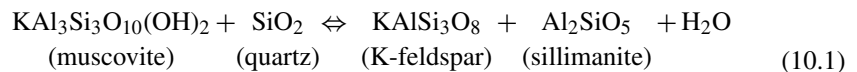


In this chapter we take a look at the chemical and mineralogical changes accompanying the formation of sedimentary and metamorphic rocks. Marine mud is consolidated into sediment through early diagenetic reactions. These sediments and the other rocks that form the bedrock may be affected by percolating hot water, mineralized to varying degrees, and acids. This is hydrothermal metamorphism. When rock is dragged deep down by subduction and thereby heated and dehydrated, it is transformed, producing a great variety of different mineral assemblages. This process is termed “metamorphism.” Some of these thermal processes concern the transformation of organic matter, whose ultimate products are the fossil fuels such as natural gas, petroleum, and coal.

The principal geochemical issues raised by these processes are to identify the nature of the rock before its transformations, the physical conditions (temperature and pressure) of the transformations, and the nature and intensity of exchanges between the transformed rocks and the interstitial solutions. Once again the essential analytical tool is thermodynamics and readers may wish to refresh their knowledge of this by referring to [Appendix C](#).

Transformations are often controlled by water pressure and temperature. Let us take the example of the important reaction whereby muscovite (white mica) disappears from gneiss and schist, and which characterizes the entry of metamorphic rocks into granulite facies:

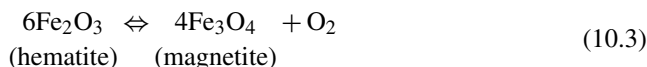


Equilibrium between pure solid and gaseous phases (Appendix C) allows us to write:

$$\ln P_{\text{H}_2\text{O}} = \frac{\Delta H}{RT} + \text{constant} \quad (10.2)$$

where ΔH is the heat (enthalpy) of the reaction. Other reactions involve other gases, such as carbon dioxide, but they are treated in the same way.

The behavior of oxygen is particularly important. The redox reaction between two types of common oxides in igneous and metamorphic rocks:



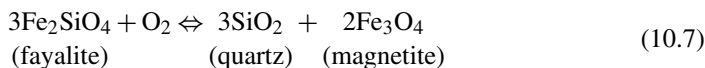
is equivalent to the sum of the two half-reactions:



This shows that redox reactions are merely a trade in electrons between acceptors (oxidants such as oxygen) and donors (reducing agents such as Fe^{2+}). There is nothing wrong, for example, in considering ferrous iron Fe^{2+} as a complex of ferric ion Fe^{3+} with an electron. As the vast majority of rocks are good electrical insulators, electrons must be conserved throughout mineralogical reactions and phase changes. Appealing to an externally imposed oxygen “fugacity” would be misleading: each and every reduction reaction, i.e. any gain in electrons by one species, must be offset by loss of electrons by another species. No local surplus or deficit of electrons is permitted and species having more than one state of oxidation (above all Fe, C, and S) must engage in balanced electron exchanges. As with water, oxygen pressure can be formulated by the mass action law. For example, for the relationship between hematite and magnetite, we write the equation:

$$\ln \frac{[\text{Fe}_3\text{O}_4]_{\text{magnetite}}^4 P_{\text{O}_2}}{[\text{Fe}_2\text{O}_3]_{\text{hematite}}^6} = \frac{\Delta H}{RT} + \text{constant} \quad (10.6)$$

in which the square brackets indicate the molar fraction of the species in question in each of the solid solutions containing hematite and magnetite, and P_{O_2} is oxygen pressure. Relationships like this can be used either for estimating temperature if the redox state of the system is known, or vice versa for measuring oxygen pressure if temperature is known. The fugacity of oxygen in many natural rocks is distributed around the famous QFM (quartz–fayalite–magnetite) buffer:



This equation does not mean that these minerals are present in the rocks, but that the electron balance of the actual mineral assemblage is on average close to that of this buffer.

10.1 Early diagenesis

We have already introduced this issue in [Chapter 8](#). Let us go back to our observers on the sea floor watching the sediment sinking beneath their feet ([Fig. 10.1](#)) and draw up the balance sheet of matter for one species, say sulfate, between two levels at depth Δz one above the other ([Fig. 10.1](#)).

