Table 12.7   Equilibrium constants for metal ion–organic ligand complexation.

Log β						
	Glycine[1]	Glutamate[2]	Acetate[3]	Citrate[4]	Malonate[5]	Salicylate[6]
H^+	9.78	9.95	4.76	6.4	5.7	13.74
Na^+				1.4	0.7	
K^+				1.3		
Mg^{2+}	2.7	2.8	1.3	4.7	2.9	
Ca^{2+}	1.4	2.1	1.2	4.7	2.4	0.4
Al^{3+}			2.4			12.02
Ba^{2+}	0.8	2.2	1.1	4.1	2.1	0.2
Fe^{3+}	10.8	13.8	4.0	13.5	9.3	17.6
Fe^{2+}	4.3	4.6	1.4	5.7		7.4
Ni^{2+}	6.2	6.5	1.4	6.7	4.1	7.8
Cu^{2+}	8.6	8.8	2.2	7.2	5.7	11.5
Zn^{2+}	5.4	5.8	1.6	6.1	3.8	7.7
Pb^{2+}	5.5		2.7	5.4	4.0	
Hg^{2+}	10.9		6.1	12.2		
Ag^+	3.5		0.7			

[1]$NH_2CH_2(COO)^-$
[2]$(HOOC)(CH_2)_2CHNH_2COO^-$
[3]$C_2H_5COO^-$
[4]$(HOOC)CH_2C(OH)(COOH)CH_2COO^-$
[5]$CH_3CH_2COO^-$
[6]$HOC_6H_4COO^-$
From Morel and Hering (1993) Table 6.3. With permission from John Wiley & Sons.

constants in excess of 10^{30}, so they are indeed very strong chelators. Iron in aerobic environments is in the ferric form and as such highly insoluble. Consequently, concentrations of dissolved Fe^{3+} are quite low in the surface waters of the ocean. Iron is biologically essential for a number of reasons, including its role in photosynthesis. In some areas of the ocean, iron appears to be the nutrient limiting photosynthesis. Some iron-specific chelators, known as *siderophores*, are released by marine heterotrophic bacteria and cyanobacteria for the express purpose of acquiring iron. In such iron-poor surface waters, as much as 99% of the dissolved Fe^{3+} appears to be bound to organic complexes (Hutchins *et al.*, 1999).

Just as for inorganic metal–ligand complexes, we can define stability constants (β) and apparent stability constants (β^*) for metal–organic ligand complexes. Table 12.7 lists some examples of stability constants for metal–organic complexes that we might expect to find in natural waters. Several generalizations may be made. First, as we saw for inorganic ligands, the higher the valence state

of the metal, the stronger the complex. Thus in Table 12.7, Fe^{3+} forms stronger complexes with all listed ligands than does Fe^{2+}. Second, there is high degree of correlation between the equilibrium constants of all organic ligands for a given metal. For the divalent metals, stability of metal–organic complexes follows the Irving-Williams series (Chapter 6), $Pb^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+} > Mg^{2+}$.

It is the functional groups of organic molecules that are primarily responsible for metal ion complexation. Amines, azo- compounds (compounds containing a –N=N– group linking two other groups), ring nitrogen, carboxyl, ether, and ketone are all important in complex formation. Tetrapyrrole pigments, or porphyrins such as chlorophyll are very strong metal ion complexing agents, particularly for transition metals such as Zn and Ni. In the case of chlorophyll and similar molecules, complex formation occurs through replacement of Mg with a transition metal ion. In this instance, the metal is bound to two nitrogens (see Figure 12.15).

Multidentate complexes are generally more stable than corresponding unidentate ones. We can see this in Table 12.7, where the stability constants for citrate, with 3 carboxyl-binding sites, are higher than those for acetate with one carboxyl-binding site. Another interesting property of multidentate ligands is that the degree of complexation decreases less strongly with dilution than for monodentate complexes.

As was the case for inorganic complexes, the stability of metal–organic complexes is invariably strongly pH-dependent. The reason for this is simple: hydrogen ions will be major competitors for sites on functional groups. Indeed, we can write the complexation reaction as:

$$m\,M + l\,HL \rightleftharpoons M_mL_l + H^+$$
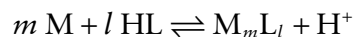
the equilibrium constant for this reaction is then:

$$K = \frac{[M_mL_l]a_{H^+}}{[M]^m[HL]^l} \qquad (12.5)$$

or in log form:

$$\log K = \log[M_mL_l] - m\log[M] - l\log[L] - pH \qquad (12.6)$$

We should also note that for multidentate ions, mixed hydrogen–metal and hydroxide–ligand complexes are possible. These will become increasingly important at low and high pH respectively. For example, at pH values below about 3, the CuHCitrate complex will be dominant over the simple Cu-citrate complex. In another example, the FeOHGlycolate complex will be more important at all pH values than the simple Fe-glycolate complex. For clarity, we have omitted stability constants for these mixed complexes from Table 12.7. Nevertheless, as these examples show, these mixed complexes must often be considered in speciation calculations, particularly at high and low pH. A more complete compilation of stability constants for metal–organic complexes may be found in Morel and Hering (1993).

Humic and fulvic acids are, as we have seen, usually the most abundant dissolved organic compounds. The functional groups on these substances are capable of complex-ing metals. A variety of experiments suggest the majority, 50–90%, of these functional groups are carboxyl groups, followed in importance by phenol and alcohol groups. When two or more of these functional groups are present in close proximity on the molecule, humic substances will act as chelators and complex metals in a manner similar to simpler multidentate organic molecules. Salicylic acid, with a carboxylic and phenolic group, can be used a simple analog for humic substances in this respect. Considering the stability constants for salicylate complexes listed Table 12.7, we would expect humic substances to complex strongly with trace metals. This appears to be the case, although the situation is somewhat complicated because the different binding sites of humic substances have differing metal affinities. Experiments suggest that overall stability constants for trace metal–humic substance complexes are in the range of 10^5 (for Zn^{2+}, Cd^{2+}, and Ni^{2+}) to 10^{10} (for Cu^{2+}) (e.g., Buffle et $al.$, 1980; Zuehlke and Kester, 1983).

It is not possible, however, to assign specific values to stability constants (or acidity constants for that matter) for humic substances. This seems to be a reflection of several factors, including electrostatic interaction between neighboring functional groups and distortions of the molecule that result from cation binding and neighboring charges in solution. The latter leads to a strong dependence of apparent stability constants on ionic strength. There has been some success in modeling humic and fulvic acids using simple empirical models (e.g., Cabaniss and Shuman, 1988) as well as more theoretical ones that assume the binding properties can be described by combining the complexation properties of a few simple organic compounds (e.g., acetate, malonate, and catechol) together with a consideration of the coulombic attraction of neighboring groups (Bartschat et $al.$, 1992; Morel and Hering, 1993).

The degree to which dissolved trace metals in natural waters are complexed by organic ligands varies by environment. There is now a good body of observational evidence showing that a large fraction of at least some trace metals (particularly Fe, Cu, and Zn) is complexed by organic ligands in streams, lakes, and ocean surface waters (e.g., Ellwood, 2004; Hoffmann et $al.$, 2007). In some cases,

Example 12.1   Speciation of organic ligands in fresh water

Using the stability constants in Table 12.7, and the calculated free ion activities for major cations in Example 6.8, calculate the speciation of glycine, citrate, and salicylate. Assume total activities of glycine, citrate, and salicylate of 1.25×10^{-8}, 5×10^{-8}, and 1×10^{-8} M/l respectively.

Answer: For each ligand, we can write a conservation equation:

$$\Sigma L = L^- + HL + AL + BL + CL + \dots \tag{12.7}$$

where L^- is the free ligand, HL is the undissociated acid, and AL, BL, CL, etc., are the various metal ligand complexes. For each species we may also write:

$$[ML] = \beta \times [M] \times [L^-] \tag{12.8}$$

where [ML], [M], and [L^-] are the concentrations of the complex, free metal ion or proton, and free ligand respectively. Substituting eqn 12.8 into 12.7, we have:

$$\Sigma L = [L^-] + \beta_{HL}[H][L^-] + \beta_{AL}[A][L^-] + \beta_{BL}[B][L^-] + \dots \tag{12.9}$$

Rearranging, we have:

$$[L^-] = \frac{\Sigma L}{1 + \beta_{AL}[A] + \beta_{BL}[B] + \dots} \tag{12.10}$$

Since the concentrations of the organic ligands are much lower that those of the major cations, we can assume that organic complexation does not affect activities of the major cations. Equation 12.10 gives us the free ion concentration. From that, we can calculate the concentration of each of the complexes using eqn 12.8. The result is shown in the adjacent table. We see that at the pH of this example (8), glycine and salicylate are esssentially completely undissociated. Citrate is almost completely dissociated, but is 95% complexed by Mg and Ca.

Speciation of organic ligands			
	Glycine	**Citrate**	**Salicylate**
H	98.24%	0.11%	100.00%
Na	0.00%	0.03%	0.00%
K	0.00%	0.01%	0.00%
Mg	0.11%	31.77%	0.00%
Ca	0.01%	63.55%	0.00%
Free ligand	1.63%	4.53%	0.00%
Activity of free ligand	2.04×10^{-10}	2.26×10^{-9}	1.82×10^{-14}

more than 99% of the metal in solution is present as organic complexes. In the ocean surface water, the extent of complexation seems to be somewhat variable; in deep water, far smaller fractions of metal ions appear to be organically complexed. (e.g., Baars and Croot, 2011). The organic ligands complexing these metals can have stability constants in excess of 10^{20} (e.g., Witter *et al.*, 2000). Many of these complexing agents, such as trihydroxamate siderophore desferriferriox-amine B, are produced by organisms to acquire essential trace metals such as Fe. They may produce others to defend themselves against the toxicity of others, such as Cu and Pb. It is interesting in this respect that Zn falls into both categories. It is toxic at high concentrations, yet essential for a number of biological processes such as nucleic acid transcription.

