

Chapter 12: Organic Geochemistry, the Carbon Cycle, and Climate

12.1 INTRODUCTION

Organic compounds are ubiquitous on the surface of the Earth: some form living organisms, some are a result of pollution, some have been leaked or excreted from living cells, but most are break-down products of dead organisms. Organic substances may be either water insoluble or water-soluble. Rain typically contains about $1\text{ }\mu\text{g/l}$ dissolved organic carbon (DOC), the ocean around 0.5 mg/l DOC, and soils up to 250 mg/l . In general, insoluble organic compounds in soil are more abundant than water soluble ones. In addition to their value as fuel (as peat, coal, petroleum, and natural gas), organic substances are also important in controlling the properties of soil, as weathering agents, and as a significant fraction of surficial carbon, which cycles between the ocean, the atmosphere, the biosphere, soils, and rocks as both inorganic carbon in carbonates and organic carbon. Organic carbon reservoirs (soils and coal, petroleum, etc.) exchange with the atmosphere, where carbon (as CO_2 and CH_4) plays an important role in regulating the Earth's surface temperature. Hence, organic carbon plays an indirect role in climate regulation. All of these provide very good reasons for acquiring a better understanding of organic substances and the role they play in geological processes.

In this chapter, we begin with a brief review of some basic biology and organic chemistry. We then examine how organic compounds are produced and used by organisms. We continue on to survey the distribution of organic compounds in water and soil. We then examine their geochemical properties and their roles as complexing agents and adsorbents. We then examine the processes by which sedimentary organic matter evolves into important energy and chemical resources such as coal, gas, and oil. In the final section, we examine how carbon cycles between various organic and inorganic forms at the surface of and within the Earth. Because CO_2 and CH_4 are strong greenhouse gases, this cycling affects and is affected by climate. We'll see that the abundance of these gases in the atmosphere has controlled the Earth's climate throughout its entire history.

Before we do that, however, we need to define the term "organic" in a chemical sense. One definition of an "organic" compound is one produced biologically. However, some compounds generally considered "organic" can be produced both abiologically* and biologically, so this is not very useful. A common definition of an "organic compound" is one that contains carbon atoms. However, carbonates, carbides, simple carbon oxides (e.g., CO_2 , CO), carbonates, and native carbon (graphite, diamond) are not considered organic compounds. An alternative, and perhaps preferred definition of an organic compound is one containing at least one carbon-hydrogen bond.

12.2 A BRIEF BIOLOGICAL BACKGROUND

Living organisms are the ultimate source of most, but not all, organic compounds in the environment. While life forms are extremely varied, the basic principles of cell operation are the same in all organisms. For example, all derive the energy they require through oxidation of organic compounds, all contain DNA (deoxy- ribonucleic acid), which is the blueprint for synthesis of proteins that carry out various intracellular functions, and all use ATP (adnosine triphosphate) in intracellular energy transactions. This commonality suggests all organisms have evolved from a common ancestor.

Over the years there have been a variety of schemes for classifying organisms, and one may still find any one of several in biological textbooks. Figure 12.01 presents a simplified version of the Woese system, based on ribosomal RNA sequencing, which has now achieved wide acceptance. It divides organ-

* For example, abiogenic methane is found in hydrothermal fluids on mid-ocean ridges.

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isms into three kingdoms: *archeobacteria*, *eubacteria*, and *eukaryotes*. The first two of these kingdoms consist only of simple unicellular organisms; all other organisms, including all multicellular organisms, are eukaryotes. Eubacteria and archeobacteria are collectively called *prokaryotes*. They are distinguished from eukaryotes in that their DNA is not contained within a membrane-bound nucleus as is the case with eukaryotes; rather the DNA of prokaryotes is simply concentrated within one or more regions, called nucleoids, of intracellular fluid, or cytoplasm (a protein solution). In contrast, the DNA of eukaryotes is contained within the cell nucleus, usually organized into chromosomes. In both eukaryotes and prokaryotes, messenger RNA (m-RNA) carries information from DNA, in the form of a complement of a portion of a DNA strand, to *ribosomes*, which consist of RNA and proteins, where proteins are synthesized by transcription RNA (t-RNA) from amino acids.

An additional contrast between prokaryotes and eukaryotes is that eukaryotes contain a variety of specialized intracellular structures whereas, except for ribosomes, prokaryotes do not. These include *mitochondria*, where energy is generated by oxidation of carbohydrates, *chloroplasts* (in plants), where *photosynthesis* takes place, the Golgi apparatus, which is involved in modifying proteins, and networks of structural proteins that, among other things, participate in changing the shape of the cell so that it can move. Some of these *organelles*, such as the mitochondria and chloroplasts, have their own DNA with affinities to that of prokaryotes. This and other evidence suggests these organelles may have evolved from prokaryote cells living symbiotically within eukaryote hosts. Eukaryotic cells typically have dimensions of about 10μ , and are therefore much larger than prokaryotes, which generally have largest dimensions of 1μ or less. The eukaryotes may be further divided into single-celled organisms (such as algae and foraminifera) called *protists* and multicellular organisms or *metazoans* (such as us). Prokaryotes, also called *monera*, are divided into Eubacteria and Archeobacteria. These groups differ in the nature of their cell walls and lipid chemistry.

Organisms may also be divided between *autotrophs*, which supply their energy needs through *photosynthesis* or *chemosynthesis*, and *heterotrophs*, whose energy needs are supplied by assimilating organic compounds previously produced by autotrophs. Thus all plants are autotrophs, and all animals are heterotrophs. The bacteria include both autotrophs, such as photosynthetic cyanobacteria (previously called blue-green algae), and heterotrophs.

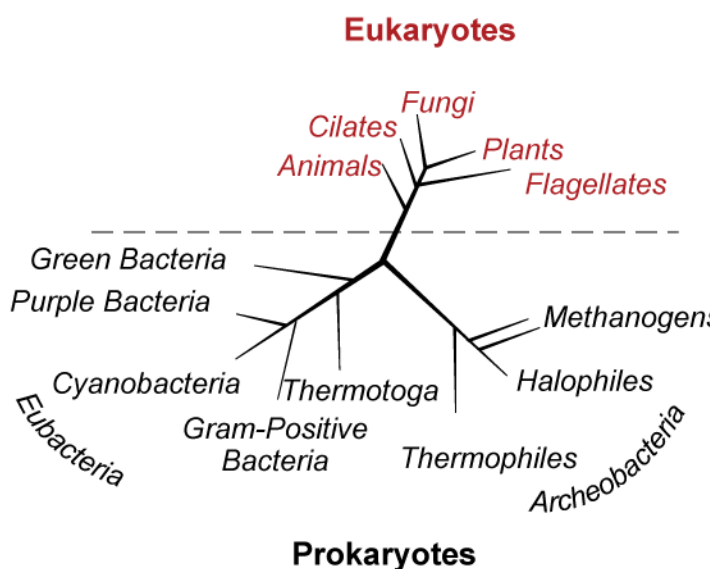


Figure 12.01. Phylogenetic relationships among organisms. The eubacteria and the archeobacteria constitute the prokaryotes; all other organisms are eukaryotes.

Perhaps because we are most keenly aware of the presence of bacteria when they infect us, we often think of bacteria as "bad". However, bacteria are ubiquitous and play essential roles in every ecosystem; only a small fraction are pathogenic. All chemosynthetic organisms are prokaryotes, as are most organisms capable of living without free oxygen (anaerobes). Archeobacteria may be found in extremely hostile environments such as saline lakes and fumaroles. Prokaryotes play the most important roles in converting the chemical products of life to organic substances found in sediments ("geopolymers") and soils; thus they are of particular interest in geochemistry. Some prokaryotes reduce sulfate, others oxidize sulfide, some produce methane, others

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consume it. Some bacteria reduce nitrogen to ammonia, a process called nitrogen fixation, others oxidize ammonia to nitrate (nitrification), yet others convert nitrate to nitrogen (denitrification). Symbiotic bacteria are essential to the digestive systems of higher animals. *E. coli* in the human gut, for example, synthesize a number of essential nutrients that are then assimilated through intestinal walls. On the whole, bacteria, and more generally the unicellular organisms, or *microbes*, play a much more important role in biogeochemical cycling and geochemical processes than do the metazoans.

12.3 ORGANIC COMPOUNDS AND THEIR NOMENCLATURE

Organic chemistry can be an intimidating subject involving a bewildering array of compounds, and names for each, whose properties depend as much on the details of their structures as on their composition. A complex nomenclature of organic chemistry has evolved because simply referring to an organic compound by its chemical formula is not sufficient to identify the compound. Compositionally identical compounds can have different structures and different properties. This is, of course, true of inorganic compounds as well, for example, quartz and tridymite or graphite and diamond, but isomers, i.e., compositionally identical but structurally distinct compounds, are particularly common among organic compounds. Organic nomenclature is in some sense a language unto itself. Like any language, organic nomenclature has a “grammar”. Once this grammar is mastered, the exact composition and structure of a compound can be communicated through its name alone. We will need to concern ourselves with only a part of that language.

We will make one simplification in the brief review of organic chemistry that follows: we will ignore the phenomenon known as *stereoisomerism*. Organic compounds that are otherwise structurally identical but are mirror images of one and other are said to be *stereoisomers*. The difference in physical properties of stereoisomers can be quite small, no more than rotation of the plane of polarized light in an opposite sense, but the difference is often biochemically important. Stereoisomerism is usually less important from a geochemical perspective (but see Example 5.03), so in the interest of clarity, we will not discuss it further.

12.3.1 Hydrocarbons

Hydrocarbons are the simplest group of organic compounds in that they consist only of

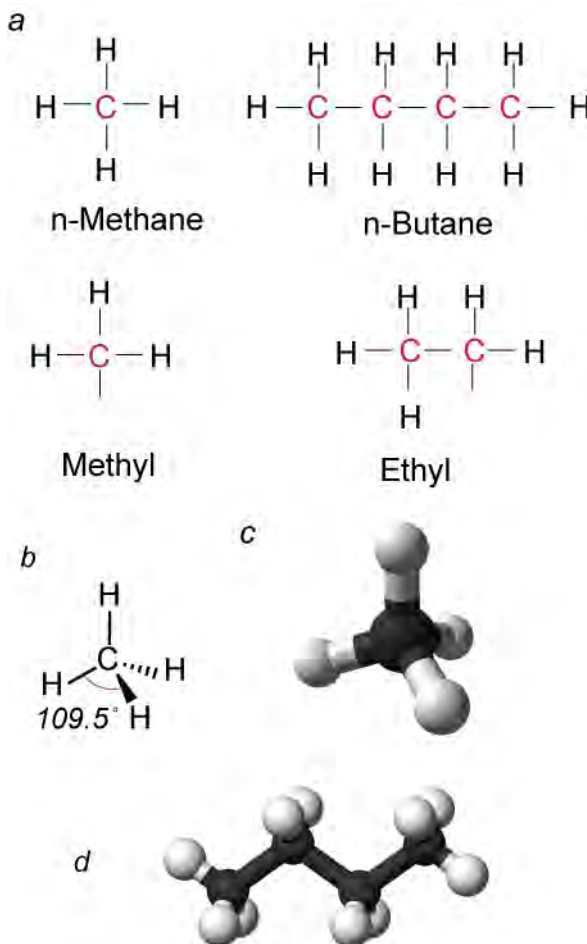


Figure 12.02. a. Simple *n*-alkanes or chain hydrocarbons. The suffix “-ane” is used for molecules and the suffix “-yl” is used to refer to equivalent radicals formed by removing a hydrogen. b. A stereochemistry illustration of the methane molecule, showing the 109.5° angle between H-C-H bonds. Solid wedge indicates a bond coming out of the paper toward the viewer, hashed wedge is one pointing away from the viewer, and straight line is a bond in the plane of the paper. c. Stick-drawing illustration of methane. d. stick illustration of n-butane.

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carbon and hydrogen. We can think of hydrocarbons, and indeed all organic compounds, as consisting of a basic skeleton of carbon atoms to which various functional groups can be attached to form other

sorts of organic compounds. The simplest skeleton is that of the *acyclic* or *aliphatic* hydrocarbons, also called *paraffins*, or *alkanes*, which consist of a straight or branched chain of carbon and hydrogen atoms. If they are unbranched, they called *normal* or *n-alkanes*.

the name is based on the Greek word for the number of carbon atoms in the chain (i.e., pentane for 5 carbons, hexane for 6, heptane for 7, etc.). Radicals formed by removing a hydrogen from a terminal carbon are named by replacing the "-ane" suffix with "-yl", e.g., methyl, butyl. As a group, the radicals formed from alkanes in this way are called *alkyls* (and thus the group name also conforms to the naming convention).