The sediment porosity (proportion of interstitial water) is φ and the sulfate concentration in the water is $C(z)$. In the stationary state, i.e. after “some” time, we can write that the difference between the influx of sulfate at z less the outflux at $z + \Delta z$ is equal to the quantity of sulfate destroyed by biological activity. For our observer, the advective flux of sulfate is equal to $\varphi v C(z)$, where v is the sedimentation rate, corrected where necessary for compaction, which progressively expels water from the sediment. Likewise, the diffusive flux of sulfate is $-\varphi D dC(z)/dz$, where D is the diffusion coefficient of sulfate in salt water. We can then write the diagenesis equation, standardizing it to a unit area:

$$\left[\varphi v C - \varphi D \frac{dC}{dz} \right]_z - \left[\varphi v C - \varphi D \frac{dC}{dz} \right]_{z+\Delta z} = -P(z)\Delta z \quad (10.8)$$

where $P(z)$ is the rate of destruction of sulfate by microbial activity. The rate $P(z)$ will be expressed in a suitable form, probably by a first-order kinetic with an appropriate stoichiometric coefficient (see [Chapter 5](#)) involving the availability of organic carbon. Solutions to the diagenetic equation are usually combinations of exponentials. By examining (10.8) above, we can infer that the concentration of sulfate in pore water, like the abundance of organic particles, must decrease with depth: [Fig. 10.2](#) shows the concentrations of sulfate ion in the interstitial water of sediments collected from the Saanich River fjord (west coast of Canada). It could be shown that (10.8) implies exponential decrease in sulfates from the initial sulfate concentration of seawater, which [Fig. 10.2](#) confirms. The reduced sulfur is in

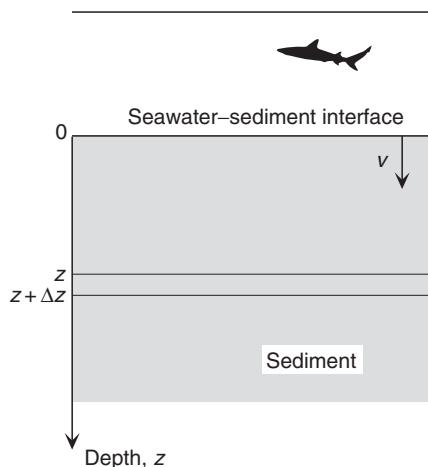


Figure 10.1 The diagenesis reference frame. Sediment sinks beneath the ocean floor at the rate v .

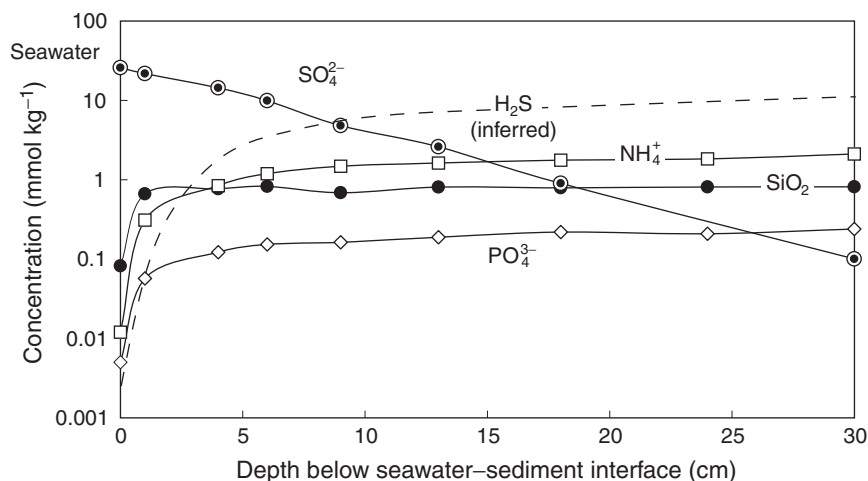


Figure 10.2 Concentration of various species dissolved in interstitial water of the Saanich River fjord (western Canada). With burial, sulfate is reduced to sulfide, organic nitrogen is reduced to ammonia (denitrification), and phosphate and silica of organic origin are remobilized by diagenesis. Data from Murray *et al.*, 1978.

the form H₂S, which eventually causes pyrite to precipitate, but in this core the sulfur data are missing. Laboratory measurement of diffusion coefficients and estimates of sedimentation rate by radiochronometric methods allow us to determine, by resolving the diagenesis equation, the rate at which sulfate is converted to sulfide and equally the rate of oxidation of the organic matter. Similar behavior is observed for nitrates in seawater. Dissolution of organic matter is reflected by a large increase in ammonia produced by the reduction of nitrogen in proteins and other organic compounds (denitrification). The increase in remobilized phosphate from phospho-organic compounds of soft matter and hard parts of certain organisms (fish teeth, ichthyoliths) is responsible for diagenetic reprecipitation of calcium phosphate (apatite), which may be intense enough to produce phosphate deposits of economic value. The silica remobilized by dissolution of diatom and radiolarian tests is locally reprecipitated as flint and the enclosing rocks can be further silicified as cherts. As seawater is highly undersaturated in SiO₂, the expulsion of interstitial water also provides an important source of silica for the ocean.

Until complete, these bacteria-controlled reactions are accompanied by substantial isotopic fractionation, of the order of 25 per mil for carbon and 20 per mil for sulfur, invariably with organic matter and sulfide having a preference for the lighter isotope.