Example 12.2 demonstrates that glycine, a common amino acid, and citrate, a common hydroxy-carboxylic acid, and salicylate, a

Example 12.2   Speciation of Cu in fresh water

Cu stability constants	
	log β
CuOH⁺	6.3
Cu(OH)₂	11.8
CuCl⁺	0.5
CuCO₃	6.7
CuSO₄	2.4

Use the adjacent stability constants as well as those for glycine, citrate, and salicylate in Table 12.7 to calculate the speciation of Cu in the water sample analysis in Example 6.8, assuming $\Sigma Cu = 10^{-9}\,M$. Use the calculated free ion concentrations of anions in Examples 6.8 and 12.1.

Answer: In calculating trace element speciation, it is common to assume that complexation with trace metals does not reduce the free ion concentrations of the anions. For this assumption to be valid, the free ion concentrations of the anions should greatly exceed those of the trace metal. This condition is met in this case for the inorganic anions, but not for the organic ones. Nevertheless, we will proceed by making this assumption initially and subsequently examine its validity and make the necessary corrections. We proceed much as we did in Example 12.1, by writing a conservation equation for copper:

$$\Sigma Cu = [Cu^{2+}] + [CuOH^+] + [Cu(OH)_2] + [CuCl^-] + [CuCO_3] + [CuSO_4] + [CuGly] + [CuCit] + [CuSal] \tag{12.11}$$

For each species, we also write a mass action equation, for example:

$$CuCit = \beta_{CuCit} \times [Cu^{2+}] \times [Cit] \tag{12.12}$$

Substituting the mass action equations into eqn 12.11 and solving for $[Cu^{2+}]$, we have:

$$[Cu^{2+}] = \frac{\Sigma Cu}{1 + \sum_i \beta_{CuL_i}[L_i]} \tag{12.13}$$

We can then calculate the concentrations of the individual species using eqn 12.12. The results are shown in the adjacent table. We see that Cu is dominantly complexed by hydroxyl and carbonate. The three organic complexes account for only about 1% of the total copper.

Calculated copper speciation		
	Conc.	**%**
CuOH⁺	2.12×10^{-10}	21.22%
Cu(OH)₂	6.71×10^{-11}	6.71%
CuCl⁺	7.03×10^{-14}	0.01%
CuCO₃	5.97×10^{-10}	59.69%
CuSO₄	4.41×10^{-12}	0.44%
CuGly	8.63×10^{-12}	0.86%
CuCit	3.82×10^{-12}	0.38%
CuSal	6.12×10^{-13}	0.06%
Cu²⁺	1.06×10^{-10}	10.63%

Now let's examine our initial assumption that Cu speciation does not reduce the free ion activities of the anions. With the exception of copper salicylate, the concentration of each species is far less than the free ion concentration of the corresponding anion. In the case of salicylate, however, the concentration exceeds the total free ion concentration of salicylate, a clear indication that our initial assumption was invalid. We could address this problem by performing an iterative calculation such as that used in Example 6.8. However, an examination of the situation reveals a simpler approximate solution. The concentration of free salicylate is far below that of free copper. Furthermore, the stability constant for copper salicylate is very large. In these circumstances, all available salicylate will be complexed with free copper, so we may replace our calculated CuSal concentration with that of the free salicylate concentration we calculated in Example 14.1, 1.82×10^{-14} M. This is a trivial fraction of the total copper. Stream and lake water is likely to contain trace concentrations of other metals that are strongly bound by salicylate, such as Fe. This would further reduce the copper salicylate activity.

common phenolate, will complex only a small fraction of the total Cu in fresh water with typically low concentrations of these substances. We see that this is due to several factors. First, at this pH, most of the glycine and salicylate are undissociated (Example 12.1), and therefore unavailable to bind Cu, and 95% of the citrate is complexed with Ca and Mg. Second, the greater abundance of inorganic anions such as hydroxyl and carbonate results in their dominating the speciation of Cu. However, one should avoid drawing the conclusion that organic trace metal complexes are inevitably insignificant. We considered only three species in this example, and while they strongly bind copper, all are at fairly low concentrations. Other organic anions, particularly including humates, are often present at sufficient concentration to complex a significant fraction of some trace metals. Problems 5 and 6 at the end of this chapter illustrate that situation.

The complexing behavior of humic substances is, well, complex, and cannot be characterized by a single stability constant. This is true for several reasons. First, different functional groups can be present on a single molecule, each of which will have a different intrinsic stability constant and pK_a. Second, these functional groups are close enough to one another that the electrostatic charge of one site can affect the complexing properties of an adjacent one (recall that this was also true of surfaces: see Chapter 6). In particular, protonation and deprotonation changes the charge on the humate molecule, which will affect its attraction for metal ions. As a result,
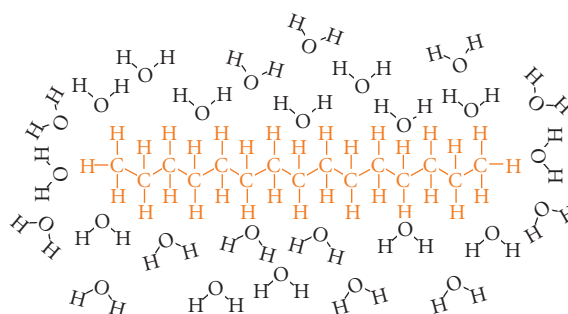

Figure 12.27 Disruption of water molecules by a large nonpolar organic molecule, in this case a C_{15} n-alkane.

metal–humate stability constants vary as a function of pH. A full treatment of this problem is beyond the scope of this book, but may be found in Morel and Hering (1993).

12.6.3   Adsorption phenomena

12.6.3.1   *The hydrophobic effect and hydrophobic adsorption*

Water molecules near large nonpolar molecules such as long chain hydrocarbons cannot orient their polar OH bonds as they normally would (Figure 12.27). Since water molecules normally orient themselves in a manner that reduces electrostatic repulsions and minimizes interaction energy, the presence of a large nonpolar molecule is energetically unfavorable. As a result, solution of such substances, called *hydrophobic substances*, in water is associated with a large ΔH_{sol} and large ΔG_{sol}.

Thus one characteristic of hydrophobic substances is limited solubility in water. A second characteristic is that when they are present in solution, they are readily absorbed on to nonpolar surfaces, such as those of organic solids.

Hydrophobic adsorption differs from other types of adsorption phenomena in that adsorption occurs not as a result of an affinity of the surface for the solute, but because of incompatibility of the hydrophobic compound with water. When a hydrophobic molecule is located on a surface, water molecules are present on one side only, and there is less disruption of water structure than when water molecules are located on both sides. Thus the interaction energy is lower when the substance is located on a surface rather than in solution. Other types of adsorption involve electrostatic or van der Waals interactions or formation of bonds between the surface and the solute. While electrostatic and, particularly, van der Waals interactions generally contribute to hydrophobic adsorption, they are of secondary importance compared to the minimization of interaction energy between the solute and water.

Hydrophobic adsorption can be described by a simple model of partitioning of the hydrophobic species between water and an absorbent. The adsorption partition coefficient, K_P, is defined as:

$$K_P = \frac{moles\ sorbate\ /\ mass\ solid}{moles\ solute\ /\ volume\ solution} \quad (12.14)$$

and is typically expressed in units of liters/kilogram. The magnitude of the adsorption partition coefficient for hydrophobic species is related in a simple way to the solubility of the species in water, as illustrated in Figure 12.28a: the least soluble compounds are most strongly adsorbed. The aqueous solubility of such species may be further related to the octanol–water partition coefficient (Figure 12.28b). Octanol is a largely nonpolar molecule, so that there is little structure or ordering of molecules in liquid octanol as there is in water. Thus there is no disruption of solvent molecules when a nonpolar solute is dissolved in octanol. The octanol/water partition coefficient is thus a measure of the "hydrophobicity" of organic molecules. The adsorption coefficient for hydrophobic substances on
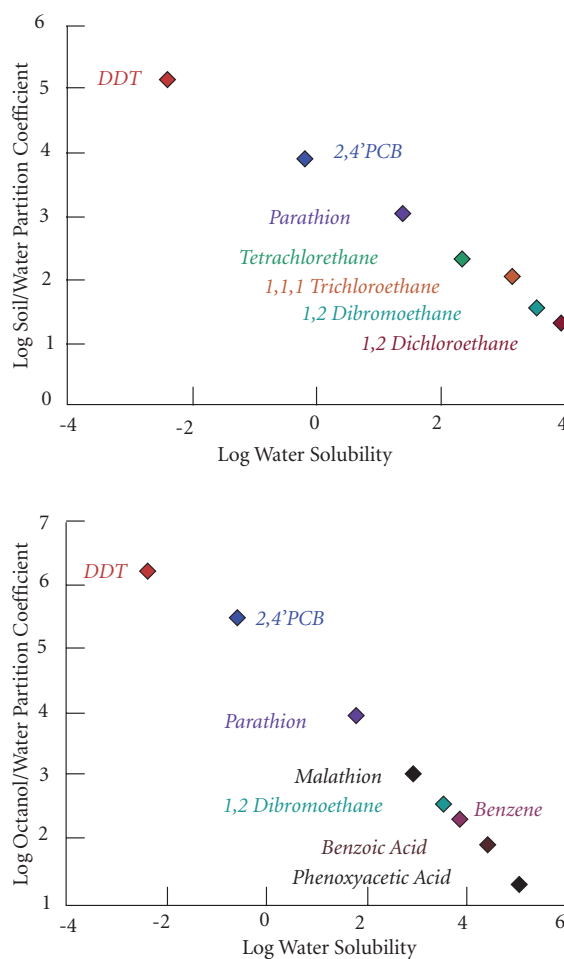

