absorption on clay minerals which usually have a negative surface charge. K^+, Rb^+ and Cs^+, on the other hand, have larger ionic radii and consequently are less strongly hydrated. This leaves them with a more effective positive surface charge which facilitates their adsorption onto clay minerals, etc.

This is demonstrated in nature during weathering and transport. While similar amounts of potassium and sodium are dissolved during weathering of basement rocks, the potassium concentration in the sea is much lower (K/Na ratio of only 1:30). This is because K^+ is more effectively removed by adsorption because it is less protected by hydration. The same is true to an even greater extent for Rb^+ and Cs^+, which are adsorbed even more readily. These ions therefore have a relatively short residence time in seawater, between being delivered by rivers and then removed by accumulating sediment.

With regard to Group 2 elements, Mg^{++} for example will be more strongly hydrated than Ca^{++} because it is a smaller ion. As a result, Mg^{++} has a greater tendency to remain in solution in seawater. However, despite the fact that the Mg/Ca ratio in seawater is 5, it is calcium carbonate which is the first to form through chemical and biological precipitation. Dolomite or magnesite do not precipitate directly from seawater and this is in part due to the strong hydration of Mg^{++}. Normally, if we had naked (unhydrated) ions, $MgCO_3$ and $FeCO_3$ would be more stable than $CaCO_3$ because Mg^{++} and Fe^{++} have greater ionic potentials and stronger bonding to the CO_3^{2-} ion. However with increasing temperature the hydration declines because the bonds with the dipole of the water molecules become weaker. Mg^{++} is then more likely to be incorporated into the carbonate mineral structures. Therefore during diagenetic processes at 80–100°C, magnesium carbonates precipitate more readily even if the Mg^{++}/Ca^{++} and Fe^{++}/Ca^{++} ratios are low. Even if Mg is preferred in the carbonate structure and also in the clay minerals, very little magnesium is usually available in the deeper parts of sedimentary basins except in the presence of evaporites with Mg salts.

3.2 Redox Potentials (Eh)

Oxidation potential (E) is an expression of the tendency of an element to be oxidised, i.e. to give up electrons so it is left with a more positive charge. This potential can be measured by recording the potential difference (positive or negative) which arises when an element functions as one electrode in a galvanic element. The other electrode is a standard one, normally hydrogen. The oxidation potential of the reaction $H_2 = 2H^+ + 2e$ (electrons) is defined as $E^0 = 0.0\,V$ at 1 atm and H^+ concentration of 1 mol/l at 20°C. Different conventions have been used to assign plus and minus values. In geochemical literature, metals with a higher reducing potential than hydrogen are assigned negative values, e.g. $Na = Na^+ + e^- = -2.71V$, while strongly oxidising elements are given a positive sign, e.g. $2F^- = F_2 + 2e = 2.87V$. A list of redox potentials shows which elements will act as oxidising agents, and which will be reducing agents. Reactions which result in a negative oxidation potential (E) will proceed spontaneously, while those which have positive voltage will be dependent on the addition of energy from an outside source. We can predict whether a redox reaction will occur by using Nernst's Law (see chemistry textbooks).

3.3 pH

The ionisation product for water is $[H^+] \cdot [OH^-] = 10^{-14}$. The concentration of H^+ in neutral water will be 10^{-7}. pH is defined as the negative logarithm of the hydrogen ion concentration, and is therefore 7 for neutral water (at 25°C). However, the ionisation constant (product) varies with temperature, e.g. at 125°C the ionisation constant for water is $[H^+] \cdot [OH^-] = 10^{-12}$. In other words, neutral water then has a pH of 6. It is important to remember this when considering the pH of hot springs or in deep wells, for example oil wells.