10.2 Hydrothermal reactions

This term is reserved for all medium temperature reactions, typically from 100 to 500 °C, between aqueous solutions and the rock through which they circulate. These are largely, but not exclusively, hydration reactions. Hydrothermal solutions and ores are the sources of many metals of economic significance. The familiar thermal springs at the surface of

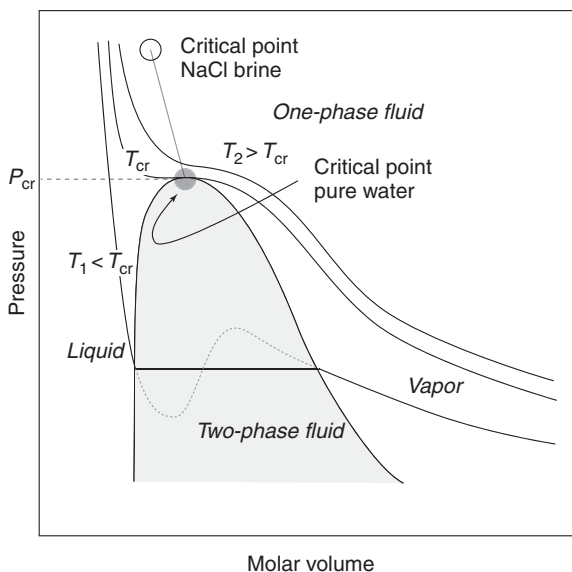


Figure 10.3

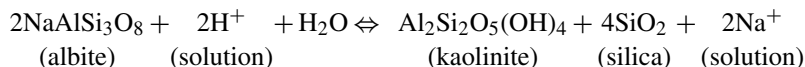
The critical behavior of aqueous solutions. At $T_1 = 100^\circ\text{C}$, boiling of pure water upon decompression proceeds by phase separation (the dotted line shows a metastable trajectory). The horizontal segment connects the two points representing the molar volumes of the liquid and the vapor. At the critical temperature T_{cr} , these molar volumes become equal and transition from liquid to vapor takes place in a continuous manner. The state referred to as one-phase fluid is a continuum between the liquid state and the gas state. The lowest temperature and pressure T_{cr} and P_{cr} at which this can happen define the critical point. Note that adding salt to water significantly increases both T_{cr} and P_{cr} .

the continents give an imperfect sampling of hydrothermal solutions: because the boiling point of hydrous solutions increases from 100°C at ambient pressure to more than 350°C at a few kilometers below the surface, the compositions and temperatures of thermal springs do not faithfully represent the properties of the solutions in contact with deep rock. Most hydrothermal springs therefore have been affected by intense boiling, to which they are subjected as they rise to the surface. In contrast, the emergence temperatures of the solutions spouted by the black smokers along mid-ocean ridges can reach 400°C because of the high pressure prevailing at the ocean floor (200–450 atmospheres), and better represent the original hydrothermal solutions. Many geologically (and economically) important hydrothermal reactions take place at even higher temperatures ($400\text{--}600^\circ\text{C}$). High-temperature solutions are often trapped in some minerals, such as quartz, in the form of fluid inclusions.

In order to understand hydrothermal reactions, we must examine phase changes and critical phenomena in high-temperature hydrous solutions. Let us first take some liquid water at 100°C in an autoclave pressurized by a neutral gas such as air and progressively release the pressure to the ambient value (Fig. 10.3): boiling goes on until all the liquid has changed into vapor. For the time it takes to evaporate the liquid, we have a two-phase fluid with liquid and vapor separated by a visible interface. If we measure the molar volume, it slightly increases upon decompression in the liquid domain, remains fixed during boiling,

and increases again, but much more rapidly, in the vapor domain. Let's now repeat the experiment at higher pressure and therefore at higher temperature: a similar sequence of events is obtained, but the difference between the molar volumes of the vapor and the liquid decreases with pressure, until we reach the critical pressure of 22 MPa. Then the volumes of both phases are identical and we pass continuously from the liquid field into the vapor field without seeing any interface. The temperature of the critical transition also is fixed at 374 °C. In nature, water is rarely pure and salts are dissolved, sometimes in large proportions (highly saline solutions are called brines). Adding salt to the solution increases both the temperature and pressure of the critical point. For example, a brine with 10 weight percent NaCl has a critical point at 700 °C and 120 MPa. Brine boiling produces rather light and dilute vapors and other brines, dense and even more concentrated in salt than the original solution. Highly concentrated brines with several tens of percent salt are important because they can dissolve enormous amounts of metals such as transition elements and rare-earth elements which, upon cooling, produce ore bodies of occasionally economical value. A hydrothermal fluid rich in Cl^- , most likely because it derives from seawater, must contain a heavy load of cations simply to equilibrate the negative charges. Another reason why hot brine chemistry is different from that of low-temperature solution is the low dielectric constant of water which enhances the recombination of ionic species, such as Na^+ , H^+ , and Cl^- , into molecular species, such as NaCl and HCl. Such molecular species are true complexes and increase the apparent solubility of metals in hydrothermal solutions. Hydrothermal deposits may form, however, from more diluted solutions at relatively low temperatures: this is the case of the Pb–Zn (base metal) Mississippi Valley-type ore deposits.