Figure 12.28 (a) Soil/water adsorption partition coefficients for a variety of organic compounds as a function of water solubility, determined by Chiou *et al.* (1979). (b) Octanol/water partition coefficients as a function of water solubility of organic compounds, determined by Chiou *et al.* (1977). Reprinted with permission of AAAS.

organic substrates may be empirically estimated by the following relationship:

$$K_{om} = b(K_{O/W})^a \quad (12.15)$$

where K_{om} is the partition coefficient between organic solids and water, $K_{O/W}$ is the octanol/water partition coefficient, and *a* and *b* are empirical constants, with the value of *a* being around 0.8. From this, a more general expression for mixed organic/inorganic surfaces may be derived:

$$K_P = bf_{OC}(K_{O/W})^a \qquad (12.16)$$

where f_{oc} is the fraction of organic matter in the solid. Comparing eqns. 12.15 and 12.16, we see that:

$$K_{om} = K_P/f_{OC} \qquad (12.17)$$

In general, the solubility of organic molecules decreases with increasing molecular weight. This observation, known as *Traube's Rule*, is apparent from Figure 12.28. Small polar molecules such as phenoxyacetic acid and benzoic acid have higher solubilities and lower octanol/water partition coefficients than do large nonpolar ones such and DDT and PCBs (polychlorinated biphenols). It is easy to understand why this should be so: the larger the molecule, the greater the volume of water whose structure is disrupted. In addition, the tendency of a molecule to be absorbed and the strength of this adsorption increases with atomic weight. In part, this is true for the same reason solubility decreases: a greater volume of water is disrupted by large molecules. However, as we noted above, van der Waals interactions between the adsorbed substance and the surface also contribute to hydrophobic adsorption. These interactions increase with increasing size of the molecule. Van der Waals interactions contribute a surface binding energy of roughly 2.5 kJ/mol per CH_2 group on the surface. Clearly, the more CH_2 groups involved, the more strongly the substance will be bound to the surface. For this reason, polymers are readily adsorbed to surfaces even if the adsorption free energy per segment is small. Adsorption of large polymers can be virtually irreversible.

Hydrophobic molecules are adsorbed preferentially to organic surfaces, which are largely nonpolar, rather than inorganic ones. Thus the degree to which hydrophobic substances are absorbed will depend on the fraction of organic matter that makes up solid surfaces. This is illustrated in Figure 12.29.

12.6.3.2   Other adsorption mechanisms

Many naturally occurring organic molecules contain both a polar and a nonpolar part. Such molecules are called *amphipatic*. A good example is fatty acids, which, as we have seen, consist of hydrocarbon chains with a carboxyl
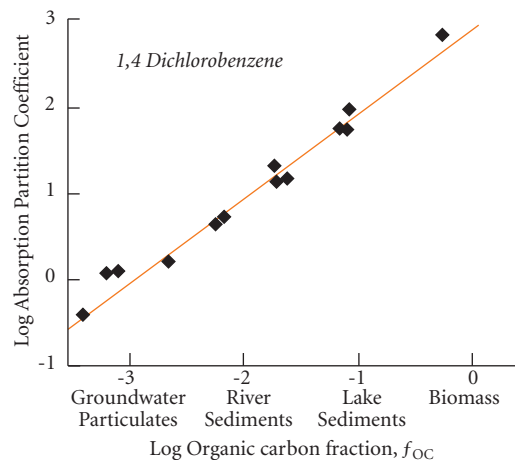

Figure 12.29 Adsorption partition coefficient for 1,4 dichlorobenzene plotted as a function of fraction of organic carbon in the solid absorbent. Other hydrophobic molecules show similar relationships. Schwarzenbach and Westall (1981). Reprinted with permission from the American Chemical Society.

group attached to one end. The hydrocarbon chain is nonpolar and hydrophobic. The carboxyl group, however, is quite polar upon dissociation. The carboxyl group itself is readily soluble in water (as demonstrated by the high solubilities of simple carboxylic acids such as formic and acetic acids) and is hence *hydrophilic*. Carboxyl groups are therefore not subject to hydrophobic adsorption except at very low pH, where they are undissociated. They can, however, bind to polar solid surfaces in much the same way as inorganic ions. These include reactions such as *ligand exchange*:

$$\begin{aligned} S{-}OH + COOH(CH_2)_n CH_3 \\ \rightleftharpoons S{-}COO(CH_2)_n CH_3 + H_2O \end{aligned} \qquad (12.18)$$
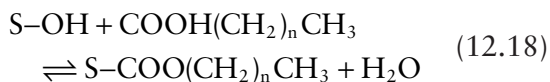
where the carboxyl group, less its hydrogen, exchanges for an OH group bound to surface S. Polar function groups or organic anions may also bind to surfaces through *water bridging*, in which complexation with a water molecule solvating an exchangeable cation at a surface occurs:

$$\begin{aligned} S{-}M^+(H_2O) + COOHR \\ \rightleftharpoons S{-}M^+(H_2O){-}COOHR \end{aligned} \qquad (12.19)$$
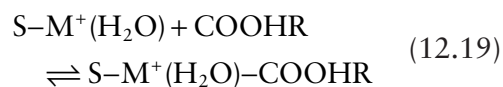
This mechanism is most likely to occur where M is strongly solvated (Mg^{2+} for instance). Where M is not strongly solvated, *cation bridging*, in which there is a direct bond between the acid functional group and the metal, can occur:

$$S-M^+ + COO-R \rightleftharpoons S-M^+-COO-R \quad (12.20)$$
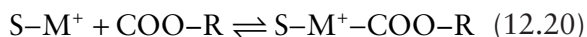
For cationic functional groups, such as quarternized nitrogen, *cation ion exchange* reactions such as:

$$S-M^+ + NH_3^+R \rightleftharpoons S-NH_3^+R + M^+ \quad (12.21)$$
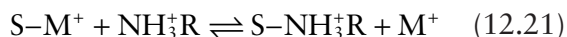
where an organic cation replaces a metal cation at a surface are possible. For anionic functional groups, such as carboxylic acids, anion ion exchange can occur. This is the analogy of reaction 12.18 with the signs reversed, for example, a carboxyl group in anion form replacing a surface OH^- group.

All the above reactions may occur at either organic or inorganic surfaces. *Hydrogen bonding* in which a hydrogen is shared between a surface O atom and an O atom in a dissolved organic such as a carboxyl or phenol group, can occur at organic surfaces, for example:

$$S-H^+ + COO-R \rightleftharpoons S-H^+-COO-R \quad (12.22)$$
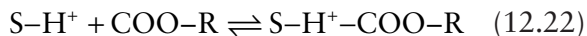
Hydrogen bonding is not restricted to acids. Organic bases, notably those containing nitrogen groups such as amines and pyridines, can also form hydrogen bonds with a hydrogen at a solid surface. Hydrogen bonding between dissolved organics and mineral surfaces is less important because the oxygens of mineral surfaces are not as electronegative as in organic compounds.

Many organic compounds will thus be subject to several types of adsorption: nonpolar parts may be adsorbed to surfaces through hydrophobic bonding, while polar groups may bind through the mechanisms just described.

12.6.3.3 Dependence on pH

Figure 12.30 shows the effect of pH on the adsorption of humic acid on Al_2O_3; the extent of adsorption is greatest at a pH of about 3 and is generally greater at low pH than at high pH. This pH dependence arises because
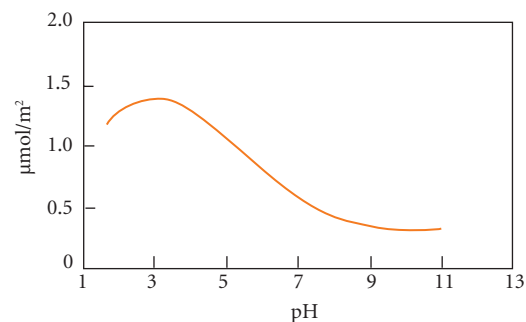

Figure 12.30 Adsorption of humic acid on $\delta\text{-}Al_2O_3$ as a function of pH. Stumm (1992). With permission from John Wiley & Sons.

the availability of hydrogen ions in solution will affect the charge on a solid surface in contact with that solution. At pH below the isoelectric point of a mineral, mineral surfaces will be protonated and will carry a positive charge; at higher pHs the mineral surface will bear a negative charge. Furthermore, dissociation and protonation of organic functional groups, which will affect the extent of adsorption through the mechanisms discussed above, is pH-dependent.

Clearly, pH will also affect the mechanism of adsorption. Carboxyl acid groups of a humic acid molecule might bind to a surface through cation bridging at high pH where the surface has a net negative charge. At low pH, carboxyl groups will bind to a protonated surface through hydrogen bonding. At a pH close to that of the isoelectric point of a mineral, its surface will be neutral, in which case a humic acid would be subject to hydrophobic adsorption through its nonpolar parts. Thus the mechanism of adsorption and the strength of the bond formed between adsorbent and adsorbate will be influenced by pH.