Alkanes are not, however, actually straight chains, although they are often represented that way, as they are Figure 12.02a, which shows methane and butane with bonds drawn as right angles. Figure 12.02b provides a 'stereochemistry' illustration of methane, showing that the bond angles between hydrogens is actually 109.5°, not 90°. Figure 12.02c and d shows stick model illustrations of the methane and n-butane molecules.

Branched chains are formed by replacing one of the hydrogens by a carbon atom, to which additional hydrogens are attached. These are named by prefixing the designations of the side chains to the name of the longest chain in the formula. A number is prefixed indicating the carbon, counting from the nearest end, to which the secondary chain is attached. An example is 3-methylpentane (Figure 12.03). If more than one secondary group is attached, the groups are listed in alphabetical order, for example, 3-ethyl-4-methylhexane shown in Figure 12.03. When several of the same group are attached, a multiplier corresponding to that number precedes the name of the group. An example is 2,4-dimethylhexane, shown in Figure 12.03.

Compounds where all carbon atoms have single bonds to 4 other atoms are said to be *saturated* (the term saturated arises from carbon being bonded to the maximum possible number of hydrogens; i.e., the carbon is hydrogen-saturated). Carbon atoms that are double bonded are termed *olefinic units*. Compounds containing one or more pairs of doubly bonded carbons are said to be *unsaturated*. Unsaturated, unbranched acyclic hydrocarbons having one double bond are named by replacing the suffix "-ane" by "-ene", e.g., ethylene: $\text{CH}_2=\text{CH}_2$. A number is used to specify the location (the carbon atom)

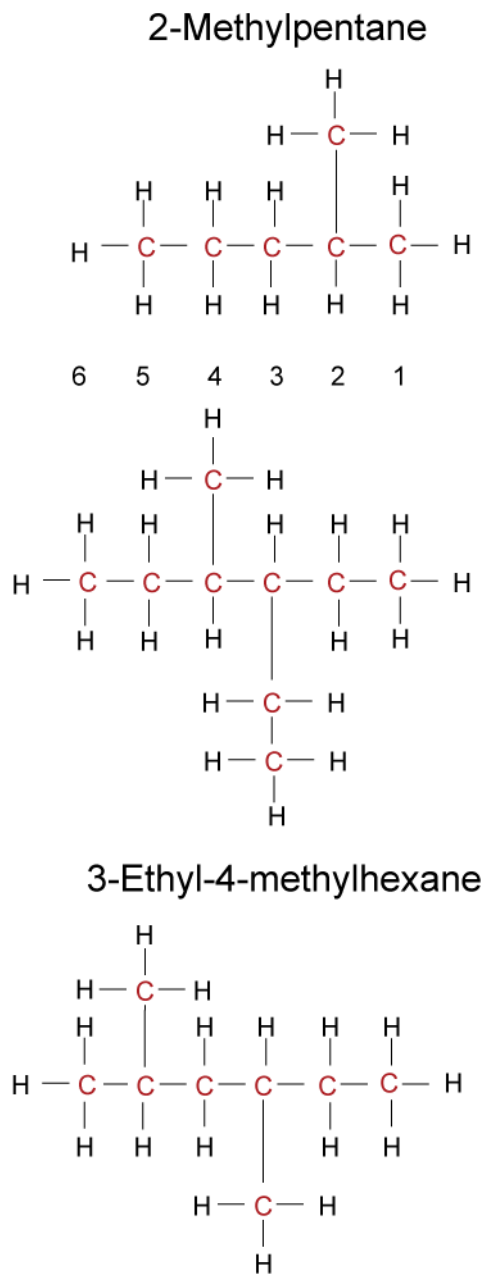


Figure 12.03. Some simple and branched hydrocarbon chains.

of the double bond, for example, 2-butene, shown in Figure 12.04. If there are more than 2 double bonds the ending becomes "-adiene", "-atriene", etc. Generic names are *alkene*, *alkadiene*, etc. Triple car-

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bon bonds are also possible, in which case the suffix becomes "yne" for a single triple bond. Acetylene* (Figure 12.04) is an example of a compound containing triply bonded carbon. Particularly stable compounds result when carbon bonds are *conjugated*, that is, alternately singly and doubly bonded, e.g., $-C=C-C=C-C=C-$.

Instead of forming chains, the C atoms may form rings; the resulting compounds are called *cyclic hydrocarbons*. Naming conventions for the simple groups are similar to those for chains, with the prefix "cyclo-" used to indicate the cyclic nature, e.g., cyclopropane.

A particularly important cyclic structure is the benzene ring, which consists of 6 conjugately bonded (i.e., alternating single and double bonds) carbon atoms lying in a single plane (Figure 12.05) with. Compounds based on this structure are particularly stable and are referred to as *aromatic*†. Representation of this structure as alternating single and double bonds is not entirely accurate. The carbon-carbon bond in a saturated alkane such as ethane is 1.54 Å in length; the double bond in ethylene is 1.33 Å in length. All carbon-carbon bonds in the benzene ring are found to be intermediate in length (1.40 Å). Thus bonding is delocalized, that is, all carbon-carbon bonds in the ring are of approximately equal strength and the double bonds appear to be shared among all carbon atoms in the ring. This delocalization is responsible for the particularly stability of this structure. Several rings may be joined to form *polyaromatic units*.

12.3.2 Functional Groups

From these basic hydrocarbon structures, a great variety of other organic compounds may be formed by attachment of atoms or functional groups by replacement of hydrogen or carbon atoms. The basic naming conventions discussed above for hydrocarbons also apply to these other organic molecules. Additional names, prefixes, and suffixes are used to indicate the presence of attached groups replacing hydrogen or other atoms replacing carbon in the basic structure.

The most important functional groups are summarized in Figure 12.06. The *hydroxyl* (OH) unit may be attached to an aromatic ring to form *phenols* or to aliphatic units to form *alcohols*. The biologically important *carbohydrates*, e.g., sugars and starches, are compounds with the general formula of $(CH_2O)_n$. They are either aliphatic or cyclic hydrocarbons in which some hydrogens have been replaced by OH. The carbonyl group ($C=O$) forms aldehydes when the "R" in Figure 12.06 is H, ketones when "R" is either an aliphatic or aromatic group, and quinones when the carbon in the group is incorporated into an aromatic ring.

A particularly important functional group from a geologic perspective is the *carboxylic acid* group: COOH. The suffix "-oic acid" is used to designate

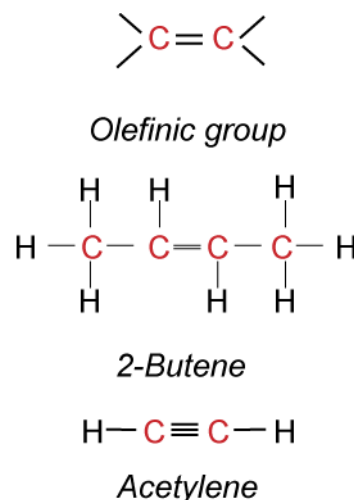


Figure 12.04. Some simple doubly and triply-bonded hydrocarbons.

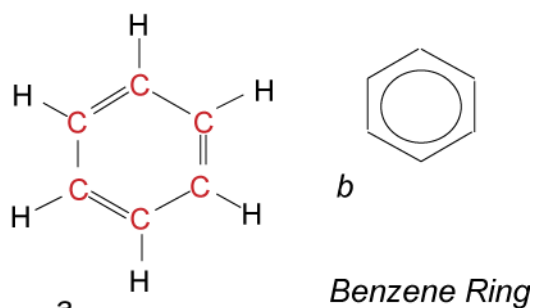


Figure 12.05. Two illustrations of the benzene ring, the foundation of aromatic hydrocarbons. In (b) the C and H atoms have been removed for clarity. Since all carbon-carbon bonds in the benzene ring are equivalent, (b) is actually a better representation than (a).

* As is the case in most languages, there are words in the lexicon of organic geochemistry that do not conform to the standard grammar. Acetylene, named before the names conventions were developed, is an example of such an irregular term.

† Some aromatic compounds, such as benzene, toluene, and a variety of chlorinated phenols, are highly toxic. Because of the stability imparted by the conjugate bonding, they are particularly environmentally hazardous.

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Group	Name	Resulting Compound
—OH	Hydroxyl	<i>Phenols (Aromatics)</i> <i>Alcohols (Aliphatics)</i>
—O—	Oxo	<i>Esters</i>
R—C=O H	Carbonyl	<i>Aldehydes</i> <i>Ketones, Quinones</i>
—C=O OH	Carboxyl	<i>Carboxylic Acid</i>
—NH ₂	Amino	<i>Amines</i>
—C=O NH ₂	Amido	<i>Amides</i>
—SH	Thio	<i>Thiols</i>

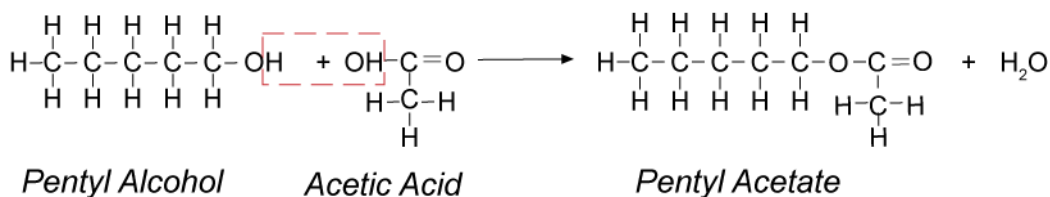
Figure 12.06. Important functional groups found in organic compounds.

compounds formed by carboxylic acid groups: for example, menthanoic acid is a carboxyl group with an attached H, ethanoic acid is a carboxyl group with an attached CH₃, benzoic acid is a carboxyl group with an attached benzene ring. Many of the carboxylic acids also have more familiar names, for example, ethanoic acid is more commonly called *acetic acid*, methanoic acid is also called *formic acid*. Two carboxyl units bound together form *oxalic acid*. A compound formed by replacement of the dissociable hydrogen in the carboxyl group with some other group is designated by the suffix “-ate”.

Carboxyl groups attached to hydrocarbon chains form *fatty acids*, which are important components of lipids. If one or more of the hydrogens attached to the carbon chain or ring is substituted by a hydroxyl group, the compound is known as an *hydroxy acid* (for example, salicylic acid illustrated in Figure 12.07). If a doubly bonded oxygen is substituted for two hydrogens attached to the chain (forming a *carbonyl group*),

the compound is known as a *keto acid*. Hydroxy acids such as lactic acid and keto acids such as pyruvic acid are important in both the Calvin Cycle, by which autotrophs synthesize organic compounds, and the Krebs Cycle, by which organisms oxidize organic compounds to release energy.

Esters form by combining a carboxylic acid and an alcohol. In the reaction between these two, the OH is removed from the carboxyl group and the H removed from the alcohol, leaving the two units bound by an oxygen atom[†]. An example of such a reaction is the formation of pentyl acetate (which gives bananas their familiar odor) from acetic acid and pentyl alcohol:



Another geologically and biologically important functional group is the *amino group*, NH₂ (the name being derived from ammonia, NH₃). *Amino acids*, the building blocks of proteins, consist of molecules containing both amino and carboxylic groups. Other important functional groups include the carbonyl group, consisting of a carbon that is double bonded to oxygen, and thiol groups, where S replaces O in the OH group (i.e., SH). Figure 12.07 illustrates a few of the important compounds formed by replacement of hydrogen in basic hydrocarbons by one or more of these functional groups.

Organic compounds can contribute significantly to the pH balance of natural waters. The acid-base properties of organic compounds depend on the attached functional groups rather than the basic structure. Functional groups may be classified as acidic or basic depending on their tendency to give up (acidic) or accept (basic) hydrogen ions. Carboxyl groups tend to be strongly acidic, phenols and quinones tend to be mildly acidic. Alcohols, ethers, ketones, and aldehydes are generally classified as neu-

[†] Such a reaction, in which two molecules combine to form a larger molecule with the elimination of a small molecule (H₂O in this case), is called a condensation reaction or simply *condensation*. The reverse of this reaction is termed *hydrolysis*.