Balancing hydrothermal reactions requires a combination of cation-exchange reactions between the rock and the solution and the principle of electrical neutrality. First we need to draw up an inventory of proton/cation exchange reactions such as (7.22), which can be simply re-written:



For pure mineral phases, this equation leads to:

$$\ln \left(\frac{[\text{Na}^+]}{[\text{H}^+]} \right)_{\text{solution}} = \frac{\Delta H}{RT} + \text{constant} \quad (10.9)$$

At a given temperature, this ratio is constant. The enthalpy ΔH of the reaction varies from one reaction to another. A solution rich in H^+ therefore displaces cations from the rock more efficiently than a high-pH solution. This phenomenon is heavily dependent on temperature. Moreover, the positive charges must balance the negative charges, which are very often dominated by Cl^- , an anion scarcely involved in any mineral reactions and whose concentration remains virtually constant. The chemistry of the solution and therefore its capacity to modify the chemistry of the rock depends essentially on all the thermodynamic properties of exchange reactions and on temperature.

Among all the parameters of hydrothermal activity that need to be understood, temperature is, along with Cl concentration, the most important. For thermometry, it is

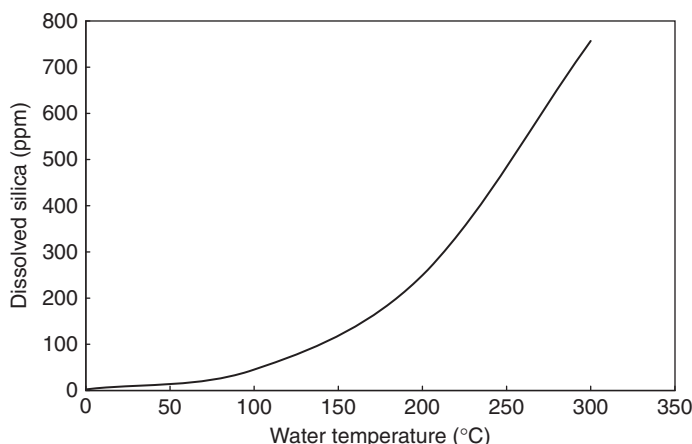
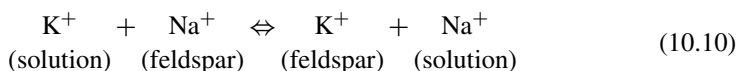


Figure 10.4 Solubility of silica in water. Silica contents of thermal waters can be used as a thermometer to a temperature of about 220 °C, and thus indicate the depth of equilibration. Above this temperature, amorphous silica precipitates as the fluid rises.

commonplace to utilize analysis of the water–rock equilibria for hydrothermal reaction thermometry, particularly K/Na fractionation induced by the exchange reaction between feldspar and the solution:



Assuming that feldspars in the reservoir zone of the solution have the compositions of common feldspars from granites and metamorphic rocks, the mass action law yields the equation:

$$\log_{10} \left(\frac{[\text{Na}^+]}{[\text{K}^+]}\right)_{\text{solution}} = \frac{908}{T} - 0.70 \quad (10.11)$$

The sodium and potassium contents of a hydrothermal solution therefore allow an equilibrium temperature with feldspar to be deduced. Solutions can also dissolve minerals without any reaction product: this is the case for silica, the content of which in spa water is used as a thermometer by writing the thermodynamic law of saturation (Appendix C):

$$\frac{d \ln [\text{SiO}_2]_{\text{solution}}}{d(1/T)} = \frac{\Delta H}{R} \quad (10.12)$$

where ΔH is the heat of dissolution of silica in water. By means of a few approximations and by introducing experimental values, the silica thermometer equation is:

$$\log_{10} [\text{SiO}_2]_{\text{solution}} = -\frac{1306}{T} + 0.38 \quad (10.13)$$

(note the logarithms with different bases). Assuming that there is surplus silica, which is true for most continental rocks, the measurement of the silica content of thermal water gives, with this equation, the equilibration temperature of the solutions with the deep rocks (Fig. 10.4).