12.6.3.4 Role in weathering

Adsorption and the formation of surface complexes play a key role in weathering reactions. Organic acids can play an important role in accelerating weathering reactions in several ways: (1) by forming surface complexes, particularly surface chelates that weaken metal–oxygen bonds in the crystal and thus promote removal of metals from the surface; (2) by forming complexes with metals in solution,

reducing the free ion activities and increasing ΔG of the weathering reaction; (3) by lowering the pH of solution (Drever and Vance, 1994; Bennett and Casey, 1994); and (4) by precipitating and stabilizing soil minerals (as reviewed in Lucas, 2001). Mycorrhiza, a symbiotic association of the fungi and plant roots, are most often responsible for these processes rather than plants themselves (Leake *et al.*, 2004). In addition, organic substances serve as electron donors in the reductive dissolution of Fe and Mn oxides and hydroxides. These effects have been demonstrated in a variety of laboratory experiments (e.g., Furrer and Stumm, 1986; Zinder *et al.*, 1986) and electron microscopy of minerals exposed to high concentrations of organic acids in both natural and laboratory situations (e.g., Bennett and Casey, 1994).

Furrer and Stumm (1986) investigated the effect of a variety of simple organic acids on dissolution of δ-Al$_2$O$_3$ and demonstrated a first-order dependence of the dissolution rate on the surface concentration of organic complexes:

$$\mathfrak{R} = k\,[S{\equiv}L]$$

where [S≡L] is the surface concentration of organic complexes. Bidentate ligands that form mononuclear surface complexes seemed particularly effective in increasing dissolution rate. (There appears to be some evidence that formation of polynuclear surface complexes retards dissolution; Grauer and Stumm, 1982.) Five- and six-member chelate rings were more effective in enhancing dissolution rate than seven-member rings (Figure 12.31). Though monodentate ligands such as benzoate were readily adsorbed on to the surface, they had little effect on dissolution rate. Similarly, Zinder *et al.* (1986) demonstrated a first-order dependence of the dissolution rate of goethite (FeOOH) on oxalate concentration.

In general, low molecular weight organic acids are more effective in accelerating mineral dissolution than larger molecules, such as humic and fulvic acids. Zhang and Bloom (1999) found that the relative effectiveness of ligands in promoting dissolution of hornblende was oxalic > citric > tannic > polygalacturonic > fulvic acid. Similarly, Khademi *et al.* (2010) showed that the addition of
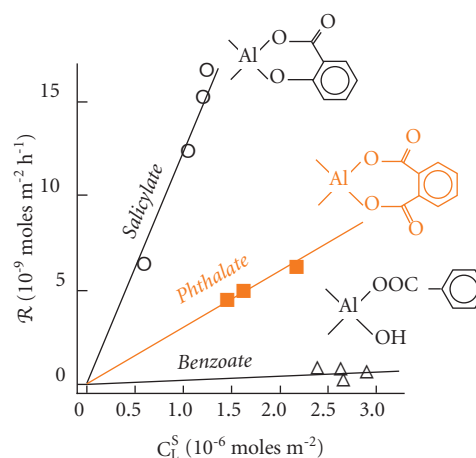

Figure 12.31 Rate of ligand-promoted dissolution of δ-Al$_2$O$_3$ as a function of organic ligand surface concentration. Chelates forming 5- and 6-member rings, such as those formed by salicylate, produced faster dissolution than 7-member rings, such as those formed by phthalate. Unidentate ligands, such as benzoate, have only a small effect on dissolution rate. Furrer and Stumm (1986). With permission from Elsevier.

oxalic acid, a dicarboxylic acid (Figure 12.7), to soil significantly increased soluble P concentrations and enhanced plant uptake of P, while addition of citric acid, a tricarboxylic acid, had a lesser effect. Thus similar organic acids can have dissimilar weathering effects.

Field studies show that high concentrations of organic acids, either natural or anthropogenic, clearly accelerate weathering (Bennett and Casey, 1994). However, in most circumstances, the concentrations of organic acids are low, and probably have only a small effect on weathering rates (Drever and Vance, 1994). Organic acids dissolved in formation waters of petroleum-bearing rocks may also enhance porosity by dissolving both carbonates and silicates (Surdam *et al.*, 1984). This enhanced porosity is essential to the migration and recovery of petroleum.

12.7   SEDIMENTARY ORGANIC MATTER AND COAL AND OIL FORMATION

Essentially all bodies of water harbor life, and therefore the production of organic carbon in
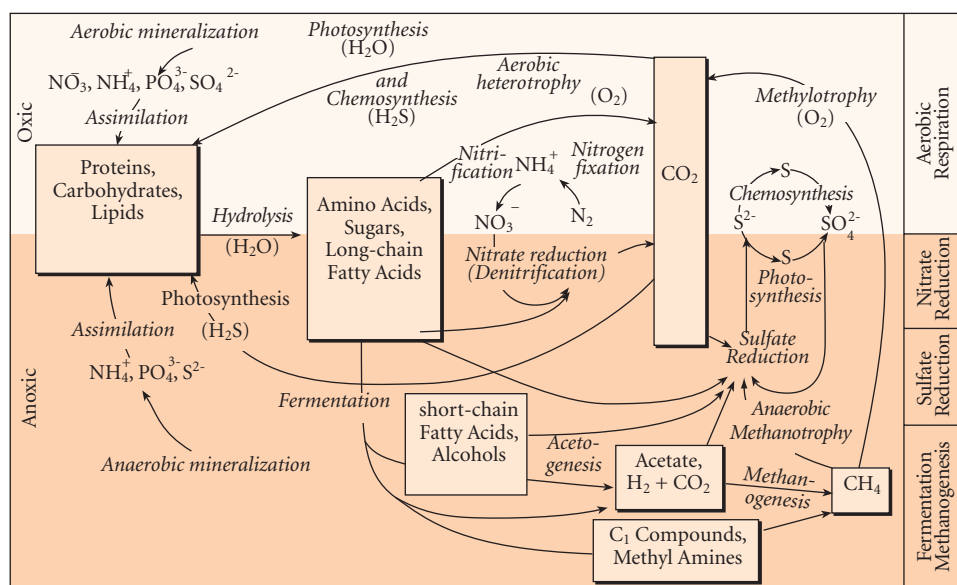
Figure 12.32   The role of bacteria in the cycling of carbon, nitrogen, and sulfur between inorganic and various organic forms. Killops and Killops (2005). With permission from John Wiley & Sons.

aquatic and marine environments is ubiquitous. Most sedimentary rocks, however, contain rather little organic matter (a fraction of a percent is typical). This is a testament to the efficiency of life: virtually all organic carbon produced by autotrophs is subsequently oxidized to CO_2 by respiration, a process called *remineralization*. Indeed, most of the organic carbon synthesized in the oceans and deep lakes never reaches the sediment; it is consumed within the water column. Organic carbon that does manage to reach the bottom is subject to consumption by organisms living on and within the sediment. Although macrofauna play a role in remineralization, it is bacteria that are responsible for most of it (in soils, by contrast, fungi are often the dominant consumers of organic matter). Concentrations of bacteria in the surface layers of marine sediments are typically in the range of 10^8 to 10^{10} cells per gram dry weight (Deming and Baross, 1993). The role of bacteria in the cycling of carbon, nitrogen, and sulfur is summarized in Figure 12.32.

These observations raise the question of why any organic matter survives. Why do most sediments contain some organic matter? How does it escape bacterial consumption? And why do some sediments, particularly those that give rise to exploitable petroleum and coal, contain much more organic matter?

What special conditions are necessary for this to occur?

Organic matter preserved in ancient sediments, and particularly coal, gas, and oil, differ chemically from living organisms. Since these resources derive from the remains of once-living organisms, we might ask how these chemical differences arise. Are the differences due to chemical transformations of simple organic molecules or selective preservation of more complex ones? Do the differences arise early, during the diagenesis of still young, poorly compacted sediment, or late, under the influence of heat and pressure? We explore these questions in the following sections, where we examine sedimentary organic matter, its diagenesis, and the formation of petroleum, gas, and coal deposits.

12.7.1   Formation and diagenesis of organic-rich sediments

12.7.1.1   Preservation of organic matter

It is primarily the particulate remains of phytoplankton that form organic matter in most marine and many aquatic sediments. Factors that affect preservation of these remains include the flux of organic matter to the sediment, bulk sediment accumulation rate, grain size, and availability of oxygen (Henrichs,

1993). The flux of organic matter to the sediment depends in turn on its rate of production in surface waters (biological productivity) and the depth of the overlying water column. Free-floating single-celled autotrophs (algae and photosynthetic bacteria), collectively called phytoplankton, are responsible for almost all the primary production of organic carbon in marine ecosystems, as well as many fresh water ones. Productivity depends mainly on the availability of nutrients, which in the ocean depends on the proximity to coasts and ocean circulation. Organic matter falling though the water column from the upper photosynthetic zone (200 meters at most) is rapidly remineralized by bacteria and animals in the water column. Hence the greater the water depth, the less organic matter reaches the sediment. In marginal marine environments, that is, those adjacent to continents, such as river deltas, bays, estuaries, and marginal seas, the land-derived remains of higher plants constitute a significant fraction of the accumulating organic matter. Such material is said to be *allochthonous* (i.e., derived from sources external to the water body). Organic matter produced within the immediate water body is called *autochthonous*.