In nature the pH of surface water mostly lies between 4 and 9. Rainwater is frequently slightly acid due to dissolved CO_2, which gives an acid reaction:

$$H_2O + CO_2 = H_2CO_3 \text{ (carbonic acid)}$$
$$H_2CO_3 = H^+ + HCO_3^- = 2H^+ + CO_3^{2-}$$

Humic acids may give the water in lakes and rivers a low pH. Sulphur pollution from burning oil and coal gives SO_2, which is oxidised in water to sulphuric acid:

$$2SO_2 + O_2 + 2H_2O = 2H_2SO_4$$

In areas with calcareous rocks or soils this sulphuric acid is immediately neutralised and the water becomes basic, as is the case across much of Europe. By contrast, in areas with acidic granitic rocks as in the south of Norway and large areas of Sweden, the rock does

not have sufficient buffer capacity to counteract acid rain or acidic water produced by vegetation (due to humic acids). Organic material also contains a certain amount of sulphur, and drainage of bogs, or drought, can produce an acidic reaction. This is because H_2S from organic material is oxidised to sulphate when the water table is lowered, allowing oxygen to penetrate deeper in these organic deposits.

The water near the surface of large lakes and the sea can have a high pH because CO_2 is consumed due to high organic production (photosynthesis). If the organic material decomposes (oxidises) on its way to the bottom, CO_2 is released again, causing the pH to decrease with depth since the solubility of the CO_2 increases with the increasing pressure.

CO_2 is also less soluble in the warm surface water than in the colder water at greater depth.

Seawater is a buffered solution, with a typical pH close to 8, though this varies somewhat with temperature, pressure and the degree of biological activity.

Eh and pH are important parameters for describing natural geochemical environments, and the diagram obtained by combining these two parameters is particularly useful.

The lower limit for Eh in natural environments is defined by the line $\mathrm{Eh} = -0.059\,\mathrm{pH}$, because otherwise we would have free oxygen, and the upper limit corresponds to $\mathrm{Eh} = 1.22 - 0.059\,\mathrm{pH}$, beyond which free oxygen would be released from the water. If we also set pH limits at 4 and 9 in natural environments, we can divide the latter into four main categories:

1. Oxidising and acidic
2. Oxidising and basic
3. Reducing and acidic
4. Reducing and basic

Variations of pH and Eh are the major factors involved in chemical precipitation mechanisms in sedimentary environments where there is not strong evaporation (evaporite environments).

The solubility of many elements is highest in the reduced state and they are precipitated by oxidation. This is particularly characteristic of iron and manganese, whereas others such as uranium and vanadium are least soluble in the reduced state.

3.3.1 Distribution Coefficients

When a mineral crystallises out of solution, the composition of the mineral will be a function of the composition of the solution and the temperature and pressure. Trace elements which are incorporated in the mineral structure are particularly sensitive to variations of these factors. With constant temperature and pressure, the concentration of an element within a mineral which is being precipitated, is proportional to its concentration in the solution. The ratio between the concentration of an element in the mineral and its concentration in the solution (water) is called the distribution coefficient.

A number of elements substitute for Ca^{++} in the calcite lattice: Mn^{++}, Fe^{++} and Zn^{++} have distribution coefficients (k) < 1. This means that they will be captured, so that the mineral becomes enriched in these elements relative to the solution.

$$\mathrm{Mn^{++}/Ca^{++}(mineral)} = k \cdot \mathrm{Mn^{++}/Ca^{++}(solution)}$$

k here is about 17, that is to say the manganese concentration in the calcite is 17 times greater than in the solution.

At low temperatures (25°C) Mg^{++}, Sr^{++}, Ba^{++} and Na^{+} have distribution coefficients <1. This means that the mineral phase will contain proportionately less of these elements than the aqueous phase. For Sr^{++}, k is about 0.1 (0.05–0.14) in calcite, such that the Sr content in calcite is relatively low. The Sr content in aragonite is considerably higher because the Sr^{++} ion, which is larger than the Ca^{++} ion, is more easily accommodated within the lattice. By analysing trace elements in minerals like calcite we can infer something about the environment when the minerals precipitated. Limestones with a high content of strontium may have had much primary aragonite which was replaced by calcite. Calcite containing significant amounts of iron must have precipitated under reducing conditions because only Fe^{++} would be admitted into the calcite structure.

3.4 Isotopes

A number of elements occur in nature as different isotopes: the atomic number (protons) is constant but there are different numbers of neutrons. They

therefore have the same chemical properties although their masses are slightly different. Isotopes which are radioactive (unstable) break down at a specific rate characteristic for the isotope species (the disintegration constant). By analysing the reaction products formed in the minerals they can be dated. The $^{87}Rb - ^{87}Sr$ and the $^{40}K - ^{40}Ar$ methods are the ones most commonly used in determining the age of rocks. The ratios between lead isotopes can also be employed because of the $^{235}U - ^{207}Pb$, $^{238}U - ^{206}Pb$ and $^{238}Th - ^{208}Pb$ reactions.