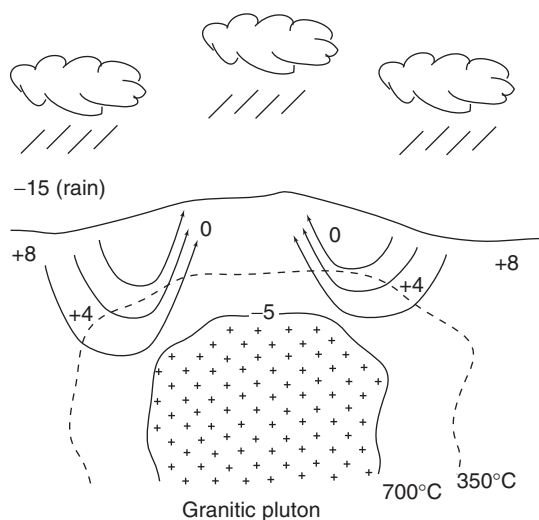


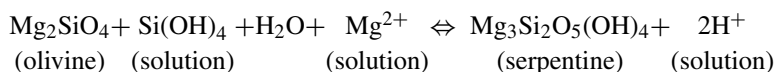
Figure 10.5 Geothermal system controlled by the emplacement of a granite pluton: rain water infiltrates and when heated in proximity to the intrusion becomes less dense and percolates back to the surface. Values shown (in ‰) are those of $\delta^{18}\text{O}$ of rock (and of precipitation). Rain water is strongly depleted in ^{18}O and changes the values of rocks, initially here at +8‰, to lower values of $\delta^{18}\text{O}$, depending on temperature and the water/rock ratio. Crystallization of the granite magmas may release magmatic waters.

From these solubility relationships, we gain some understanding of the mineral associations present in the fractures observed in granitic and metamorphic basements. Pegmatites, characterized by large crystals of albite and K-feldspars, precipitate from relatively high-temperature hydrous fluids (400–600°C), while the quartz veins, which are commonly associated with ore deposits, form at lower temperatures (200–400°C).

Water–rock interactions may also leave a profound mark on the isotopic compositions of the geothermal systems associated with magmatic provinces, such as Wairakei in New Zealand, Larderello in Italy, and the Geysers of California. Felsic intrusions emplaced at a few kilometers below the surface act as deep heat engines; they promote convection of the pore fluids and isotopic exchange between meteoric water and the rock matrix (Fig. 10.5). Rain water being particularly depleted in the heavy isotopes of oxygen and hydrogen, the $\delta^{18}\text{O}$ and δD of the magmatic intrusions themselves and of their country rocks are significantly shifted towards lower values upon exchange with meteoric water.

The markedly marine signature of isotopic compositions of oxygen and hydrogen in solutions from black smokers indicates that these formed by seawater infiltrating the edges of the ridges and by reaction at depth with the still hot basalt. Hydrothermal reactions at the mid-ocean ridges play an important role in the magnesium cycle and in controlling the alkalinity of the ocean. It has been observed that water from the black smokers of the ocean ridges is particularly acidic, i.e. its pH is much lower (typically 3) than that of deep ocean

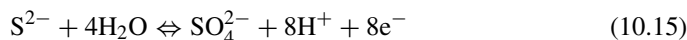
water (7.6), and that it is totally devoid of magnesium. This can be explained by reactions of seawater with common basalt minerals:



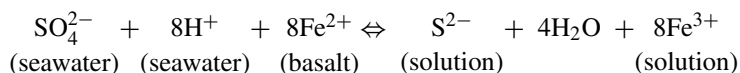
whose effect is to exchange the abundant Mg^{2+} in seawater for protons and therefore to reduce its alkalinity. In such reactions, the silica in the solution comes from dissolution of various enclosing igneous rocks (basalt, gabbro).

The redox reactions between seawater and hot basaltic rock first explains why hydrogen, methane, and ammonia continuously seep out from mid-ocean ridges and in aquifers located in ultramafic rocks, notably those of ophiolitic environments. The most important reactions are probably the oxidation of the ferrous component of Fe-olivine (fayalite) by water and its complement, the serpentinization of Mg-olivine (forsterite), which we discussed in the previous chapter; and the reaction of hydrogen with CO_2 and N_2 to produce methane and ammonia.

As the state of oxidation of the oceanic crust at the time it is subducted also dictates the long-term evolution of the redox state of the mantle, similar reactions involving iron and sulfur are also important. The two following half-reactions of oxidation–reduction:



can be represented schematically by oxidation in an acidic medium of the ferrous iron of magmatic rocks offset by reduction of marine sulfate into sulfide ions (see above for the origin of H^+ ions). By multiplying the first equation by eight and subtracting the second, we obtain:



Ferric ion precipitates as hydroxide Fe(OH)_3 and S^{2-} as sulfide minerals of iron and copper (chalcopyrite), and zinc (sphalerite) forming the mineralized submarine chimneys of the black smokers. Sulfur isotopes indicate, however, that, within the mid-ocean ridge hydrothermal systems, sulfur derived from seawater through the previous reaction is dominated by sulfur leached from the basaltic rocks. The sulfate-reduction reaction also transforms part of the ferrous iron of the oceanic crust into ferric iron stored as oxides or silicates (epidote). Subduction of the oceanic crust therefore controls not only mantle hydration but also its relative proportions of ferric and ferrous iron, and its electrical conductivity. The Earth's mantle, into which enormous amounts of oxidized crust have been recycled over the Earth's history, is thus far more oxidized than the Moon's mantle.