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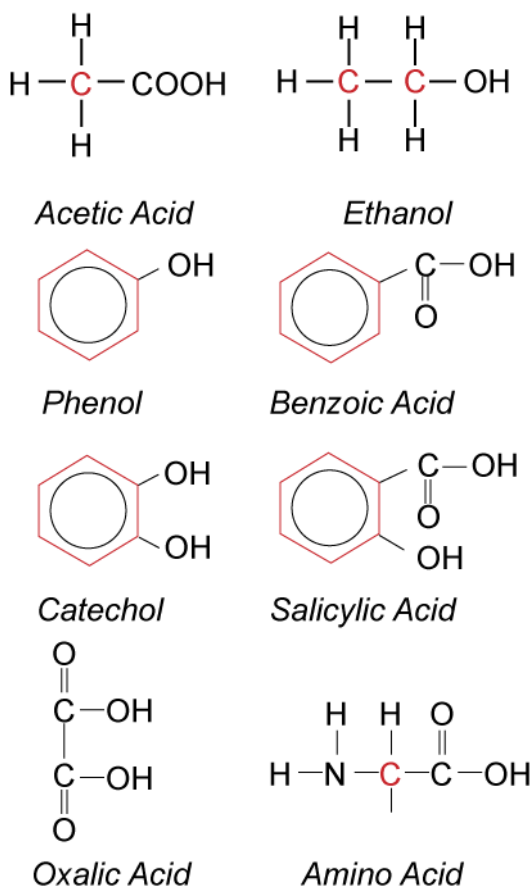


Figure 12.07. Some examples of compounds formed by substituting functional groups for hydrogen in basic hydrocarbon structures.

script indicating the number or repetitions, for example $(\text{CH}_2)_6$. Groups placed on the ends then precede and follow. Thus for example stearic acid, a fatty acid consisting of a 17 carbon chain with a hydrogen on one end and a carboxyl group on the other, can be denoted as $\text{CH}_3(\text{CH}_2)_{16}\text{C}(\text{O})\text{OH}$. If a double carbon bond occurs, this is designated by $\text{CH}=\text{CH}$ inserted at the appropriate place. Thus palmitoleic acid, a common unsaturated fatty acid with the formula $\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{C}(\text{O})\text{OH}$ is a 15

carbon aliphatic compound with a olefinic unit between the 7th and 8th carbons, an H on one end, and a carboxyl acid group on the other. If an attached group occurs in the middle part of the chain, then the formula for the group is inserted in parentheses after the appropriate number of repetitions of the CH_2 unit, and a second $(\text{CH}_2)_n$ follows, n indicating the number of subsequent repetitions. Thus the formula for 3-

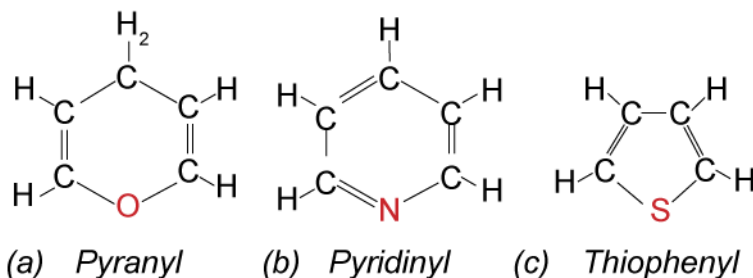


Figure 12.08. Examples of functional groups formed replacing one carbon atom in the cyclic skeleton with atoms of O, N and S. The names of the functional groups are given in the figure;

tral. The nitrogen in amines and amides binds free hydrogen ions fairly easily, hence these groups are basic.

The acid-base properties of organic substances are also directly related to their solubility in water. Because water can more easily dissolve ionic substances than neutral ones, strongly basic or strongly acidic compounds (those that have given up or accepted a proton) tend to be more soluble than neutral compounds. Thus carboxylic acids are very water soluble, amines somewhat less soluble, and neutral compounds such as esters and ether least soluble.

It is also possible to substitute other elements for carbon in the basic hydrocarbon structure; such atoms are known as *heteroatoms*. Examples are illustrated in Figure 12.08. The pyranyl group is a particularly important one because it forms the basis of many cyclic carbohydrates; the pyridinyl group is an important component of nucleic acids.

12.3.3 Short-hand Notations of Organic Molecules

For both aliphatic and cyclic molecules, the number of carbons in the ring or chain is commonly denoted with C followed by a subscript corresponding to the number of carbons, e.g., C_6 for hexane. It is often convenient to use this notation in condensed structural formulae of long-chained aliphatic compounds. The basic repeating unit of such chains is CH_2 . The number of repetitions can be expressed by enclosing the CH_2 in parentheses followed by a sub-

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methylhexane would be $\text{CH}_3(\text{CH}_2)_2(\text{CH}_3)(\text{CH}_2)_2\text{CH}_3$.

There are also several conventions for illustrating the structure of organic molecules. We have already seen one: the hexagon with an enclosed circle to denote the benzene ring (Figure 12.05). As in this illustration, carbons and hydrogens bonded to them are often omitted from representations of organic molecules. We infer a carbon at each bend of the line as well as hydrogens bonded to it. A similar short-hand may be used for aliphatic molecules as well, as illustrated in Figure 12.09. We may summarize these abbreviated illustrations as follows. A carbon is inferred at each change in angle of the line as well as at the ends. Double bonds are indicated by double lines. Each carbon may have one or more hydrogens bonded to it. Since carbon always forms 4 bonds, the number hydrogens is easily deduced as 4 less the number of other bonds shown.

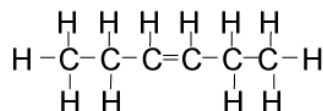
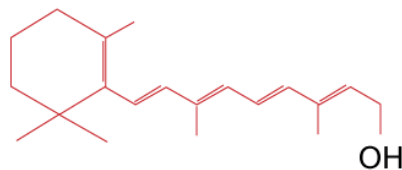
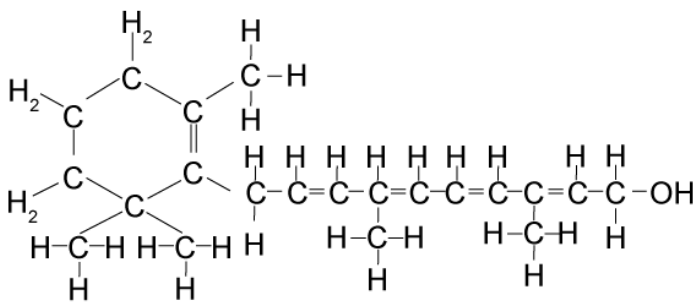
12.3.4 Biologically Important Organic Compounds

Life is, of course, based upon organic compounds. A remarkable variety of organic compounds can be found in even the simplest cells. Many of these compounds are incredibly complex, commonly having molecular weights exceeding 10,000 u. The most important of these compounds can be divided into a few fundamental classes: carbohydrates, proteins, lipids, nucleotides, and nucleic acids. Essentially all naturally occurring organic compounds originate from these classes, and most from the first three. Here we briefly review the chemistry of these biologically important compounds.

12.3.4.1 Carbohydrates

Carbohydrates are the most fundamental of the biologically important compounds in the sense that they are the direct products of photosynthesis. Virtually all life is ultimately dependent on photosynthesis, and virtually all other compounds necessary for life are synthesized in cells from carbohydrates. Some organisms, such as those of hydrothermal vent communities, depend on chemosynthesis rather than photosynthesis, but carbohydrate is also the immediate product of chemosynthesis. Thus carbohydrates may be regarded the fundamental substance of life. Furthermore, carbohydrates, cellulose in particular, are the most abundant organic compounds in nature.

Carbohydrates, as we mentioned earlier, are related to hydrocarbons by substitution of hydroxyl groups for hydrogen atoms. Two of the simplest carbohydrates are the sugars glucose and fructose, both of which have the composition $\text{C}_6\text{H}_{12}\text{O}_6$. Both can exist as straight chains or cyclic structures (Figure 12.10), though the cyclic structures predominate. Glucose and fructose are examples of *monosaccharides*, the mono-prefix indicating they consist of single chains or

(a) 3-*n*-hexene

(b) Retinol (Vitamin A)

Figure 12.09. Short-hand structural representation of 3-*n*-hexene and retinol. Carbon and hydrogen atoms are not shown in the short-hand representations. Carbons occur at each joint in the lines as well as at ends of lines. Number of hydrogens bonded to each carbon is equal to 4 less the number of other bonds shown.

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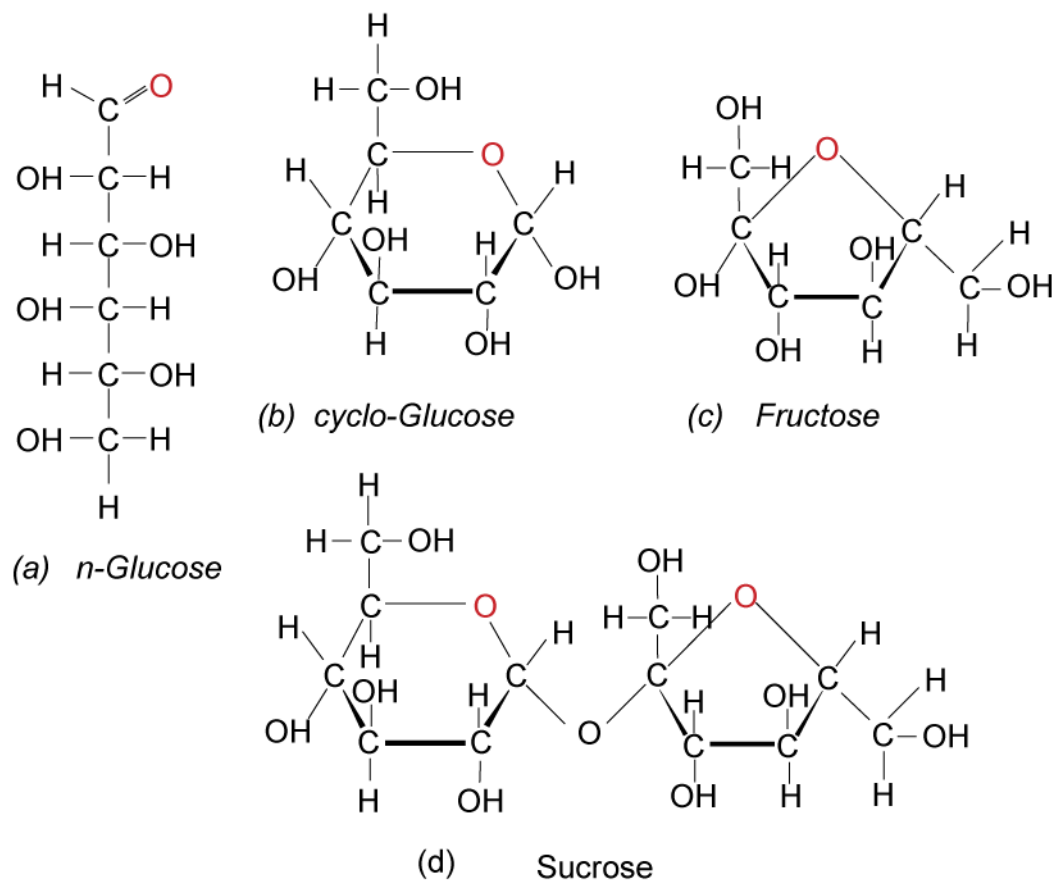


Figure 12.10. Some simple sugars. (a) linear glucose, (b) cyclic glucose, (c) fructose, and (d) sucrose, a disaccharide formed by condensation of glucose and fructose.

rings. General names for these compounds are formed from the Greek prefix corresponding to the number of carbons and the suffix *-ose*. Thus fructose and glucose are pentose sugars and ribulose (a building block of nucleic acids) is a hexose sugar. Two monosaccharide units may be linked together by elimination of H_2O to form a disaccharide (another example of a *condensation* reaction). Sucrose, or common table sugar, is the condensation product of glucose and fructose.

Molecules consisting of 10 or more monosaccharide units are called *polysaccharides*. Among the biologically most important polysaccharides are *cellulose* and *starch*. Cellulose, the basic structural material of plants, has the general formula of $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ and consists of long (i.e., $n \geq 10,000$) chains of glucose units. The chains are cross-linked to each other by hydrogen bonds, building up fibrils. In cell walls of vascular plants these fibrils are interwoven or cemented by other polysaccharides called *hemicellulose*. Cellulose is an example of a *homogeneous polysaccharide*, i.e., one that is formed by linkage of a single kind of monosaccharide. *Chitin*, the material forming hard structures in arthropods, molluscs, and some fungi and algae, is also a homogeneous polysaccharide. It is related to cellulose by replacing one of the hydroxyl groups with an amido group. Starch, which serves to store energy in plants, is also a $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ polysaccharide in its simplest form. Amylose, for example, which represents about 25% of starch, consists of long, unbranched chains of (cyclo-) glucose. Starches, however, also include heterogeneous polysaccharides, i.e., polysaccharides containing more than one kind of monosaccharide unit. Water-soluble starches consist of relatively short chains ($n \approx 25$); insoluble starches are typically longer, up to 500,000 u. Glycogen, a polysaccharide used for energy storage in animals, is closely re-

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lated to starch. From a geochemical perspective, an important difference between cellulose and starch is that the former is much more stable and less readily metabolized. Although organisms generally store energy in the form of complex carbohydrates and lipids, these are always first converted to back to glucose before oxidation releases this energy.