Organic carbon concentrations are inversely correlated with grain-size for several reasons. First, low-density organic particles can only accumulate where water velocities are low enough to allow finer particles to settle out. Second, a significant fraction of the organic matter in sediments may be present as coatings on mineral grains (Mayer, 1993). Small grains have higher surface areas per unit mass or volume, and therefore would have higher organic content. Mayer (1993) also argued that adsorbed organic matter is more refractory than that in discrete particles, meaning it is more likely to survive consumption by heterotrophs in the sediment. Third, the permeability of fine-grained sediments is lower than that of coarse-grained ones. Where permeability is low, the flux of oxygen into the sediments will also be low.

The availability of oxidants, and particularly oxygen, is, as one might expect, among the most important factors in the survival of organic matter. Simply put, the preservation of significant amounts of organic matter in sediment requires that the burial flux of organic matter exceeds the flux of oxidants. The flux of oxidants depends on sedimentation rate, bioturbation, and diffusion, and their availability in the overlying water. Where the burial flux of organic carbon exceeds the downward flux of oxygen, the latter will ultimately be completely consumed and conditions will become reducing. At that point aerobic respiration must cease. This may occur either within the sediment, or within the water column itself. Situations where deep water becomes anoxic are rare in the modern ocean (indeed, in most of the deep ocean, conditions do not become anoxic even in the upper few meters of sediment); it occurs only in a few basins where circulation of deep water is restricted, such as the Black Sea. However, anoxicity appears to have been more common at certain times in the geologic past, such as the Cretaceous, when ocean circulation was different. Anoxicity is perhaps more common in lakes, where the abundance of nutrients is higher than in the open ocean.

Whether preservation of high organic matter concentrations in sediments requires anoxic bottom water is a matter of debate. Calvert and Pederson (1992) pointed out that sediments accumulating in oxic and anoxic basins have similar organic carbon contents and argued that the primary control is primary production in surface waters. They also argued that the extent of decomposition of marine organic matter is similar under oxic and anoxic conditions, although terrestrial organic matter tends to be degraded less by sulfate reducers. On the other hand, Killops and Killops (2005) pointed out that high fluxes of organic matter resulting from high productivity makes anoxic conditions in the sediment more likely. Anoxic conditions inhibit the macrofauna, whose bioturbation mixes oxygen downward and organic matter upward toward more oxygen-rich layers. They argued that ancient lipid-rich sediments of the sort likely to give rise to petroleum are generally finally laminated, implying a lack of bioturbation and therefore anoxic conditions at the sediment–water interface.

12.7.1.2   Diagenesis of marine sediments

Diagenesis in the context of organic matter refers to biologically induced changes in organic matter composition that occur in recently deposited sediment. Actually, these changes begin before organic matter reaches the sediment, as organic matter sinking

Table 12.8   Free energy changes for bacterial reactions.

Reaction	ΔG (kJ/mol CH$_2$O)
$CH_2O + O_2 \rightarrow CO_{2(aq)} + H_2O$	−493
$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_{2(aq)} + 3H_2O$	−472
$CH_2O + 3CO_{2(aq)} + H_2O + 2MnO_2 \rightarrow 2Mn^{2+} + 4HCO_3^-$	−348
$^\dagger 3CH_2O + 4H^+ + 2N_2 + 3H_2O \rightarrow 3CO_{2(aq)} + 4NH_4^+$	−125
$CH_2O + 7CO_{2(aq)} + 4Fe(OH)_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 3H_2O$	−103
$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$	−99
$2CH_2O \rightarrow CH_4 + CO_{2(aq)}$	−88
$^* 3CH_2O + 2N_2 + 7H_2O \rightarrow 3CO_{2(aq)} + 4NH_4(OH)$	−54

Modified from Berner, Robert A: Early Diagenesis © 1980 Princeton University Press. Reprinted with permission of Princeton University Press.
*Because the speciation of ammonia is pH-dependent, the ΔG of the nitrogen fixation reaction depends strongly on pH.

through the water column is fed upon by both the macrofauna and bacteria. Roughly 98% of the organic matter reaching the sediment is already degraded (Wakeman *et al.*, 2002), although its overall composition (e.g., amino acid fraction, lipid fraction, etc.) is little changed. Indeed, a significant proportion of the organic matter reaching the sediment does so in the form of fecal pellets of everything from zooplankton to whales. Decomposition continues once the organic matter reaches the sediment surface. Burial by subsequently accumulating sediment eventually isolates it from the water. Where the burial flux of organic matter is high enough, oxygen is eventually consumed, but life and decomposition persist. Once oxygen is consumed, respiration continues through fermentation, which narrowly defined refers to reactions in which an internal, rather than external, source of electron acceptors (oxidants) is used. An example familiar to brewers and vintners is the fermentation of glucose to alcohol:

$$C_6H_{12}O_6 \rightarrow 2\,C_2H_5OH + 2\,CO_2$$

In this example, part of the glucose molecule is reduced to ethanol and part is oxidized to CO_2. There is a limit to how much of the organic matter can be oxidized in this way, however. Remaining organic matter is subsequently attacked by a series of bacterial communities utilizing a progression of electron receptors (oxidants) at decreasing pε. We can predict the order of the use of these oxidants from the ΔG of the redox reactions involved, shown in Table 12.8. Thus, moving downward in a column of accumulating sediment, we expect to see, following consumption of free oxygen, a series of zones where nitrate, Mn(IV), Fe(III), sulfate, and nitrogen reduction occur. Each of these zones will be colonized by a bacterial flora adapted to conditions in that zone.*

The bulk of the organic matter in sediments exists in solid form, yet only dissolved compounds can cross cell membranes and be a useful source of nutrition to microbes. For this reason, bacteria release exoenzymes that first break insoluble complex organic molecules into smaller soluble ones. Complex organic molecules usually cannot be oxidized completely by a single organism, because no single organism is likely to produce all the necessary enzymes. Instead, consortia of bacteria break down macromolecules. In each step, some energy is released and smaller molecules are produced as waste; these are subsequently attacked by other bacteria. Thus proteins, carbohydrates, and lipids are broken down into amino acids, simple sugars, and long-chain fatty acids. These smaller molecules can be attacked by fermenting bacteria that produce acetic acid, other short-chained carboxylic acids, alcohols, hydrogen, and CO_2. In the final step, these are converted to methane (CH_4) by methanogenic bacteria. During this process, the remains of bacteria themselves can become a significant part of the sedimentary organic matter.

The stepwise oxidation results in an interdependence between the various bacterial

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*Examined at the microscopic level, separation of bacterial species is not quite this simple or complete. For example, within the oxic zone, there are anoxic microenvironments where anaerobic bacteria flourish.

species within each community, as many species are dependent on the "waste" products of other species. There is also a more general interdependence between communities in sediments. For example, anaerobic communities depend on aerobic ones to produce an anoxic environment. Reduced compounds, for example sulfide, ammonia, and methane, which are waste products of anaerobic communities in the deep levels, diffuse upward into the oxic zone where they are oxidized by various photosynthetic, chemosynthetic, and methanotrophic bacteria.

Both the abundance of organic matter and of bacteria decrease with depth in marine sediments, the highest concentrations of both being found in the upper 10 cm. There is also evidence that decomposition rates decrease when conditions become anoxic (summarized in Henrichs, 1993). Thus most remineralization occurs in the uppermost couple of meters, and the bulk of the organic matter buried beneath this depth is preserved long-term (Henrichs, 1993).

What molecules are preserved? As we might expect, the simple organic molecules such as amino acids, sugars, and short-chained carboxylic acids are rapidly decomposed by bacteria (time-scales of days to weeks). DNA is particularly subject to degradation in most circumstances. More complex molecules, such as polysaccharides and fatty acids, appear to decompose over a few months to a few years (Henrichs, 1993). Certain classes of compounds, principally ones that serve as cellular structural materials (e.g., components of cell walls), appear to be particularly resistant to bacterial decomposition and form the bulk of the preserved organic matter. Examples of these resistant materials are algaenans, which are found in the cell walls of marine algae, and phlorotannins (de Leeuw and Largeau, 1993). Allochthonous material derived from higher plants may also contribute a number of resistant aromatic-rich compounds (see below) to sediments in marginal marine environments. However, a small fraction of readily metabolized compounds is also preserved. Even older sediment, in which there has been ample opportunity for bacterial decomposition, contains low concentrations of such compounds. These molecules may survive because they are located in micro-environments that shield them from bacterial enzymes. Thus

labile molecules packaged within resistant structures (e.g., spores, pollen) can be preserved. Adsorption to inorganic particulates may also afford a degree of protection, and most organic matter in marine sediments appears to be adsorbed on to particle surfaces. Enzyme-catalyzed hydrolysis often requires a precise and unique physical alignment of the enzyme and reactant. The part of the surface of an organic molecule adsorbed on to an inorganic surface will not be accessible to the enzyme. Furthermore, sorption promotes condensation reactions that result in more refractory compounds (Killops and Killops, 2005). Organic molecules partly or wholly contained within micropores on the solid surface will be even more protected. Similarly, we might expect proteinaceous material in carbonate shells to be somewhat protected from bacterial enzymes.