10.3 Metamorphism

Metamorphic transformations affect all rocks drawn down deep into the Earth by subduction. They are particularly perceptible where continents collide, i.e. when mountain ranges form. In contrast to hydrothermal reactions, these are largely, although not exclusively, dehydration reactions under the effect of temperature or excess CO_2 . Metamorphic facies correspond to given temperature and pressure ranges and these are usually bounded by specific mineralogical reactions: the greenschist facies (250–450 °C), the amphibolite facies (450–700 °C), and the granulite facies (> 700 °C) correspond to increasing temperatures at usual pressures; at higher pressures (> 30 km) we speak of blueschist facies, and at higher temperatures of eclogite facies.

The nomenclature of metamorphic rocks, based on their mineralogy, is fairly straightforward. Gneiss contains feldspar and quartz with variable proportions of other minerals and is frequently similar to granite in chemical composition. Schist contains little or no feldspar and is typically composed of quartz and mica; it is of similar composition to claystones. Amphibolite contains amphibole, with or without plagioclase feldspar; it is similar in composition to basalt. Most dehydrating metamorphic reactions could be described by dehydration reactions of the type described by (10.2) and represented by straight lines in a plot of $\ln P_{\text{H}_2\text{O}}$ vs. $1/T$ K, but it has become customary to represent metamorphic equilibria as curves on a simple pressure–temperature graph (T °C, $P_{\text{H}_2\text{O}}$). A metamorphic grid of this sort is commonly used to determine the temperature and pressure conditions prevailing in ancient metamorphic environments. Oxidation–reduction reactions are also used to determine temperature and oxygen pressure. Other reactions, finally, do not involve any fluid, as for example the polymorphic transformation of aluminum silicates:



Such reactions, not usually directly involving fluids, are represented by straight lines in pressure–temperature diagrams (Fig. 10.6). The position of the Clapeyron curve of these different reactions in pressure–temperature space must be carefully calibrated by experiment or obtained by thermodynamics (see Appendix C).

At this stage we should look more closely at the relationships between fluid pressure – the fluid for simplicity we take to be pure water – and the pressure of the surrounding rock. As water is about three times less dense than rock, the weight of a column of water is three times less than the weight of a column of rock of the same height. Near the surface, the pores are interconnected and interstitial fluid pressure is therefore equal to hydrostatic pressure. The weight of the water column being about one-third the weight of the rock column, pressure in the rock matrix (lithostatic pressure) is higher than that of interstitial water. With depth, the rock is compacted and the pores tend to close, progressively isolating the pore water a few kilometers beneath the surface. Fluid pressure and rock pressure are then in equilibrium. When the temperature of this unit is raised by a metamorphic event, as the water has greater thermal expansivity than rock, it is at higher pressure than the rock

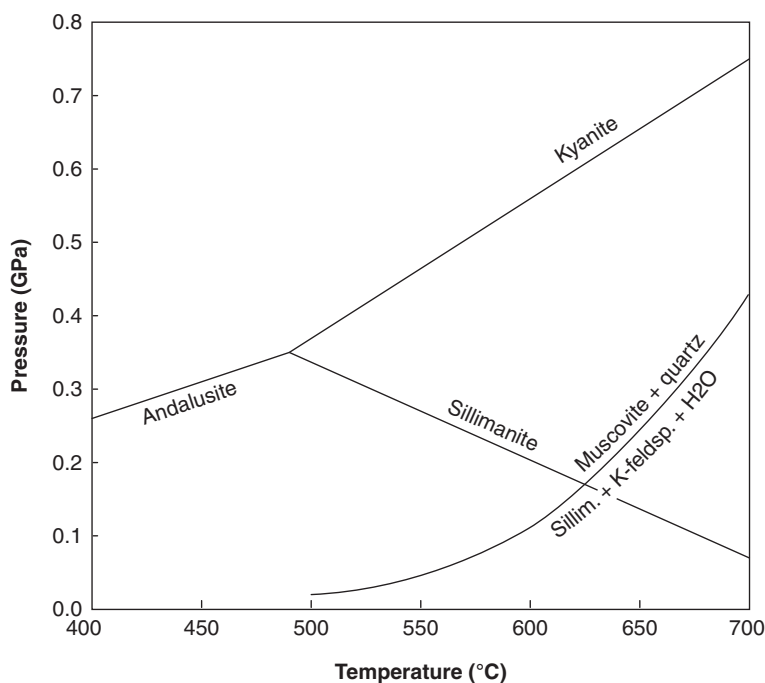


Figure 10.6 Metamorphic grid showing dehydration reaction curves that can be described by (10.2) and three solid-solid reactions for which the slopes are virtually constant.

matrix. As the tensile strength of the rock is generally low, this pressure contrast causes hydro-fracturing and water escapes.

Metamorphic dehydration reactions entail a loss of water but also of dissolved solids, and metamorphic rocks must be considered as open systems where very large quantities of water may have circulated. During this process, the chemical composition of the initial rock is transformed. As metamorphic reactions proceed, the distribution of trace elements and chronometric systems are severely disrupted but, because the system is open to fluid circulation, this rarely happens in a predictable way. Since, at the temperatures at which metamorphism occurs, ^{18}O tends to preferentially fractionate into the fluid (contrary to what happens at ordinary temperatures), the isotopic composition of the oxygen of rocks drifts toward lower $\delta^{18}\text{O}$ levels closer to those of the mantle. At temperatures in excess of 500°C , the oxygen isotope fractionation coefficients tend to unity, there is little water left to exchange oxygen with, and isotopic changes become less important.