12.3.4.2 Nitrogen-Bearing Organic Compounds: Proteins, Nucleotides, and Nucleic Acids

Amino acids are the basic building blocks of proteins. There are 20 common amino acids, the essential characteristic of which is the presence of both an amine and a carboxylic group (Figure 12.07). The simplest amino acids are *glycine*, which consists of the amino acid group with a hydrogen at the free position (Figure 12.11), and *alanine*, which has CH_3 at the free position. Amino acids may be characterized as neutral, acidic, or basic. *Acidic* amino acids have an additional carboxylic group, which acts as a proton donor. *Basic* amino acids, such as lysine ($\text{COOHCH}((\text{CH}_2)_4\text{NH}_2)\text{NH}_2$), have an additional amine group, which can act as a proton acceptor. Neutral amino acids, such as glycine and alanine have equal numbers of carboxylic and amine groups.

Proteins are formed by condensation of many amino acid units into polymers called peptides. The simplest proteins consist of 40 amino acid units; the most complex ones consist of more than 8000 units. With 20 basic building blocks, the possible combinations are virtually limitless, making the diversity of life possible. The condensation reaction forming peptides consists of linking the carboxylic group of one amino acid to the amine group of another with the elimination of water, as illustrated in Figure 12.11. This bond is referred to as a peptide linkage. The biosynthesis of proteins is performed in ribosomes by RNA molecules. The genetic information contained in DNA is essentially a set of blueprints for protein synthesis.

There are an immense variety of proteins, and they play a wide variety of roles in life. Proteins such as *collagen* (bone) and *keratin* (hair, claws) are the essential structural and connective materials of higher animals. It is contraction of proteins in muscles that provide movement. Enzymes, which are cell's catalysts, are often proteins, as are antibodies, which play an essential role in the immune system. Proteins also act to store and transport various elements and compounds; hemoglobin is a good example of such a protein. Hormone proteins serve as messengers and regulators.

This variety of function results from primary, secondary, and tertiary structures. The primary structure of proteins depends both on the kind of amino acid units composing them and on the order in which these units occur. These

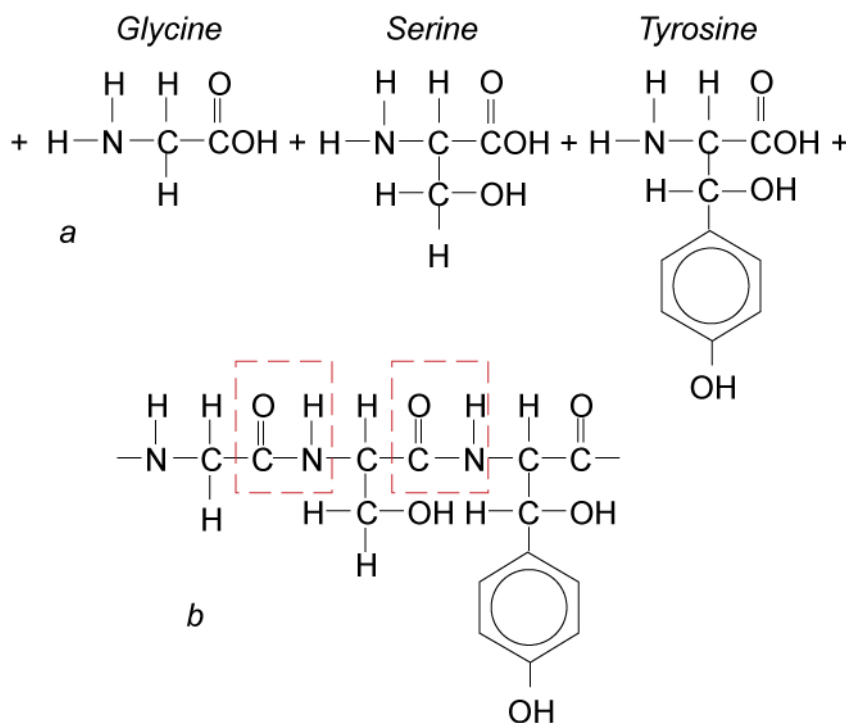


Figure 12.11. (a) Three of the twenty common amino acids that can combine to form proteins. (b) Peptide segment consisting of glycine, serine and tyrosine bound by peptide linkages (dashed boxes). Peptide linkage occurs between amine and carboxyl groups with the elimination of H_2O .

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primary structures may then be folded. The folds are locked in by hydrogen bonds between adjacent parts of the chain (secondary structures). Other proteins are twisted into α -helix structures. Folding of the α -helix results in tertiary structures. All these structures contribute to the biological function of the protein.

Nucleotides are based on pyrimidine or purine groups (Figure 12.12). The nucleotides adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADP), illustrated in Figure 12.11, play key roles in both the creation and storage of chemical energy (photosynthesis) and its transfer and release (respiration) in organisms. Another nucleotide, nicotinamide adenine dinucleotide (NAD) plays an important role in respiration. ATP can be formed from ADP (adenosine diphosphate) by the addition of an inorganic phosphate ion. This process, called *phosphorylation* involves a free energy change (ΔG) of about +40 kJ/mol. That energy is readily liberated on demand by the reverse reaction. Thus ATP serves as a general carrier of free energy within cells. NAD and NADP and their reduced equivalents (NADH and NADPH) serve as redox couples and as transport agents of reduced hydrogen.

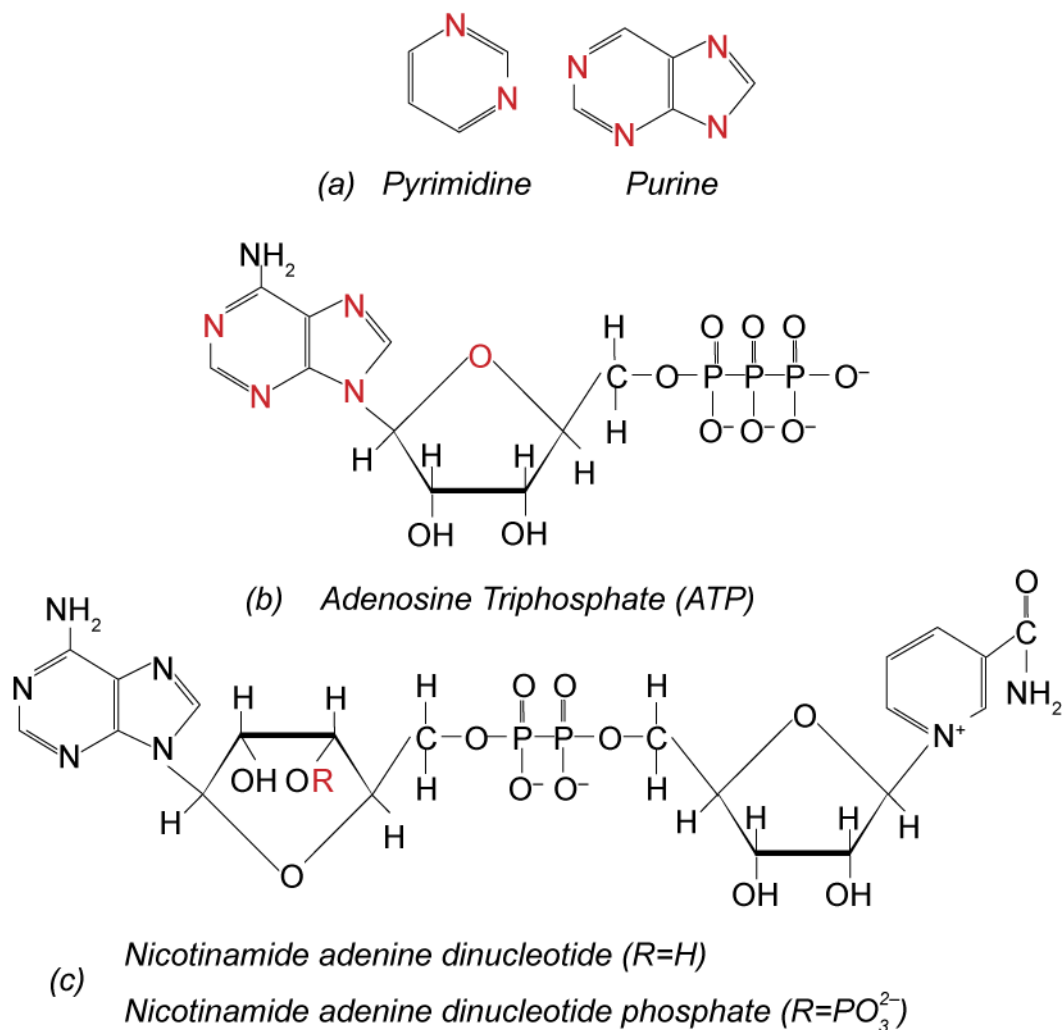


Figure 12.12. (a) The structure of pyrimidine and purine groups, essential components of nucleotides. (b) Structure of the nucleotide adenosine triphosphate (ATP). (c) Structure of NAD or nicotinamide adenine dinucleotide (when the radical labelled R is H) and NADP or nicotinamide adenine dinucleotide phosphate (when R is phosphate).

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Nucleic acids are related to proteins in the sense that are nitrogen-containing polymers built from a variety of fundamental groups. The amine, phosphate (PO_4^{3-}), and pyridinyl (Figure 12.07) groups are among the essential ingredients of nucleic acids. Unlike proteins, the carboxyl group is generally not present. The nucleic acids DNA (deoxyribonucleic acid) and RNA (ribonucleic acid) contain the genetic code and control protein synthesis within the cell. DNA consists of two backbone strands of a polymer made up of phosphate and the pentose sugar β -D-ribose connected to each other by pairs of the 4 nucleotides, cytosine, thymine, adenine, and guanine. The genetic information is encoded in the sequence of pairs.

12.3.4.3 Lipids

Unlike carbohydrates and proteins, *lipids* are defined not by their composition and structure, but by their behavior: lipids are those organic substances that are water insoluble but are soluble in organic solvents such as chloroform, toluene, acetone, and ether. Lipids include fats, oils, waxes, steroids, and other compounds. Fats and oils are generally *triglycerides*, which are esters of 3 *fatty acids* and *glycerol*, an alcohol (Figure 12.13). Fatty acids are straight-chained (aliphatic) carboxylic acids (i.e., an alkane with a carboxyl group at one end). They typically range in length from C_{12} to C_{36} . Because they are generally formed by successive additions of acetyl (C_2) units, fatty acids have predominantly even numbers of carbon atoms. Unsaturated fats, such as *oleic acid* ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}(\text{O})\text{OH}$), predominate in plants, whereas saturated fats, such as *stearic acid* ($\text{CH}_3(\text{CH}_2)_{16}\text{CH}(\text{O})\text{OH}$), predominate in animals. In *phospholipids*, one of the fatty acids in the triglyceride is replaced by a phosphate unit, which is in turn often linked to a nitrogen base. Many *glycolipids*, which are combinations of lipids and carbohydrates, are triglycerides in which one of the fatty acids is replaced by a sugar. Ether lipids are glycerides formed from straight-chained alcohols, called *n-alkanols* or fatty alcohols, rather than fatty acids.

Waxes are a mixture of many constituents. Among the most important are wax esters, which are esters of straight-chained fatty acids and fatty alcohols, both of which have chain lengths generally in the range of C_{24} to C_{28} . The fatty alcohols also have predominantly even number of carbon atoms because they are synthesized from fatty acids. Plant waxes also contain long, straight-chained hydrocarbons (C_{23} to C_{33}). These hydrocarbons typically have odd numbers of carbons because they are formed by *decarboxylation** of fatty acids. *Cutin*, which forms protective coatings on plants, is a polymerized hydroxy fatty acid (commonly C_{16} or C_{18}).

Another important class of lipids is the *terpenoids*. Terpenoids display a great diversity of structure, but the basic unit of all terpenoids is the isoprene unit, a branched, 5-carbon chain with a methyl group attached to the second carbon atom (Figure 12.14a). Terpenoids are named on the basis of the number of isoprene units present: monoterpenoids have 2, sesquiterpenoids have 3, diterpenoids have 4, triterpenoids have 6, tetraterpenoids have 8. Molecules consisting of more than 8 isoprene units are termed polyterpenoids. Terpenoids may be cyclic (e.g., methanol, Figure 12.14b) or acyclic, saturated or unsaturated.