Dating sedimentary rocks is a complicated procedure and the results are often difficult to interpret. The main problem is that clastic sediments are comprised of fragments and minerals which have been eroded from older rocks and the measured radiometric age may be strongly influenced by the age of these source rocks. Separating the newly formed (authigenic) mineral to be dated, can be particularly challenging.

The fact that isotopes have different masses causes fractionation to take place through both chemical and biological processes. The simplest example is water, H_2O, which contains two oxygen isotopes and two hydrogen isotopes. The oxygen isotopes are fractionated through evaporation, with more $H_2^{16}O$ evaporating than $H_2^{18}O$. This is because the ^{18}O isotope has greater mass and a phase change from fluid to vapour therefore requires more energy. $H_2^{16}O$ has higher vapour pressure than $H_2^{18}O$. This is the reason why rainwater and ice contain less ^{18}O than seawater.

Isotope fractionation is a function of temperature, however, and is much more effective with evaporation at low temperatures than at high ones. The explanation for this is that at high temperatures the energy of the molecules are so great that the difference in mass between ^{18}O and ^{16}O is of less consequence. At low temperatures the isotopic separation evaporation is much more selective so that the water evaporated is more enriched in ^{16}O. When water vapour condenses to rainwater, molecules with ^{18}O are most stable. Rain and snow becomes enriched in the heavier isotope (^{18}O), so that the water vapour remaining in the air becomes more enriched in ^{16}O. Most of the evaporation takes place at low latitudes and the water vapour in the air has a progressively lower ^{18}O-content towards higher latitudes as the air cools and it rains. The concentration of oxygen isotopes is expressed in relation to a standard:

$$\delta^{18}O = \left({}^{18}O/{}^{16}O_{sample} / {}^{18}O/{}^{16}O_{std} - 1 \right) \cdot 1000$$

This standard may be the average composition of seawater, called SMOW (Standard Mean Ocean Water). Another commonly used standard is PDB (Pee Dee Belemnite), which is the composition of calcite in a Cretaceous belemnite. The calcite ($CaCO_3$) was precipitated in the sea and its composition was in equilibrium with the seawater at normal temperatures (15–20°C). There is more ^{18}O in calcite than in the water (positive fractionation), but with higher temperatures the less effective fractionation of oxygen lowers the $\delta^{18}O$ values. The relationship between the two standards is:

$$\delta^{18}O_{SMOW} = 1.031 \cdot \delta^{18}O_{PDB} + 30.8$$

PDB values are preferred for carbonate minerals while the SMOW scale is mainly used for water samples and silicate minerals.

Hydrogen has two stable isotopes, ^1H and ^2H (deuterium), and an unstable one, ^3H (tritium), which has a half-life of 12 years. The hydrogen isotopes are even more strongly fractionated than oxygen isotopes during evaporation. Water molecules with deuterium (heavy water) have lower vapour pressure that water moles with hydrogen.

In meteoric water there is a linear relation between the deuterium/hydrogen ratio (D/H) and the $\delta^{18}O$.

The isotopic composition of seawater has varied through geological time, though not so much during the last 200–300 million years. During glacial periods, seawater acquires more positive $\delta^{18}O$ values because the water bound as ice has more negative $\delta^{18}O$ values. Rainwater (meteoric water) has normal $\delta^{18}O$ values from –2 to –15. The values become more negative towards higher latitudes, and near the poles one can measure $\delta^{18}O$ values of about –50 and δD (^2H) values close to –350 (see Fig. 3.4). Minerals that form in seawater show decreased $^{18}O/^{16}O$ ratios with increased ambient temperature during formation. The $\delta^{18}O/^{16}O$ ratio in carbonate secreting marine organisms, for example, is thus a function of both temperature and salinity. The seawater changes its $\delta^{18}O$ values by around 1–1.5‰. Isotopes can thus provide important proxy evidence for palaeoclimate studies.

Cold freshwater gives strongly negative $\delta^{18}O$ values, whereas evaporites are enriched in ^{18}O isotopes