Methane produced by methanogenic bacteria during diagenesis can react with water to form solid ice-like methane clathrate, which consists of a methane molecule locked in a cage of hydrogen-bonded water molecules (Figure 12.33) with the overall composition of approximately $CH_4(H_2O)_{5.75}$. Depending upon water temperature, the methane clathrate structure becomes stable at water depths of 300–400 m or more, and is favored by increasing pressure and decreasing temperature (Figure 12.34). An enormous mass of methane clathrate, in the range of 500–2500 carbon gigatons (700–3000 Gt methane), appears to exist in continental
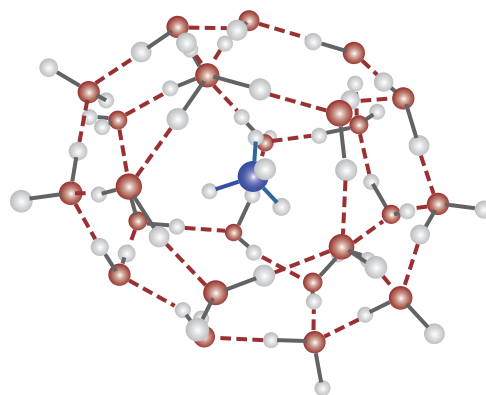

Figure 12.33   Structure of methane clathrate. Red atoms are oxygen, white are hydrogen, and black is carbon. Dashed red lines represent hydrogen bonds.
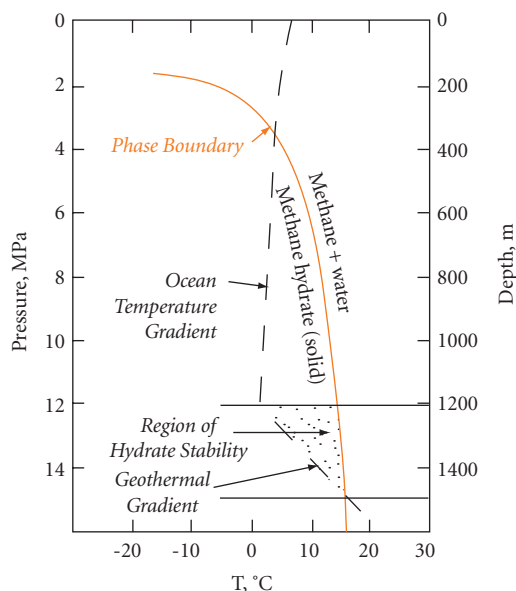
Figure 12.34 Phase diagram for the stability of methane clathrate in marine sediments. In this example, the ocean floor is at 1200 m depth and there is a roughly 200 m deep layer where methane clathrate is stable. From Kvenvolden (1993).

margin sediments (Milkov, 2004). A somewhat smaller mass of methane clathrate is also present in the deep permafrost of the Arctic tundra. This methane represents both a blessing and a threat. On the positive side, the amount of methane clathrate likely exceeds the total recoverable natural gas in other deposits by a factor of 2 to 10 and compares with an overall global inventory of fossil fuels of 5000–15,000 Gt carbon. On the negative side, methane clathrate is only marginally stable in the majority of its occurrences. Destabilization of methane clathrate, either through ocean or atmospheric warming or geologic events such as submarine landslides, could release massive quantities of methane to the atmosphere, which, because methane is a powerful greenhouse gas, could have profound climatic consequences.

12.7.1.3 Diagenesis of aquatic sediments

On the whole, diagenesis in fresh water sediment is similar to marine diagenesis. As is also the case in marine sediments, most of the organic detritus in aquatic environments orig-

inates from plants, with animals contributing less than 10%. Perhaps the principal difference in diagenesis between large lakes and the ocean is the much lower sulfate concentrations in lakes. Sulfate is important both as an oxidant and because sulfur can be incorporated into organic molecules (primarily lipids) during early diagenesis, a process known as "natural vulcanization". Because fresh waters have low sulfate concentrations, the zone of sulfate reduction is restricted and vulcanization does not occur. Otherwise, the same sequence of oxidant usage and decomposition occurs, and most of the remineralization occurs near the sediment–water interface.

In large lakes, the bulk of the organic matter reaching the sediment may be autochthonous (i.e., produced within the lake itself, primarily by phytoplankton), as is the case in marine environments. Often, however, allochthonous organic matter derived from terrestrial plants constitutes a substantial part of the organic flux to aquatic sediment. Higher plants living within the water may also contribute organic matter, and such material is dominant in swamps and marshes. The significance of this is that higher plants contain a greater abundance of aromatic compounds than algae. We found earlier in the chapter that aromatic compounds are often particularly stable. Thus it is no surprise to find that aromatics such as lignins, tannins, gums, curtans, and suberans, all produced by higher plants, are particularly resistant to bacterial decomposition and hence are more easily preserved in sediment.

Coal is formed by the compaction and diagenesis of organic-rich sediment, called *peat*, deposited in swamps and bogs. In contrast to petroleum, which can form in sediments containing only a few percent of organic matter, coal forms from sediments in which organic content is the dominant constituent. There are many examples of modern environments where such organic-rich material is now accumulating. Production of peat in these environments is a consequence of a number of factors. The first of these is productivity. Wetlands are generally characterized by high biological productivity; hence there is a high flux of organic matter to the sediment. The second factor is hydrology. Peat formation occurs where there is an excess of inflow and precipitation over outflow and evaporation. This

maintains a waterlogged soil as peat accumulates. Waterlogged conditions restrict the flux of oxygen into the sediment, resulting in conditions becoming anoxic immediately below the sediment–water interface. The third factor is the abundance of dissolved organic acids, some resulting from decomposition, others exuded by mosses and bacteria. These acids lower pH and inhibit the activity of decomposing bacteria. Finally, the primary producers in such environments are bryophytes (mosses) and vascular plants. As we noted above, these contain relatively high concentrations of aromatic compounds, which are more resistant to decomposition than the aliphatic compounds that predominate in algae and bacteria. Nevertheless, less than 10% of the organic production in these environments is preserved as peat, the rest being exported or recycled.

At present, the largest peat-forming environments are high-latitude (>45°) marshes and bogs. These marshes are typically dominated by a few species of moss (*Sphagnum*) that account for most of the accumulating organic matter. Other modern peat-producing environments include coastal swamps, such as the Mahakam Delta of Indonesia, and temperate and tropical lowland swamps.

12.7.1.4   *Summary of diagenetic changes*

Changes in sedimentary organic matter occurring as a result of diagenesis can be summarized as follows:

- Functional groups, such as carboxyl, aminos, and hydroxyl, are preferentially removed from their parent molecules.
- Loss of these functional groups decreases the oxygen, and to a lesser degree, the hydrogen, content of the organic matter.
- The abundance of readily metabolized organic compounds decreases. Nucleic acids and amino acids and related compounds appear to be the most labile (most readily destroyed), followed by carbohydrates, particularly simple ones and those synthesized for energy storage (e.g., starch) rather than structural (e.g., cellulose) purposes. The simple molecules in these groups (e.g., amino acids, glucose) are most labile of all. Lipids appear to be somewhat less labile.

- Unsaturated compounds decrease in abundance compared with their saturated equivalents due to hydrogenation of double carbon bonds.
- Aliphatic compounds decrease in abundance compared with aromatic ones. This results partly from aromatization of unsaturated aliphatic compounds and partly from the more resistant nature of aromatics.
- Short-chained molecules (e.g., alkanes, fatty acids), decrease in abundance relative to their long-chain equivalents.
- Hydrolysis of complex molecules produces a variety of molecular fragments that subsequently recombine with other molecules to produce new ones not present in the original biota. For example, phytol, produced by degradation of chlorophyll-a, and phenols, which can be produced by degradation of a variety of aromatic compounds, condense to form phenol–phytol compounds.
- In high-sulfur environments, such as marine sediments, H_2S (produced by sulfate-reducing bacteria) is incorporated into carbon double bonds in long-chain compounds such as isoprenoids to produce thiol functional groups. These can subsequently form cyclic structures and ultimately aromatic thiophenyls. This process is known as natural vulcanization.
- Condensation of a variety of molecules and molecular fragments into complex macromolecules.
- All along, bacterial remains are progressively added to the mixture, and are progressively decomposed along with the organic matter originally deposited.

The principal product of these processes is *kerogen*, the name given to the mixture of complex organic compounds that dominates the organic fraction in sediments.

12.7.2   Kerogen and bitumen

Kerogen is defined as sedimentary organic matter that is insoluble in water, alkali, non-oxidizing acids, and organic solvents (such as benzene/methanol, toluene, methylene chloride). It is usually accompanied by a smaller fraction of organic matter that is soluble in CS_2, called *bitumen*. Kerogen, an inhomogenous

macromolecular aggregate, constitutes 90% or more of organic matter in sedimentary rocks (much of the remainder being dispersed bitumen). Kerogen is by far the most abundant form of organic carbon on Earth; it is three orders of magnitude more abundant than coal, petroleum, and gas, and four orders of magnitude more abundant than the living biomass. Kerogen has the interesting and significant property that upon heating in the laboratory, a procedure known as *pyrolysis*, it breaks down to produce a variety of hydrocarbons similar to those found in natural petroleum. However, kerogen varies widely in its petroleum potential. Kerogen that is rich in aliphatic compounds, generally derived from aquatic and marine algae, has good petroleum potential and is called *sapropelic kerogen*. *Humic kerogen*, derived principally from the remains of higher plants, is rich in aromatic compounds, but has poor petroleum potential.

Carbon and hydrogen are the main constituents of kerogen. Hydrogen concentrations range from 5 to 18% (atomic), depending on type and degree of evolution. Oxygen concentrations typically range from 0.25 to 3%, again depending on type and degree of evolution. Besides C, H, and O, kerogen typically contains 1–3% N and 0.25–1.5% S (though the latter can be higher). A variety of trace metals, notably V and Ni, are also found in kerogen.