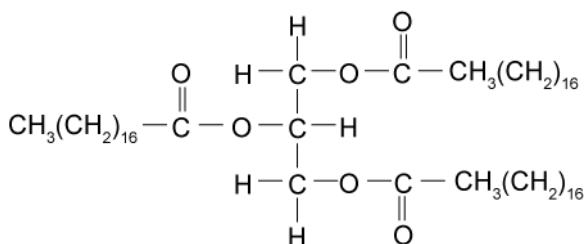


Figure 12.13. A triglyceride fat formed from the alcohol glycerol and three molecules of stearic acid.

Among other things, terpenoids serve as pheromones (scents, attractants), hormones, antibiotics, resins, and vegetable and animal oils. The noncyclic terpenoids, often referred to as acyclic *isoprenoids*, are important from a geochemical perspective because they are common component of sedimentary organic matter. Furthermore, they are also found in petroleum, apparently having survived diagenesis. Many isoprenoids in sedimentary organic matter are

* *Decarboxylation* is a process whereby a CO_2 molecule is lost from an organic compound. *Carboxylation* is the addition of a CO_2 molecule to an organic molecule.

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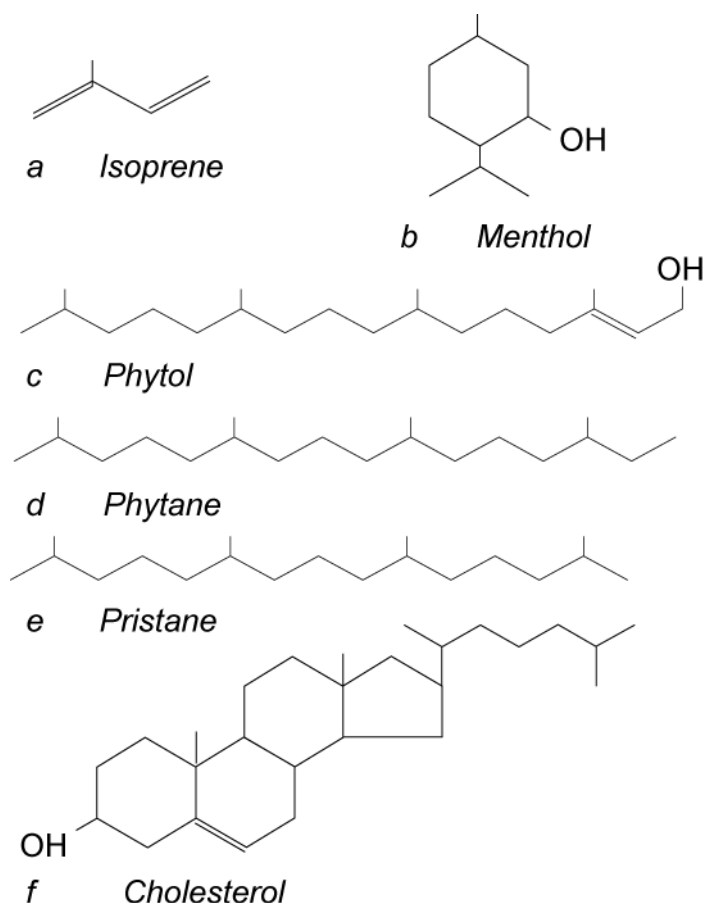


Figure 12.14. Terpenoids. a. Isoprene, the building block of all terpenoids. b. Menthol, a simple cyclic monoterpene. c. Phytol, an acyclic diterpene. d. Phytane, an acyclic diterpene derived from phytol. e., Cholesterol, illustrating the ring system shared by all steroids. The carbon atoms at the apices of the phenols and the hydrogens bound to them are not shown.

such as cutin form protective barriers. Other lipids act as sex pheromones (i.e., providing scent) or hormones, or assist in digestion. From a geochemical perspective, lipids are important because they are thought to play a dominant role in petroleum formation. Furthermore, many oils and pigments are unique to groups of organisms. Some of these, isoprenoids in particular, can survive diagenesis, and can be used in reconstructing the origin of hydrocarbon deposits. Such compounds are called *biomarkers*.

12.3.4.4 Lignin and Tannins

Lignin is another important structural material in higher plants. It forms a network around cellulose to provide structural rigidity in wood. It is second only to cellulose as the most abundant organic molecule in the biosphere. It is a rigid, high molecular weight polyphenol. As such, it is quite stable and resistant to bacterial decomposition. As a result, it is a very important contributor to soil and terrestrial sedimentary organic carbon. Because marine plants are almost exclusively algae, most of which

derivatives of *phytol*, a diterpenoid that forms part of chlorophyll-a (Figure 12.15), a key compound in photosynthesis. Under strongly reducing conditions during diagenesis, phytol (Figure 12.14c) is converted to *phytane* (Figure 12.14d), whose backbone is a 16-carbon chain, through the loss of the OH functional group and hydrogenization (loss of the C-double bond). Under less reducing conditions, phytol is converted to *pristane* (Figure 12.14e), which has one less carbon in its backbone. Another important isoprenoid is squalene, a triterpenoid ($C_{30}H_{50}$). Squalene is abundant in both plants and animals. Among other things, it is the precursor of a biologically important class of compounds called *steroids*. *Cholesterol* (Figure 12.14f) is a triterpenoid that occurs in both plants and animals. Most cholesterol is found in cell membranes and in lipoproteins. Cholesterol also serves as the precursor of other animal steroids.

Like proteins, lipids play a variety of roles in life. Phospholipids are the primary constituents of cell membranes. Per unit weight, lipids release twice as much energy as carbohydrates upon oxidation. Thus fats and oils serve as efficient stores energy for both plants and animals. Lipids include pigments that are essential in photosynthesis in plants (e.g., chlorophyll) and vitamin A production in mammals (e.g., carotenoids). Waxes

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do not produce lignin (red algae, which are often multicellular seaweeds are the exception), lignin is a much less important contributor to marine organic carbon.

Tannins, whose name derives from their use in tanning leather, are another class of compounds found only in higher plants. They occur predominantly in bark and leaves and function to make the plant less palatable to herbivores. Like lignin, they are high molecular weight (500-3000) polyphenol compounds. Functional groups include carboxyl as well as OH.

12.4 THE CHEMISTRY OF LIFE: IMPORTANT BIOCHEMICAL PROCESSES

Our main concern in this chapter is the role played by organic compounds outside living tissue. Nevertheless, given the remarkable impact of life upon the surface of the Earth and its chemistry, and

the interplay and constant exchange between living and non-living organic matter, a very brief survey of the more important biochemical processes is appropriate at this point.

As was mentioned earlier, autotrophs produce the energy they need by synthesis of organic compounds from inorganic ones. Most autotrophs are phototrophic: they use light energy to synthesize organic compounds, a process known as photosynthesis. Some bacteria use chemical energy, derived from the oxidation of H_2S or other reduced species, to synthesize organic compounds in a process called chemosynthesis.

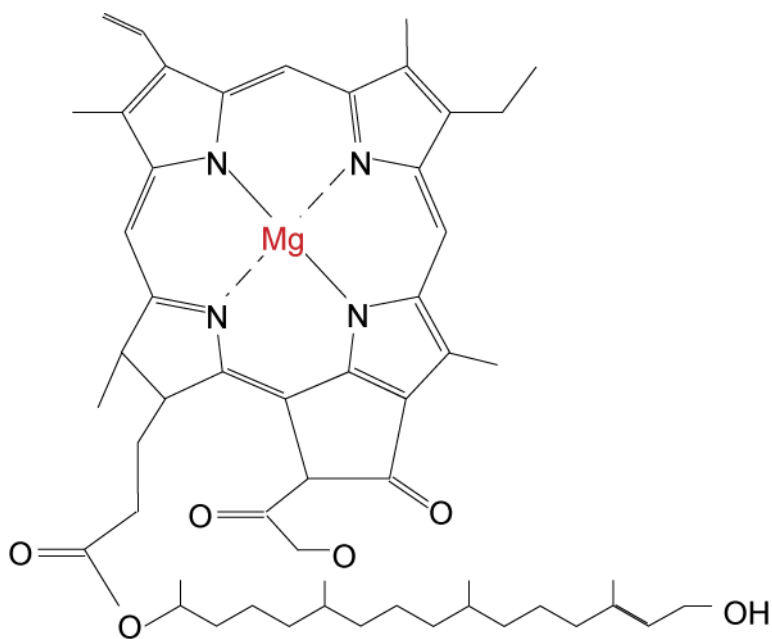
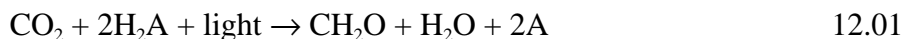


Figure 12.15. Structure of chlorophyll-a. The linear chain is a phytol unit.

12.4.1 Photosynthesis

Like most biochemical processes, photosynthesis is a complex one, involving many steps catalyzed by a variety of compounds. The details of the photosynthetic processes also vary somewhat between photosynthetic bacteria and true plants. In true plants, photosynthesis takes place within specialized intracellular organelles called chloroplasts. In prokaryotic bacteria such specialized intracellular units are absent. In these organisms, the site of photosynthesis may take place internal membranes within the cell protoplasm, as in the case of the cyanobacteria, or on the cell's plasma membrane, as in the case of the halophiles.

We can describe photosynthesis with the following reaction:



In photosynthetic eukaryotes and cyanobacteria, A is oxygen, and hence the hydrogen donor is water. However, in anaerobic photosynthesis, carried out by some photosynthetic bacteria (for example the purple sulfur bacteria), A may be sulphur, so that H_2S is the hydrogen donor; alternatively, hydrogen may be taken up directly. In oxygenic photosynthesis, carried out by plants and some photosynthetic bacteria, molecular oxygen is a by-product of photosynthesis and it is this process that is to a large degree responsible for free oxygen in the atmosphere. Some bacteria can fix CO_2 without liberating oxy-

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gen, a process called non-oxygenic photosynthesis. Our brief description will focus on oxygenic photosynthesis.

Oxygenic photosynthesis can be divided into a light and a dark stage. The former involves two separate photoreactions. The first of these, governed by Photosystem II (or PS II) is the photodissociation of water. This reaction can be described as:



Among the enzymes mediating this process is a Mn-bearing protein, which takes up the liberated electrons by oxidation of Mn. The hydrogen ions and electrons produced by PS II travel along distinct chemical pathways, which in the case of the latter include Fe- and Cu-bearing proteins, to the site of the dark reactions. The energy from the electrons liberated in PS II is used for phosphorylation of ADP to ATP. In Photosystem I (PS I), NADP^+ is reduced to NADPH. In the subsequent dark reactions, this NADPH acts as an electron donor in the reduction of CO_2 , and the energy for this reaction is supplied by ATP.