Extreme metamorphic conditions cause rocks to melt when they have a high water content; the hydrated melting of common crustal metamorphic rocks is referred to as anatexis. When water is absent or the dominant fluid is CO_2 , granulite facies conditions pertain. Circulation of CO_2 promotes migration and the loss of elements that are normally inert under hydrated conditions: it is known that granulite facies rocks, which are so common at the base of the continental crust, have lost much of their uranium and some of their thorium. The production of heat in granulites of the deep part of the continental crust by the radioactive elements U, Th, and K is therefore usually very low, with, as a consequence, a distinctive isotopic composition of lead, which is in general unradiogenic.

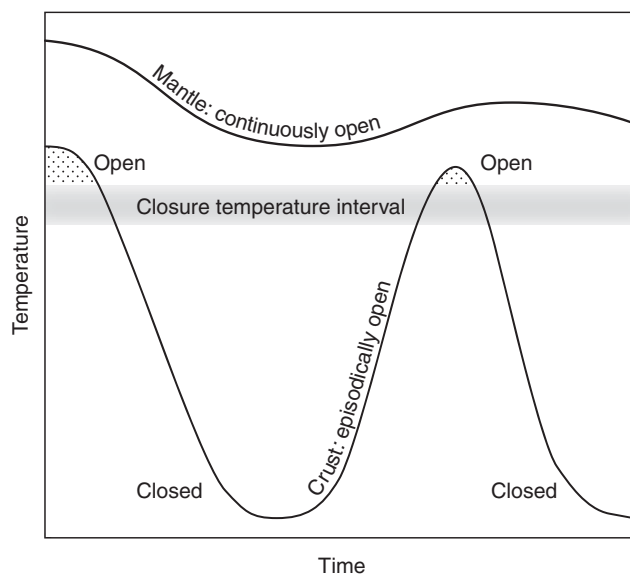


Figure 10.7

The common thermal pathways of rock samples from the mantle (top) and crust (bottom). The shaded zone represents the blocking temperature of a mineral reaction used to provide temperature and pressure estimates or the closure temperature of a chronometer such as garnet ^{176}Lu – ^{176}Hf ages. Temperatures of mantle rocks typically exceed 900°C : their minerals therefore remain continuously open to the exchange of elements and isotopes. In contrast, after original cooling to rather low temperatures, the PT -age estimates derived from crustal rocks may be episodically reset by geological events.

Metamorphic assemblages and, at depth, the metasomatic assemblages derived by reaction between mantle rocks and percolating fluids and magmas, are commonly used to derive equilibration temperatures and depth (pressure)–temperature–time (through geochronology) pathways in the mantle and the crust. Mineral assemblages can only be considered as equilibrium assemblages (they are then referred to as parageneses) and can therefore be used as thermometers or barometers if they cool rapidly enough to freeze mineral compositions under the conditions prevailing at high temperatures. In Chapter 5, we saw that, in the most general case, diffusion may maintain chemical exchange among minerals and between minerals and surrounding fluids. It is important that such exchanges do not affect a large fraction of mineral elements, in other words that cooling is fast. In the case of moderate cooling rates, metamorphic assemblages reflect not equilibrium PT -age conditions but the blocking (closure) temperature of chemical exchanges. This is a common situation of high-temperature assemblages, such as granulites and eclogites, in slowly cooling metamorphic terranes: the ubiquitous temperature range of 700 – 850°C observed for these rocks corresponds to the closure temperatures of many minerals, notably pyroxene and garnet.

Two additional complexities arise with pressure–temperature estimates in metamorphic and metasomatic assemblages (Fig. 10.7). First, it must be checked that the values observed reflect the temperature and the age of the original cooling and not those of a resetting during a subsequent reheating event above the closure temperature of the different mineral

reactions and chronometric systems. Migration of magmas or hot fluids on top of rift or subduction zones are prime potential culprits for such resetting events. Second, most rocks from the mantle and the deep crust never cooled below these blocking temperatures: they remained essentially open systems since they formed. If such an open system behavior is nearly perfect, the thermobarometric estimates can be used to derive modern geotherms, e.g. the P - T relationship in the local mantle. Such a behavior is best assessed by checking that the chronometric ages correspond to the time these rocks rose to the surface (e.g. the eruption age of ultramafic inclusions in volcanic rocks). If, however, the chronometric ages of these rocks are substantially older than the time of their final ascent, the P - T observations should be treated with utmost care. In the absence of zircons in the mantle, garnet ^{176}Lu - ^{176}Hf ages have proved to be particularly helpful in this context. It is therefore worth stressing that most rocks from the mantle should be a priori treated as open systems and that attempts to interpret the major and trace element concentrations and the isotopic properties of their minerals as reflecting those prevailing at the time they formed are probably bound to be erroneous. The lack of equilibration among minerals of mantle rocks is therefore not a sufficient indication of a metasomatic event. In contrast, most of the crustal rocks have cooled through the closure temperature and some of them have been reworked over different tectonic and magmatic events.