The structure of kerogen and the manner in which it forms is only partly understood. It forms from humus, humic and fulvic acids through condensation reactions. It appears to consist of nuclei cross-linked by chain bridges. The nuclei consist of stacks of two to four sheets of condensed aromatic rings, with roughly 10 rings per sheet, giving them a dimension of less than 10 Å. A variety of functional groups and alkyl chains are attached to the sheets. The bridges linking the nuclei may consist of linear or branched aliphatic chains, oxygen or sulfur functional bonds (e.g., ketones, esters, thiols, etc.). The bridges may also have functional groups attached to them. This structure appears to act as a "molecular sieve" and can trap compounds such as lipids within it. While condensation of low molecular weight biomolecules (amino acids, sugars, fatty acids, phenolics, etc.) produced by bacte-

rial decomposition contribute to kerogen formation, resistant biomolecules, such as tannins, cutins, polyterpenoids, and algaenans, which constitute only a small proportion of the original organic matter, contribute disproportionately to kerogen formation (Tegelaar *et al.*, 1989). This hypothesis, known as *selective preservation*, has gained wide acceptance.

Microscopic examination reveals that kerogen consists of identifiable plant remains, amorphous material, and rare animal remains. The amorphous material in kerogen may occur as mottled networks, small dense rounded grains, or clumps. The microscopically identifiable constituents are called *macerals*. Schemes for classifying macerals were first developed to describe coal and later applied to kerogen. Unfortunately, there are a number of classifications in use (see Whelan and Thompson-Rizer, 1993, for a summary), which can lead to considerable confusion. Here we follow Tissot and Welte (1984) and divide them into four groups. These groups differ in both composition (Figure 12.35) and origin. The *inertite* group consists of carbonized remains formed by rapid oxidation under aerobic conditions. One mechanism of inertite formation is probably wildfires in peat-producing environments.[*] Inertite may include
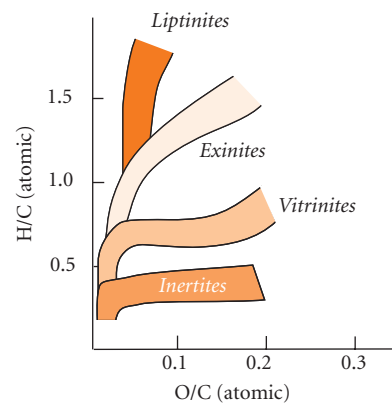

Figure 12.35 Compositional difference between kerogen maceral groups liptinite, exinite, vitrinite, and inertite. A plot of the H/C ratio versus the O/C ratio such as this is commonly called a *van Krevelen diagram*. van Krevelen (1961). With permission from Elsevier.

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[*] One such modern environment is the Okefenokee Swamp in southern Georgia (US). Wildfires often follow major droughts that occur at ~25 year intervals. These fires may burn the peat to a depth of 30 cm.

the carbonized remains of just about anything: woody tissue, fungi, spores, cuticles, resins, algae, and so on. Inertite has low H/C and O/C ratios and, as its name implies, is rather inert. *Vitrinite* is preserved woody tissue. There are two common macerals in this group: telenite and collinite. Telenite has a defined cell structure while collinite is colloidal, derived from solidified humic gels. *Exinite* includes lipid-rich materials derived from leaf cuticle, spores, pollen, algae, plant waxes, resins, fats, and oils. The fourth group, liptinite, is similar in many respects to exinites, but whereas exinites have recognizable shapes, liptinites are amorphous bodies. Liptinites are derived primarily from algal remains and usually have higher H/C ratios than exinites. These four maceral groups react differently to heating: vitrinite produces a fused carbon residue, inertites show no visible change, and exinites and liptinites transform into gas and tar.

12.7.2.1 Kerogen classification

Kerogen is usually classified into one of three types, based on bulk H/C and O/C ratios (Figure 12.36). *Type I* kerogen has a high H/C (atomic) ratio (≥ 1.5) and a low O/C (atomic) ratio (<0.1). It is rich in lipids, especially long-chain aliphatics, and has high petroleum potential. It consists primarily of liptinites derived from algal and bacterial remains, often deposited in aquatic or estuarine environments. Kerogen found in the Eocene Green River Shale of the western US is a good example. *Type II* kerogen, the most common type, has intermediate H/C (~1.25) and O/C (<0.2) ratios. It is derived primarily from planktonic and bacterial remains deposited in marine environments (though remains of higher plants can contribute as well). Because of its marine origin, it is often sulfur-rich. Its lipid content and oil potential are somewhat lower than Type I kerogen. *Type III* kerogen has low H/C ratios (<1.0) and high O/C ratios. It is rich in aromatics and poor in aliphatic structures. It is formed principally from the remains of vascular plants. Its oil potential is poor, but can be a source of gas (particularly methane). A comparison of Figures 12.35 and 12.36 shows that Type I kerogen is related to liptinite macerals, Type II to exinites, and Type III to vitrinites. High-sulfur Type II
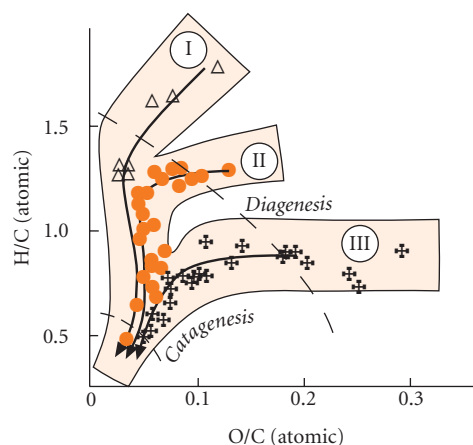

Figure 12.36 H/C and O/C ratios of the three types of kerogen. Open triangles, Type I; closed red circles, Type II; crosses, Type III. Arrows show the direction of compositional evolution during diagenesis and subsequent thermal maturation (catagenesis and metagenesis). Dashed lines show boundaries between regions of diagenesis, catagenesis, and metagenesis. Tissot and Welte (1984). With kind permission from Springer Science+Business Media B.V.

kerogen (denoted Type II-S) can contain 10% or more sulfur by weight. A fourth kerogen type (Type IV), which more or less corresponds to the inertite maceral group, is sometimes also defined. However, inertite has no petroleum potential, so there is less interest in this type.

12.7.2.2 Bitumen

The fraction of sedimentary organic matter that is soluble in carbon disulfide is called *bitumen* and includes solids, liquids, and gases. At the end of diagenesis, bitumens generally constitute less than 3–5% of the total organic carbon (the remainder being kerogen), though this figure is occasionally higher. During subsequent thermal evolution, however, the fraction of bitumen increases at the expense of kerogen (see below). Bitumen consists primarily of two fractions: *asphaltenes* and *maltenes*. These fractionations are defined, like humic substances, by their solubility. *Maltenes* are soluble in light hydrocarbons such as hexane, whereas asphaltenes are not. Asphaltenes appear to be structural similar to kerogen, consisting mainly of aromatic nuclei

linked by aliphatic units. They can be thought of as small fragments of kerogen. Maltenes can be subdivided into *petroleum*, which consists of a variety of hydrocarbons, and *resins*. Resins and asphaltenes, unlike hydrocarbons, are rich in heteroatoms such as N, S, and O. Resins tend to be somewhat richer in hydrogen (H/C atomic ~ 1.4) and poorer in N, S, and O (7–11 wt. %) than asphaltenes (H/C atomic ~ 1.2, N, S, O ~ 8–12%). Both have molecular weights greater than 500 and commonly several thousand.

The hydrocarbon fraction consists of both aliphatic and aromatic components. The aliphatic component can further be divided into acyclic alkanes, referred to as *paraffins*, and cycloalkanes, referred to as *naphthenes*. The lightest hydrocarbons, such as methane and ethane, are gases at room temperature and pressure; heavier hydrocarbons are liquids whose viscosity increases with the number of carbons. The term *oil* refers to the liquid bitumen fraction. *Pyrobitumens* are materials that are not soluble in CS_2 but break down upon heating (pyrolysis) into soluble components.

12.7.2.3   Biomarkers

Biomarkers, sometimes called "geochemical fossils", are molecules that have lost their functional groups but whose basic skeleton is preserved and which can be associated with a specific environment, class of organisms, or petroleum source rock. A few examples include:

- Odd carbon-numbered n-alkanes in the range of C_{25} to C_{33}, which are derived from even carbon-numbered fatty acid and alcohol components of cuticular waxes of higher plants through decarboxylation.
- C_{22}, C_{15}, and C_{17} n-alkanes derived from hydrocarbons and corresponding fatty acids in phytoplankton.
- Isoprenoids, most notably pristane (C_{19}) and phytane (C_{20}) derived from phytol in chlorophyll.
- Pentacyclic triterpenoids and their derivatives, including those derived from higher plant resins, and hopanoids, derived from bacteria.