Energy to drive both PS I and PS II is captured by chlorophyll (Fig. 12.15), a member of a class of lipids called *porphyrins*, or some other light absorbing pigment. There are several varieties of chlorophylls, several of which are generally present within a given plant. Chlorophyll-a is the principal photosynthetic pigment in plants and cyanobacteria. Some other bacteria, such as the green sulfur bacteria, utilize a closely related substance called bacteriochlorophyll. The halophiles, members of the archeobacteria, use retinol (the same light-sensitive pigment in the human retina) rather than chlorophyll to capture light energy. All chlorophylls strongly absorb light in the red and blue parts of the visible spectrum

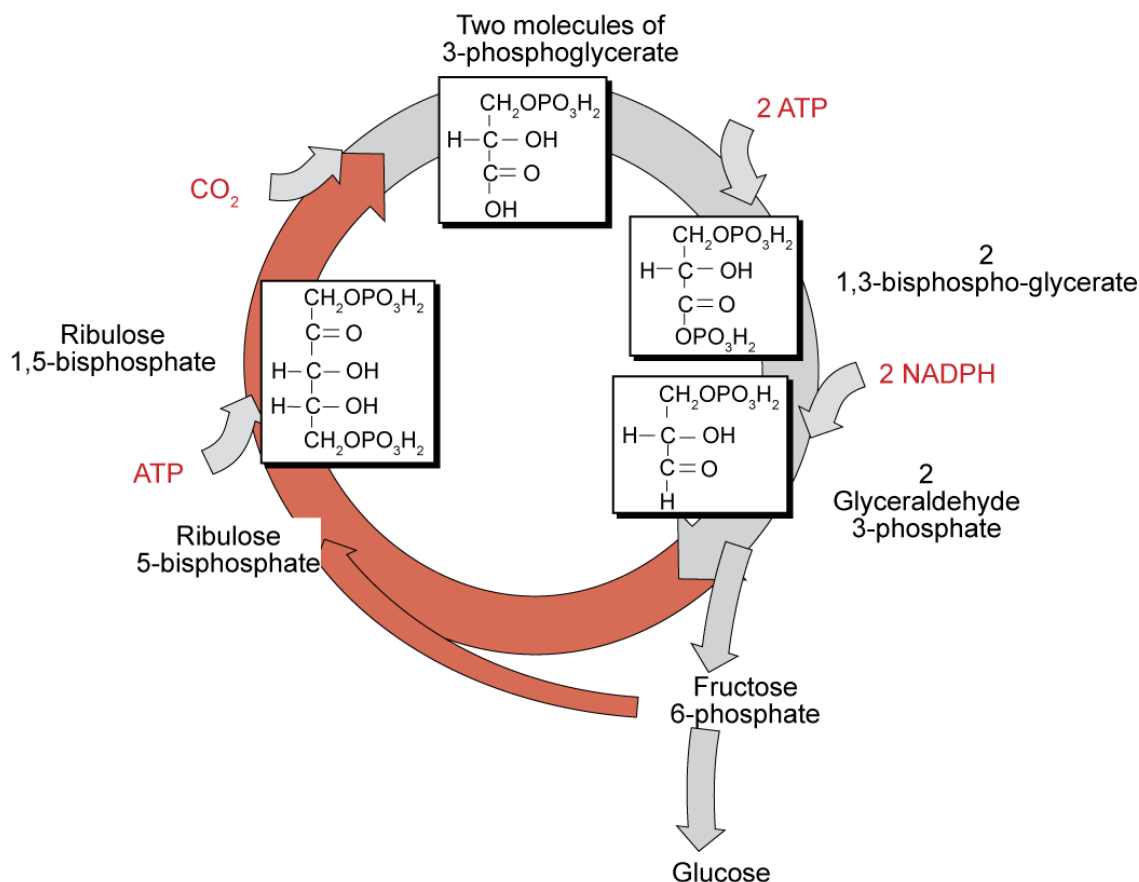


Figure 12.16. The Calvin cycle of dark reactions for the production of glucose in C₃ plants.

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(the green color of plants results from a lack of absorption of green light).

It is in the dark stage of photosynthesis that carbohydrate is actually synthesized. At this point, there is a divergence in the chemical pathways. In C_3 plants the initial carbohydrate produced (3-phosphoglycerate) is a 3-carbon chain. This process, known as the Calvin Cycle (illustrated in Figure 12.16) is used by all marine plants and about 90% of terrestrial plants. The first step is the *phosphorylation*, or the addition of a phosphate group. In this reaction, ribulose 5-phosphate, a C_5 sugar containing

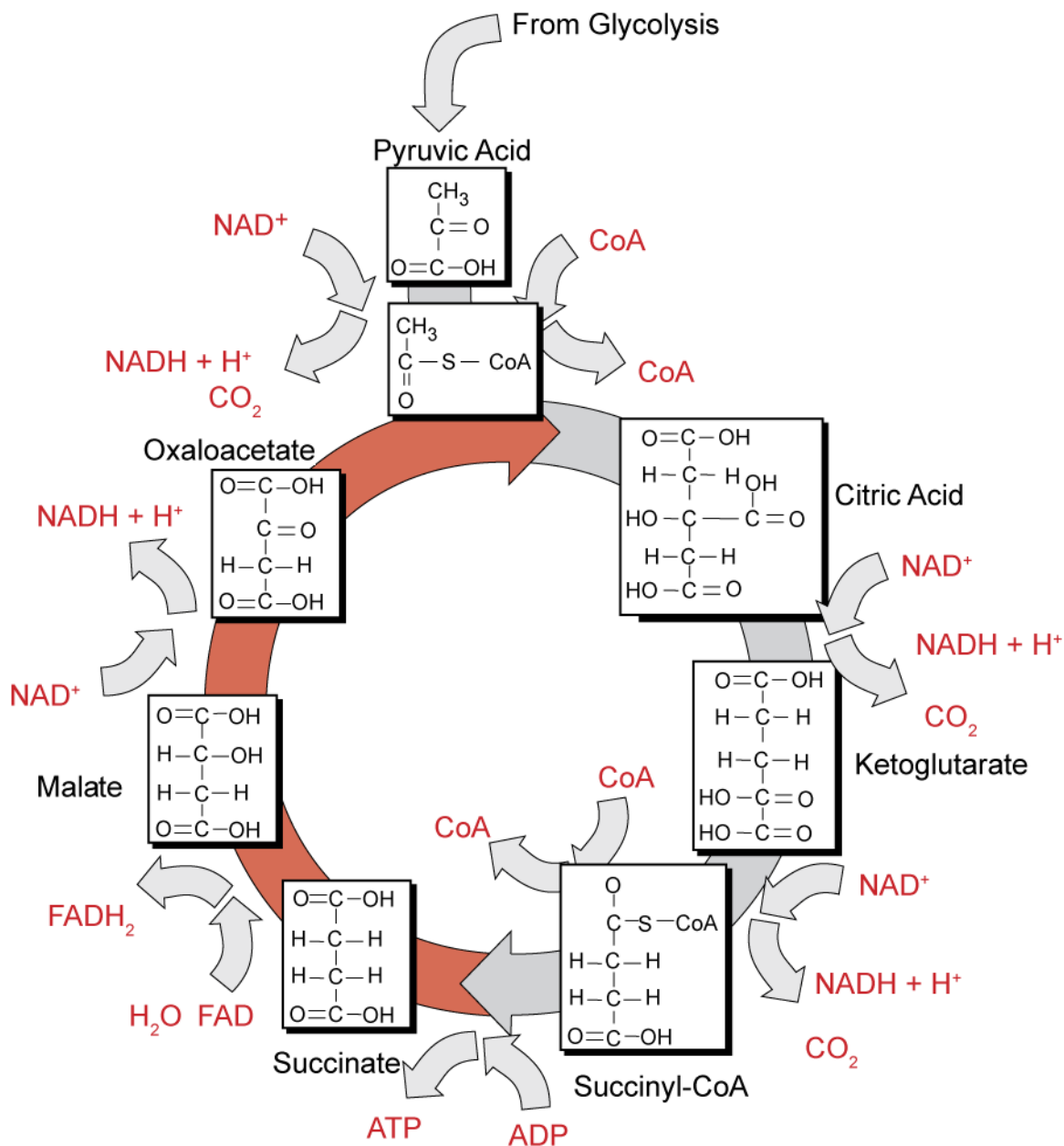


Figure 12.18. Illustration of the Krebs, or Citric Acid, Cycle, in which organic matter is oxidized by organisms to produce energy in the form of ATP. New pyruvate enters the cycle at the top, where one carbon is removed from the structure. The remaining two carbons join with a four-carbon oxaloacetate chain from a previous cycle to form citric acid, from which 2 additional carbons are successively stripped.

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1 phosphate, is converted to ribulose 1,5-bisphosphate, with the additional phosphate coming from the ATP generated during the light stage. In the next step, an enzyme called *ribulose biphosphate carboxylase oxygenase* (RUBISCO) catalyzes a reaction in which ribulose 1,5-bisphosphate reacts with one molecule of CO_2 to produce 3 molecules of 3-phosphoglyceric acid. Then an additional phosphate is added to each of these molecules to form 1,3-bisphosphoglycerate. This phosphate is then replaced by hydrogen supplied by NADPH to form glyceraldehyde 3-phosphate. It is in this step that the new CO_2 in the phosphoglycerate is reduced. The ΔG for reduction of CO_2 to CH_2O is about +480 kJ/mole. Most of this energy is supplied by the oxidation of two molecules of NADPH to NADP^+ . Most of the resulting triose phosphate is converted back to ribulose 5-phosphate for further synthesis, but some is used for synthesis of fructose or glucose. Monosaccharides produced in this way, if not immediately metabolized, are eventually converted to more complex carbohydrates or other essential compounds.

The other photosynthetic pathway is the Hatch-Slack Cycle, used by the C_4 plants, which include hot-region grasses and related crops such as maize and sugarcane. These plants use *phosphoenol pyruvate carboxylase* (PEP) to initially fix the carbon and form oxaloacetate, a compound that contains 4 carbons. CO_2 is fixed in outer mesophyll cells as oxaloacetate and is then transported, either as malate or aspartate, to inner "bundle sheath" cells, where it is decarboxylated and refixed in the Calvin Cycle (Fig. 9.14). C_4 photosynthesis appears to have evolved only recently, the oldest known C_4 plants are of late Miocene age (though there has been speculation they may have first evolved in the Cretaceous). Because the C_4 pathway is somewhat more efficient at low ambient concentrations of CO_2 , there has been speculation that their appearance may reflect an evolutionary response to low atmospheric CO_2 concentrations of the late Cenozoic.

From a geochemical perspective, the most important aspect of the difference between C_3 and C_4 plants is the difference in carbon isotope fractionation during photosynthesis. The C_3 pathway produces a $\delta^{13}\text{C}$ fractionation of from -20 to -30‰, whereas the C_4 pathway produces a much smaller fractionation of about -13‰. Further aspects of this are discussed in Chapter 9.

Some bacteria, the chemoautotrophs, obtain the energy necessary to reduce CO_2 to carbohydrate from oxidation of sulfide to sulfate or of ferrous iron to ferric iron. As in the light stage of photosynthesis, the oxidation reactions, catalyzed by an enzyme called dehydrogenase, provide both protons (for reduction of CO_2) and energy in the form of electrons. Although they require reduced species for energy, chemosynthetic bacteria are aerobic. Thus they live at boundaries between oxic and anoxic conditions.

12.4.2 Respiration

Respiration is the process by which organic carbon is oxidized to H_2O and CO_2 , liberating energy in the process. Polysaccharides serve as the primary energy storage in both plants and animals. In plants, these generally take the form of starches, while in animals glycogen serves as the primary energy store. In both cases, single glucose molecules are first liberated from these chains before being oxidized. This is accomplished through the catalytic action of an enzyme[‡]. There are a very large number of enzymes, many designed to catalyze the breaking (or formation) of a single specific bond. Glucose molecules liberated from complex carbohydrates in this fashion are then converted to two molecules of pyruvic acid in a multi-step process called *glycolysis*. The first steps involve phosphorylation and conversion of glucose to fructose diphosphate. The fructose diphosphate is then cleaved into two triose phosphates and converted to pyruvic acid (CH_3COCOOH) upon removal of the phosphates. This liberates 2 hydrogen atoms, which are consumed by the reduction of NAD^+ to NADH, per glucose molecule. The reduction of each NAD^+ consumes about 219 kJ/mol. This energy can be later used to produce ATP. Although ATP is consumed in the initial phosphorylation steps, it is produced in subsequent steps and the entire

[‡] Enzymes are denoted by the ending "-ase". Classes of enzymes that catalyze hydrolysis reactions are named by combining the name of the class of compounds whose hydrolysis they catalyze with the suffix "-ase". Thus lipases catalyze the hydrolysis of lipids, amylases catalyze the hydrolysis of starches, etc.

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process results in a net production of 2 ATP molecules per glucose molecule (and an additional energy gain of 80kJ/mole).

Glycolysis does not release CO_2 . Energy released in the process comes primarily from oxidation of hydrogen in the sugar to hydroxyl and resulting conversion of a sugar (glucose) to a carboxylic acid (pyruvic acid). Thus glycolysis releases only a small fraction of the energy stored in the glucose molecule. Under aerobic conditions, further energy may be obtained by oxidation of the pyruvic acid molecule. This oxidation of pyruvic acid occurs within the mitochondria of eukaryote cells in a process called the *Krebs Cycle* (illustrated in Figure 12.17), or alternatively the *Citric Acid Cycle* (in contrast, glycolysis occurs within the general cell cytoplasm). In the Krebs cycle, pyruvic acid is first oxidized to acetyl coenzyme A (a reactive thioester) plus CO_2 . This acetate is then combined with an oxaloacetate produced in an earlier Krebs cycle to form citrate. Two additional CO_2 molecules as well as additional hydrogens are then successively stripped, ultimately producing an oxaloacetate. Thus one pass through the Krebs cycle completely oxidizes one pyruvic acid molecule, producing 4 molecules of NADH, one of FADH_2 (FAD, flavin adenosine dinucleotide, is an oxidizing agent similar to NAD), and one of ATP. The hydrogen stored in FADH_2 and NADH are passed along through a series of protein carriers until it is finally combined with free oxygen to form H_2O . The last step generates 3 molecules of ATP per water molecule produced. In all, 36 molecules of ATP can be produced per molecule of glucose, 34 of these being produced in the Krebs cycle.