10.4 Water/rock ratios

The motivations for finding out how much water a given rock sample has “seen” during diagenetic, hydrothermal, or metamorphic processes are varied: we may want to assess the reserves of a particular element of economic value remaining in the source rock of a particular ore deposit, we may need to know how far water circulation affected the thermal regime of a given area, or we may worry that too much circulating water disturbed the initial geochemical properties of a rock, a mineral, or fossil remains. In order to provide a quick estimate of the extent of water-rock interaction, geochemists often refer to the concept of a water/rock ratio. Given a set of geochemical observations on an altered rock or a diagenetic/hydrothermal solution, geology may often give some hints at what the untransformed rock may have looked like (a basalt, a granite), while other constraints may be good enough to let us infer the geochemistry of the reacting fluid (meteoritic water at a given latitude, for instance). A number of geochemical properties can be used as well, concentrations and isotopes, but probably the most popular are $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$. Let us suppose, for instance, that we measured the $\delta^{18}\text{O}_{\text{HR}}$ of a hydrothermally altered basalt sample to be -2‰ , while examination of thin sections suggests that the rock was hydrothermally altered at 350°C in the greenschist facies. Paleogeography also suggests that when this particular basalt was erupted, the latitude was such that meteoric water had a $\delta^{18}\text{O}_{\text{MW}}$ of -10‰ . We will assume that the $\delta^{18}\text{O}_{\text{FR}}$ of the fresh basalt was in the range of mantle-derived magmas, say $+5.5\text{‰}$. Can we find out how much water interacted with this particular basaltic sample before it turned into a metabasalt?

We will note R and W the mass of rock and water, respectively, reacting with each other, and neglect the fact that water and rock contain slightly different oxygen concentrations. We can write the isotopic mass balance during the reaction as

$$R\delta^{18}\text{O}_{\text{FR}} + W\delta^{18}\text{O}_{\text{MW}} = R\delta^{18}\text{O}_{\text{HR}} + W\delta^{18}\text{O}_{\text{HW}} \quad (10.17)$$

where HW refers to the hydrothermal solution, which, unfortunately, can no longer be sampled and analyzed. Rearranging, we get the water/rock (W/R) ratio as:

$$\frac{W}{R} = \frac{\delta^{18}\text{O}_{\text{FR}} - \delta^{18}\text{O}_{\text{HR}}}{\delta^{18}\text{O}_{\text{HW}} - \delta^{18}\text{O}_{\text{MW}}} \quad (10.18)$$

It is often observed that, for mass balance reasons, the $\delta^{18}\text{O}$ value of igneous whole-rocks is similar to that of their feldspar. This property allows us to estimate the $\delta^{18}\text{O}$ of the hydrothermal water from the $\delta^{18}\text{O}$ of the altered rock and the fractionation factor of $^{18}\text{O}/^{16}\text{O}$ between feldspar and water at 350 °C, i.e:

$$\delta^{18}\text{O}_{\text{feldspar}} = \delta^{18}\text{O}_{\text{HW}} + 4 \quad (10.19)$$

Rearranging, we get the water/rock (W/R) ratio as:

$$\frac{W}{R} = \frac{5.5 - (-2)}{(-2) - 4 - (-10)} = 1.875 \quad (10.20)$$

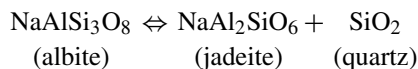
Water/rock ratios in the range 1–5 are very common. These values are in general minimum values and much higher values (up to several hundred) are not exceptional, especially during diagenesis. Examples based on Sr isotopes may be constructed in a similar way.

Exercises

1. Show that if the changes of enthalpy $\Delta H(T, P)$, entropy $\Delta S(T, P)$, and volume $\Delta V(T, P)$ of a reaction are approximately constant, (C.11) in Appendix C can be integrated into

$$\Delta G(T, P) \approx \Delta H_0 - T\Delta S_0 + \Delta V_0(P - 1) \quad (10.21)$$

where $\Delta G(T, P)$ is the free enthalpy of the reaction at T and P and the subscript 0 denotes a reference state (usually 298 K and 1 bar). Show that at equilibrium, this relation provides an equation for the reaction curve. Use the previous result to draw the reaction curve defining the onset of the eclogite facies:



in which the sodic plagioclase breaks down into a sodic pyroxene, which dissolves into ambient clinopyroxene and quartz. Use the following values: $\Delta H_0 = -2115 \text{ J mol}^{-1}$, $\Delta S_0 = -32.25 \text{ J mol}^{-1} \text{ K}^{-1}$, and $\Delta V_0 = -17.0 \cdot 10^{-6} \text{ m}^3$.