Biomarkers are useful in petroleum exploration in associating oil with its source rock. As we shall see shortly, petroleum generally migrates away from the source rock from which it was generated. In some areas there are multiple potential parents of petroleum being produced. For example, in the Gulf of Mexico, petroleum has developed in both Jurassic and Tertiary source rocks. Biomarkers in the two are different and have shown that oil generated from Tertiary sources migrated into reservoirs where it displaced oil generated from Jurassic sources. Biomarkers are also useful in determining the environment in which a particular petroleum deposit formed. For example, n-alkanes longer than C_{22} together with an odd-over-even predominance would suggest a lacustrine depositional environment, as those molecules derive from leaf waxes. Some biomarkers can constrain the age of organic matter. For example, Grantham and Wakefield (1988) showed that the ratio of C_{28}/C_{29} steranes has decreased systematically over Phanerozoic time; they attributed this to diversification of marine planktonic assemblages. The presence of dinosterane and related methyl steranes in sediments is indicative of dinoflagellates in the planktonic assemblage, which in turn constrains the age to be Mesozoic or younger. Biomarkers are also useful in deducing the oxidation state during diagenesis. As we noted earlier, phytol, derived from chlorophyll, can be converted to either of two triterpenoids, phytane or pristane, during diagenesis, depending on oxidation state. Thus the pristane/phytane ratio can be used an indicator of oxidation state, with ratios greater than 1 indicating relatively oxidizing conditions.

12.7.3   Thermal evolution of organic matter and petroleum generation

12.7.3.1   Catagenesis and metagenesis

As sedimentary organic matter is buried, it experiences progressively higher temperatures and pressures. Although most bacterial decomposition occurs quickly, in the upper meter or so, it may continue at a much slower pace almost indefinitely. Indeed, bacteria have been found in subsurface rocks at temperatures of up to 75°C and depths of nearly 3 km.

As bacterial activity ceases, a number of new reactions begin as the organic matter attempts to come to equilibrium with higher temperature and pressures. These reactions, in which kerogen breaks down into a variety of hydrocarbons and a refractory residue, are collectively called *catagenesis*. As temperatures in the range of 100–150°C are reached, a complex mixture of hydrocarbons, *petroleum*, is produced, along with lesser amounts of asphaltenes and resins. Collectively, this bitumen fraction is called oil or *crude oil* and is, of course, of great economic interest. At temperatures above 150–175°C, methane and graphite are the ultimate products, created in a process called *metagenesis*.

One of the principal effects of diagenesis is the condensation of complex macromolecules from simpler ones. During catagenesis, this process is reversed as kerogen breaks down into comparatively simple hydrogen-rich molecules (hydrocarbons) and a hydrogen-depleted carbon residue. The hydrogen-rich phase is mobile and will migrate out of the source rock if a migration pathway exists. The refractory carbon-rich residue is immobile and remains in place.

Whereas diagenesis is a result of microbial metabolic activity, catagenesis is a physical (i.e., thermodynamic) response to increasing temperature and pressure. During the latter, kerogen molecules undergo rearrangement to take on a more ordered and compact structure. As this occurs, the alignment of nuclei, each composed of two or more aromatic sheets, becomes increasingly parallel, the number of sheets per nucleus increases, and the space between them decreases. Aliphatic units that are peripheral to the aromatic nuclei as well as those that bridge nuclei are progressively eliminated, with longer chains eliminated preferentially. Since most of the remaining functional groups in kerogen are attached to these aliphatic units, these are also eliminated. Heteroatoms, N, S, and O, are also eliminated in this process. Aromatic units increase in abundance relative to aliphatic units. This results from aromatization of cyclic aliphatic structures as well as elimination of aliphatic structures. Unsaturated n-alkanes have 2 or more hydrogens per carbon atom, whereas aromatic units have 1 or fewer hydrogens per carbon. Thus the compositional effect of catagenesis on kerogen is a decrease in the H/C ratio, as well as a continued decrease in the O/C ratio. This compositional evolution is illustrated by the arrows in Figure 12.36.

The degree of thermal maturation of kerogen can be monitored from its H/C and O/C ratios. In the "oil window", the point where maximum hydrocarbon generation occurs, the H/C ratio is less than 1 and the O/C ratio less than 0.1. Kerogen with H/C ratios lower than 0.5 is over-mature, that is, it has already entered the metagenesis stage where methane is the principal hydrocarbon product. Kerogen maturity can also be monitored by measuring *vitrinite reflectance*. Kerogen in the diagenetic stage reflects light only weakly, but as its structure becomes more dense and ordered during catagenesis, more incident light is reflected. Vitrinite reflectance is determined by polishing a specimen and then comparing the fraction of incident light reflected with that of a calibrated standard using a microscope photometer. Vitrinite reflectance increases from about 0.2% in recent sedimentary organic matter to 4% or more in over-mature kerogen. In the oil-generating stage of catagenesis, vitrinite reflectance is typically in the range of 0.6–1.3%.

Figure 12.37 summarizes the generation of oil and gas as a function of temperature. During catagenesis, heteroatomic bonds are the first to be broken as they are generally weaker than carbon–carbon bonds. Hydrocarbons released during this stage are those attached to the kerogen structure with heteroatoms or merely trapped within it; often these are only slightly modified from their biomolecular form. Thus the hydrocarbon fraction of bitumen in immature kerogen is dominated by *biomarkers*.

As temperature increases, carbon–carbon bonds are also broken, in a process called *cracking*. Carbon–carbon bonds in the centers of chains are slightly weaker than those on the ends. As these begin to break, hydrocarbon fragments are released that progressively dilute biomarkers. Also because of this effect, the size of hydrocarbons evolved decreases with increasing maturity. The first hydrocarbons to evolve in the oil window have on average relatively high molecular weight, ~$C_{35}H_{54}$. This decreases to less than $C_{10}H_{18}$ at
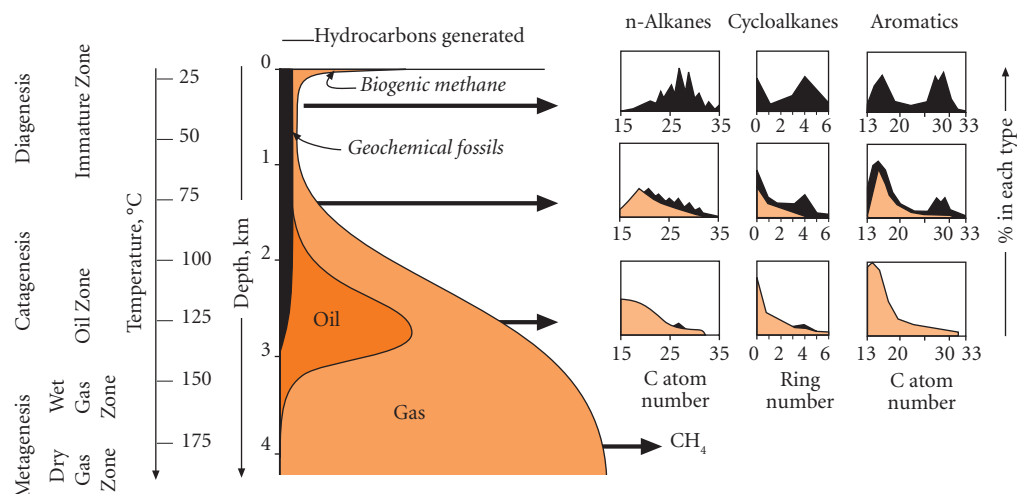
Figure 12.37 General scheme for hydrocarbon generation as a function of depth and temperature. Composition of the hydrocarbons generated is shown in the graphs to the right. Temperature and depth scales assume a geothermal gradient of 40°C per km. Tissot and Welte (1984). With kind permission from Springer Science+Business Media B.V.

the peak of the oil window and continues to decrease at higher temperatures.

As temperatures approach and exceed 150°C, even smaller hydrocarbons ($\leq C_5$) become dominant. These are gases at surface temperature and pressure. Dissolved in them, however, are lesser amounts of longer chains ($\geq C_6$). These condense to liquids upon reaching the surface and hence are called *condensates*. Hydrocarbons that are gas-dominated yet contain a significant amount of longer hydrocarbons are called *gas condensates*, and this stage of catagenesis, corresponding roughly to 150–180°C, is called the "wet gas zone". At higher temperatures, the liquid hydrocarbons are completely eliminated by C–C bond breakage. The upper temperature limit of oil stability has been revised upward in recent years as examples of n-alkanes in reservoirs at 200°C have been reported (e.g., Vandenbroucke *et al.*, 1999), and reaction modeling suggests light oil could persist to 250°C (Dominé *et al.*, 2002). Eventually, all C-C hydrocarbon bonds are broken, leaving methane as the sole hydrocarbon, accompanied by a nearly pure carbon residue. This stage of evolution is referred to as metagenesis or the "dry gas zone".

Rates of reactions involved in catagenesis show an exponential temperature dependence, as we might expect (Chapter 5). Reaction rates roughly double for every 5–10°C increase in temperature. Because of this, catagenesis depends not just on temperature, but on time as well, or more specifically, on the heating rate. Heating rate in turn depends on (1) the burial rate and (2) the geothermal gradient. The burial rate depends primarily on the rate at which the sedimentary basin subsides. The geothermal gradient at the surface of the Earth varies widely, from 10°C/km to 80°C/km or even higher in geothermal areas. Values at the low end of this range are typical of old continental shields; higher values are typical of rifts and oceanic crust. Petroleum deposits often occur in subsiding basins associated with tectonic activity, thus geothermal gradients can be high. Gradients of from 25–50°C/km are perhaps most typical for petroleum-producing environments. As a result of kinetics and variations in burial rate and geothermal gradient, the time required for petroleum generation will vary. In western Canada, Devonian sediments were slowly buried in a region of low geothermal gradient, and oil generation followed deposition by 300 million years. In contrast, 10 million year old upper Tertiary sediments in the Los Angeles Basin are already generating petroleum and much younger sediments are generating petroleum in regions of very high geothermal gradient in the Bransfield Strait of Antarctica. The temperature required for the onset of petroleum generation varies inversely with time.