Fats serve as secondary energy storage in both plants and animals. Because they contain less oxygen, they store approximately twice as much energy per unit weight as carbohydrates. Respiration of fats involves breaking them into their component fatty acid and glycerol units. The glycerol is converted to triose phosphate, much as glucose, and then enters the Krebs Cycle as pyruvate. The fatty acids undergo successive loss of C_2 units that subsequently enter the Krebs Cycle as acetyl coenzyme A.

When oxygen is absent in cells, hydrogen carried by NADH cannot be oxidized to H_2O and the Krebs Cycle cannot operate. Some organisms that normally live under aerobic conditions can switch to an alternative metabolism, called *fermentation*, which does not require oxygen. Such organisms are called *facultative anaerobes*. When such cells are deprived of oxygen, NAD^+ is regenerated from NADH by reduction of pyruvic acid. Lactic acid* ($\text{CH}_3\text{CH}(\text{OH})\text{COOH}$) is one of several possible products of this process. In alcoholic fermentation, carried out by yeast, CO_2 is removed from pyruvate leaving acetaldehyde (CH_3CHO), which is then reduced to ethanol ($\text{CH}_3\text{CH}_2\text{OH}$). Many bacteria can live only by fermentation and are poisoned by free oxygen. Such organisms are called *obligate anaerobes*. These bacteria, of which there is a great variety, carry out cellular respiration by using a compound other than oxygen as an electron acceptor. The most common such receptors are nitrate, nitrite, and sulfate, but Fe^{3+} and Mn^{4+} can be reduced by some bacteria.

12.5 ORGANIC MATTER IN NATURAL WATERS AND SOILS

12.5.1 Dissolved Organic Substances

Virtually all water at the surface of the Earth contains organic substances. These can be divided into *particulate organic matter* (POM) and *dissolved organic matter* (DOM). In a sense, though, there is a continuum, with colloids being intermediate between dissolved and particulate forms. By definition, dissolved substances are those that pass through a 0.45μ filter; particulate organic matter is anything coarser than this. Together, dissolved and particulate organic carbon are called *total organic matter* (TOM). The carbon fraction of this organic matter is called *total organic carbon* (TOC) and can likewise be divided into *particulate organic carbon* (POC), which is also called *suspended organic carbon* (SOC), and

* Animal muscle cells have the ability to switch to fermentation when oxygen cannot be supplied fast enough for NAD^+ to be regenerated. Under these circumstances, lactic acid, the formal name for which is 2-hydroxy-propanoic acid, builds up in muscle tissue. The presence of lactic acid is what produces the sore muscle feeling that often accompanies vigorous exercise. "Conditioning" involves a number of processes, including increasing efficiency of oxygen delivery and a build-up of glycogen stores in muscle tissue, but also increasing tolerance to lactic acid. Nerve and brain cells, however, cannot respire anaerobically and quickly die when deprived of oxygen.

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dissolved organic carbon (DOC). In some instances, several other distinctions are made. Those organic substances that are volatile at ambient temperature constitute volatile organic carbon (VOC). Colloids have sizes in range of 1 nanometer to $0.45\ \mu$, corresponding to molecular weights greater than about 10,000. They may be specifically referred to as colloidal organic matter (COM).

Figure 12.18 illustrates the range in concentrations of dissolved and particulate organic carbon. Groundwater and seawater typically have the lowest organic carbon concentrations, while wetland waters (bogs, swamps, marshes) have the highest. The interstitial waters of the upper layers of soils often have DOC concentrations in the range of 20-30 mg/l. Organic carbon concentrations in natural waters generally show strong seasonal variations, as factors such as rainfall, biological productivity and microbial activity all may vary seasonally. One might also note that even rain and snow typically contain some DOC. The concentration is generally less 1 mg/l or less, but much higher concentrations have been measured.

Organic substances dissolved in natural waters can be divided into *simple compounds* and *humic substances*. Simple compounds include *biomolecules*, which we will define as molecules synthesized by or-

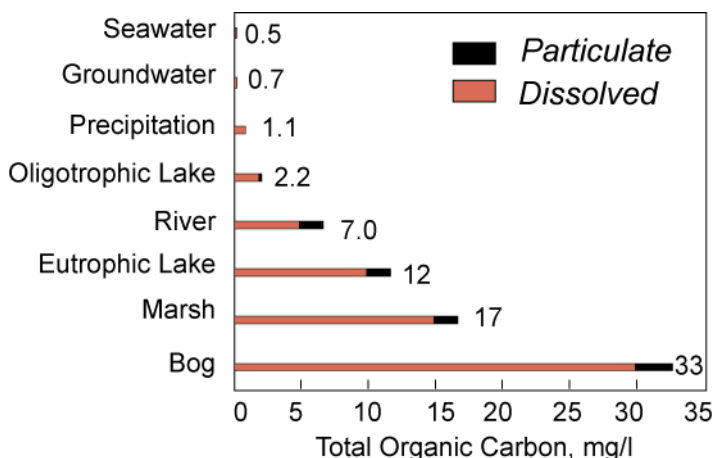


Figure 12.18. Average concentration of dissolved, particulate, and total organic carbon in various natural waters. After Thurman (1985).

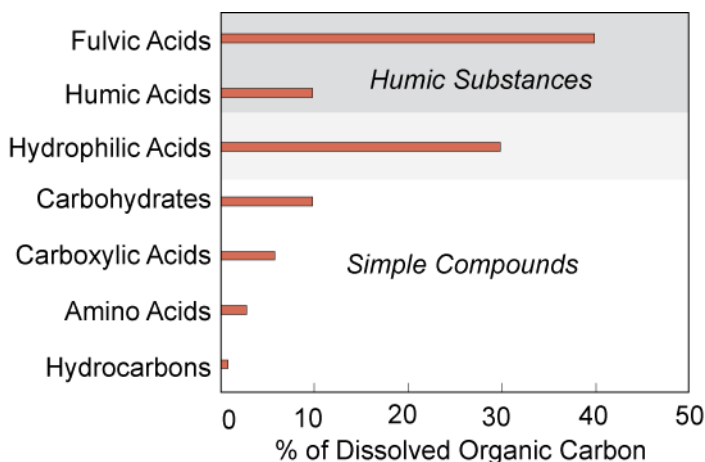


Figure 12.19. Components of dissolved organic carbon in typical river water. After Thurman (1985).

ganisms to directly support life, and breakdown products of biomolecules, as well as excreted waste products and metabolites and substances released, or exuded, by cells by organisms to assist in breaking down and assimilating nutrients. Simple compounds include carboxylic acids (including fatty acids), phenols, carbohydrates, amino acids, nucleic acids, and hydrocarbons. As we shall see, humic substances are complex and poorly understood substances found in water and soil. Their exact origin is not well understood and is still somewhat controversial, but they probably include both residues of complex biomolecules and polymers that form from condensation of simpler biomolecules. Humic substances are further divided into fulvic and humic acids based on their solubility. *Hydrophilic acids* are a third set of compounds closely related to humic substances. Hydrophilic acids are, however, more soluble (as their name implies) and generally simpler than humic and fulvic acids. Humic, fulvic, and hydrophilic acids are the most abundant organic substances in river water, as Figure 12.19 illustrates. Simple organic compounds compose a smaller fraction of DOM in deep ocean water than in river water.

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12.5.1.1 Simple Compounds

Simple compounds typically constitute 10 to 60% of dissolved organic carbon in natural waters, with an average of about 25%. Simple compounds are derived directly from cells or the breakdown of dead cells. Most of them are readily metabolized by bacteria, hence their residence time in water is usually quite short, probably a matter of minutes to days. Concentrations are maintained by continuous production by the biota. We might expect under these circumstances that the dissolved concentrations of these substances would be quite variable, and this is indeed the case. A number of instances of regular diurnal or seasonal variations in concentrations of carbohydrates and other simple compounds have been documented (reviewed in Thurman, 1985).

Fatty acids are among the most abundance of the dissolved simple organic compounds. They are also among the most important for several reasons. First, the carboxyl group acts as an acid, and hence these substances can significantly affect pH. Second, carboxylate can complex metal ions and will thus affect the concentration and activity of metal cations in solution. Third, they apparently form the basic building blocks of marine and aquatic humic substances.

The short chained carboxylic acids (C_1 to C_5), which include formic acid, acetic acid, propionic acid (CH_3CH_2COOH), butyric acid ($CH_3(CH_2)_2COOH$), and valeric acid ($CH_3(CH_2)_3COOH$) have relatively high vapor pressures and hence are known as volatile fatty acids. Acetic acid is the most abundant of these. Carboxylic acids are produced by microbial fermentation of more complex compounds and can accumulate in anaerobic environments. They are typically present in concentrations of 10 to 100 $\mu g/l$ in natural waters, but can reach higher concentrations in petroleum-related ground waters.

The longer chained, or non-volatile, fatty acids are produced by hydrolysis of triglycerides. Though these may range from C_{12} to C_{36} , C_{16} and C_{18} fatty acids (e.g., palmitoleic acid, its saturated equivalent palmitic acid, stearic acid and its saturated equivalent linoleic acid) are most common because they are most common constituents of lipids in marine and aquatic organisms. The concentrations of non-volatile fatty acids is typically 5 to 500 g/l and is generally somewhat higher than that of volatile fatty acids (Thurman, 1985).

Hydroxy and keto acids, particularly lactic, glycolic (also called hydroxy-acetic acid, $OHCH_2COOH$), and pyruvic acid, also occur in solution in natural waters in concentrations in the range of 10 to 250 $\mu g/l$. They can originate from breakdown of plant matter, but most are probably directly excreted by algae and other organisms; hydroxy acids are produced in both the Krebs and Calvin cycles, as we have seen. Other related compounds that have been identified in solution in natural waters include dicarboxylic acids such as oxalic acid and aromatic carboxylic acids such as salicylic and benzoic acid. These generally do not exceed concentrations of a few $\mu g/l$.

Phenols and other monomeric or dimeric aromatic compounds are generally present in concentrations of a few $\mu g/l$ or less in uncontaminated waters. Natural phenols result primarily from breakdown of lignins and tannins. Anthropogenic activity (i.e., pollution), however, can result in higher concentrations of phenols. An interesting example of "natural pollution" was the occurrence of high concentrations of phenol and cresol (a phenol unit with a methyl group attached to the ring) in South

Fork Castle Lake in Washington, USA. This lake was created when debris flows from the 1980 catastrophic eruption of Mt. St. Helens blocked the South Fork of Castle Creek. Concentrations of phenol approached 1000 $\mu g/l$ and that of cresol approached 100 $\mu g/l$ (McKnight et al., 1982). These compounds were presumably produced by decomposition of the many dead trees floating in the lake.

Carbohydrates constitute about

Table 12.01. Total Dissolved Carbohydrates in Natural Waters

	Concentration $\mu g/l$	% DOC
Groundwater	65-125	1-4
Seawater	100-1000	5-10
River Water	100-2000	5-10
Lake Water	100-3000	8-12

From Thurman (1985).

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10% of dissolved organic matter. Carbohydrates are found both as monosaccharides and polysaccharides, as well as a variety of other forms, such as amino sugars, and sugar alcohols. In addition, carbohydrates are present as sugars bound to humic substances. Table 12.01 summarizes typical carbohydrate concentrations in various natural waters. In fresh waters, most carbohydrates are probably derived from leaching of terrestrial plant matter. In seawater, phytoplankton are thought to be the principle source of dissolved carbohydrates. Figure 12.20 illustrates the concentrations of various carbohydrates in seawater. As this figure shows, polysaccharides are the most abundant carbohydrates, followed by saccharides associated with humic substances. Monosaccharides, sugar acids, amino sugars, methylated sugars and sugar alcohols are less abundant. Of the monosaccharides, glucose is generally the most abundant. Other important monosaccharides include fructose, arabinose, xylose, and galactose.

Carbohydrates are readily assimilated and metabolized by bacteria; hence their concentration in water is probably regulated by bacterial activity. A number of studies have demonstrated diurnal variations in carbohydrate concentration, with minimums occurring in the early morning and the maximum concentration occurring in the late afternoon. These results suggest active production of dissolved carbohydrate by phytoplankton and rapid consumption by bacteria. Thus the residence time of a carbohydrate molecule in solution may be as short as a few hours in many instances (Thurman, 1985).

Amino acids are present in natural waters both as free molecules and combined in peptides and proteinaceous substances and are also important constituents of humic substances. The concentrations of free amino acids are typically a factor of four or so lower than the concentrations of combined amino acids. The simpler amino acids, glycine, serine, alanine, lysine, and valine, are the ones most abundant as free amino acids. Typical concentrations of free and combined amino acids are 15-200 $\mu\text{g/l}$ in seawater, 15-250 in groundwater, 40-800 in rivers and lakes, 250-5000 in eutrophic lakes and marshes, and 400-9000 in interstitial waters of sediments (Thurman, 1985). Since amino acids are essential to all life, the sources of amino acids are quite varied.

A variety of hydrocarbons are also present in natural waters. These may be divided into volatile and non-volatile hydrocarbons, depending on the vapor pressure and boiling point. Short-chained hydrocarbons tend to be volatile and this volatility limits their abundance in natural waters. Longer chained hydrocarbons are not volatile. Their abundance in natural waters is often limited by their solubility, which is generally low. Hydrocarbons may originate both from natural and anthropogenic sources. Here we focus on the naturally occurring hydrocarbons; anthropogenic hydrocarbons.

Of the volatile hydrocarbons, methane is by far the most abundant. Some methane can be produced

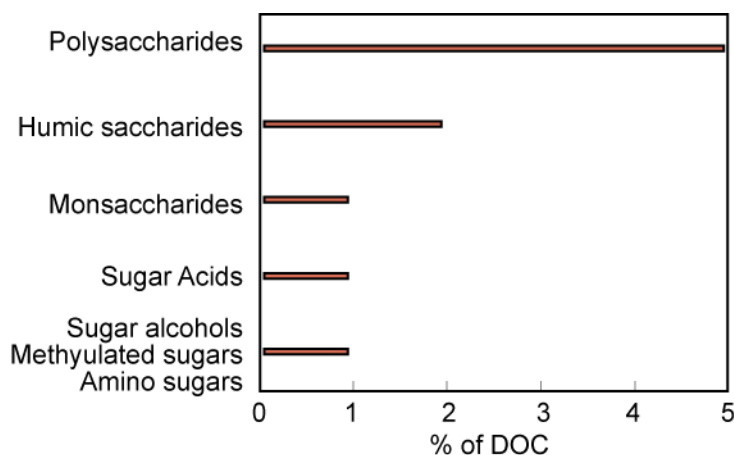


Figure 12.20. Abundances of dissolved carbohydrates in seawater as a percentage of total dissolved organic carbon. After Thurman (1985).

in the digestive tracks of higher animals, but the principal source of natural methane is methanogenic bacteria in reducing sediments. The amount of methane produced in such environments (swamps, reducing marine and lake sediments, etc.) is a significant, though minor, part of the global carbon cycle. The amount of methane released to the atmosphere from natural sources annually, primarily reducing sediments in wetlands, is 1.5×10^{14} g; anthropogenic activities release about 3.6×10^{14} g (Graedel and Crutzen, 1993). The abundance of methane in natural waters is summarized in Table 12.02. The solubility of methane in water is

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800 $\mu\text{g/l}$ (at 20°C and 0.1 MPa). At concentrations above this level, methane bubbles will form and this process is undoubtedly important in the transport of methane from sediment interstitial waters of swamps and shallow lakes to the atmosphere. Some of this methane redissolves in the lake water and is oxidized by methanotrophic bacteria.

Among the most common non-volatile and semi-volatile hydrocarbons in seawater are C_{15} and C_{17} n-alkanes (penta-decane and heptadecane) and isoprenoids. C_{15} and C_{17} originate by decarboxylation of C_{16} and C_{18} fatty acids (palmitic and stearic acids), which are derived from zoo- and phytoplankton. The isoprenoids, primarily pristane and phytane, are derived from the phytol chain in the chlorophyll molecule. *Halogenated hydrocarbons*, i.e., hydrocarbons where one or more hydrogens are replaced by a halogen, are of particular interest because of their toxicity. Most halogenated hydrocarbons in natural waters are anthropogenic, having been directly manufactured and discarded or leaked into natural waters. Others, such as chloroform and trichloromethane, can arise indirectly through chlorination of drinking water. However, some halogenated methanes do occur naturally in seawater at very low abundance levels.

12.5.1.2 Humic Substances

Humic substances are high molecular weight (> 500 u) compounds that are produced by partial degradation of complex biomolecules and recombination of these with simple biomolecules and their breakdown products. They are complex molecules: their exact structures are not known and in any case variable. As we noted earlier, humic substances dominate dissolved organic matter in natural waters. They are also important contributors to particulate organic matter.

The exact definition of humic substances is analytical and varies somewhat between dissolved humic substances and soil humic substances. Aquatic and marine humic substances are defined as colored (yellow, brown, or black), polyelectrolytic acids that can be removed from solution through absorption on weak-base ion exchange resins (e.g., the acrylic-ester resin XAD-8) or through some similar procedure. Humic substances tend to be highly refractory in the biological sense, that is, they resist decomposition by organisms. As a result, their residence time in water is on the scale of weeks to thousands of years. Their exact molecular structures are variable and therefore difficult to characterize, but in general they consist of a flexible chain with limited branching and cross-linkage to which smaller molecules and molecular fragments such as sugars and amino acids are attached. To which a variety of functional groups are attached. While the overall structure is poorly characterized, the chemical composition and functional groups are well characterized. The most important of these functional groups are carboxylic, phenolic, alcoholic, carbonyl, amino, and sulfhydryl (SH) groups. Because of the predominance of the carboxyl groups, humic substances are acidic (i.e., they act as proton donors). *Hydrophilic acids* are closely related to humic substances: they are molecules too complex to fully describe, but are not absorbed as readily onto ion exchange resins. They are slightly colored, highly branched, and highly substituted organic acids. They appear to have lower molecular weight and a greater number of acid functional groups than humic substances.

Soluble humic substances in waters are divided into *fulvic acid* and *humic acid*. The definition of these two is again analytical. Humic acids are defined as those humic substances that precipitate when the solution is acidified with HCl to a pH of 1. Fulvic acids are those substances remaining in solution at this pH.

Table 12.02. Dissolved Methane in Natural Waters

	Concentration $\mu\text{gC/l}$
Groundwater	10-10,000
Seawater	10-100
Lake Water	10-10,000
Interstitial Water	100-10,000

From Thurman (1985).

where one or more hydrogens are replaced by a halogen, are of particular interest because of their toxicity. Most halogenated hydrocarbons in natural waters are anthropogenic, having been directly manufactured and discarded or leaked into natural waters. Others, such as chloroform and trichloromethane, can arise indirectly through chlorination of drinking water. However, some halogenated methanes do occur naturally in seawater at very low abundance levels.

Table 12.03. Humic Substances in Natural Waters

	Concentration mg C/l
Groundwater	0.03-0.10
Seawater	0.06-0.60
Lake Water	0.5-4.0
Rivers	0.5-4.0
Wetlands	10-30

From Thurman (1985).

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The concentration ranges of humic substances are given in Table 12.03. As a proportion of dissolved organic carbon, hydrophilic acids predominate in seawater and groundwater, constituting about 50% of DOC. They are only slightly less important in lake waters. In wetlands, streams and rivers, fulvic acids are the most important fraction of dissolved organic carbon, constituting 60% of wetland DOC and 40% of stream and river DOC. Humic acids are always

less abundant than fulvic and hydrophilic acids. Humic acids constitute 15% of wetland DOC and less than 10% of DOC in other waters (Thurman, 1985).

While the definition of humic and fulvic acids is based on their acid solubility, there is nevertheless a compositional difference between the two. Table 12.04 compares the compositions of humic and fulvic acids from several environments. The table shows that the whole, humic substances are H-poor compared to most biomolecules. For example, carbohydrates have a C:H weight ratio of 6; the C:H ratios in Table 12.04 range from 7 to 17. Humic acid is on average poorer in hydrogen and richer in nitrogen than fulvic acid and usually poorer in oxygen as well. These compositional differences are better developed in soil humic substances than in dissolved ones.

Fulvic acid tends to have a lower average molecular weight (800-2000 u) than humic acid (>2000 u). In addition, fulvic acid has a higher content of carboxyl acid groups than does humic acid, while humic acid is richer in phenolic groups (Table 12.05). The higher content of carboxyl groups in fulvic acid and the greater abundance of aromatic structures in humic acid helps to explain the higher solubility of fulvic acid. In general, dissolved humic substances have higher concentrations of carboxyl groups than soil humic substances. The average concentration of carboxyl groups in dissolved fulvic acid, 5.5mM/g, corresponds roughly to one carboxyl group per 6 carbon atoms. In contrast, dissolved humic acid has about one carboxyl group per 12 carbon atoms.

In addition to functional groups, humic substances incorporate a variety of biomolecules in their structures. Carbohydrates account for 1% of the carbon in dissolved humic substances, and their abundances appear to be higher in humic than in fulvic acids. Many of these carbohydrates appear to be bound to the humic structure only through hydrogen bonds. Amino acids are also present in humic substances, although in smaller amounts. The most abundant are glycine, aspartic acid, glutamic acid, and alanine. Aquatic humic acids contain about 120 nM/mg amino acid; aquatic fulvic acids generally contain less: 15-120 nM/mg. Soil humic substances contain higher amino acid concentrations: roughly 500 nM/mg for soil humic acids and 150

Table 12.04. Composition of Fulvic and Humic Acids Dissolved in Natural Waters

	C	H	O	N	P	S	Ash
Groundwater							
Biscayne Aquifer Fulvic	55.4	4.2	35.4	1.8			0.04
Biscayne Aquifer Humic	58.3	3.4	30.1	5.8			10.4
Seawater							
Saragasso Sea Fulvic	50.0	6.8	36.4	6.4		0.46	
Lake Water							
Lake Celyn Humic	50.2	3.1	44.8	1.9			
Lake Celyn Fulvic	43.5	2.7	51.6	2.2			
Stream Water							
Ogeechee Stream Fulvic	54.6	4.97	38.2	0.87	0.62	0.74	0.86
Ogeechee Stream Humic	55.9	4.19	36.5	1.27	0.25	0.93	1.13

Data from Aiken et al. (1985). Concentrations in weight percent.

Table 12.05 Functional Groups in Dissolved Fulvic and Humic Acids

	Carboxyl meq/l	Phenolic meq/l
Groundwater Fulvic	5.1-5.5	1.6-2.0
Groundwater Humic		2.5
Seawater Fulvic	5.5	—
Lake Fulvic	5.5-6.2	0.5-2.1
Lake Humic	5.9	3
Stream & River Fulvic	5.5-6.4	1.5-2.1
Stream & River Humic	4.0-4.7	1.9-2.0

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nM/mg for soil fulvic acids. Hydrogen bonding appears to play a role in molecular aggregation.

Soil humic substances have core structures that are highly aromatic (20 to 70% of total C). It was originally thought that this was also true of aquatic humic substances as well. However, a variety of studies over the last 20 years have led to the view that the core structures of aquatic and marine humic substances are primarily aliphatic rather than aromatic (Malcom, 1985; Thurman, 1985; Steinberg and Muenster, 1985; Harvey and Boran, 1985). Nuclear magnetic resonance studies suggest only 15-20% of the carbon in aquatic fulvic acids and about 30% of the carbon in aquatic humic acids are aromatic. Figure 12.21 illustrates one proposed hypothetical structure of aquatic fulvic acid. This molecule has a molecular weight of about 1000 u.

There are differences between marine and aquatic humic substances. Derivatives of lignin appear to be important in the backbone of aquatic humic substances, but not marine. Marine humic acids appear to have even a smaller proportion of aromatic carbon than aquatic ones, and marine fulvic acids have essentially none. Aromatic structures are far more common in terrestrial plants than marine ones, so this suggests that terrestrial humic matter doesn't contribute substantially to marine humic matter.

The shape of humic substances is strongly influenced by pH. At low pH, humic and fulvic molecules are fibrous. At neutral pH, these fibers tend to mesh together to form a sponge-like structure. This mesh structure is capable of trapping smaller molecules. For example, fatty acids and acyclic alkenes, which are found in most humic and fulvic acids, may be simply trapped rather than bonded to the molecular backbone. Under alkaline conditions the structure becomes plate-like.

The origin of dissolved humic substances is not well understood. At one time it was widely held that aquatic humic substances consist of soil fulvic acid that had been leached or eroded from soils. However, most recent works on the subject express the view that at least a substantial fraction of aquatic humic substances is autochthonous, that is, produced within the body of water itself. The evidence favoring this view includes the compositional and structural differences between aquatic and soil humic substances. Aquatic humic substances are primarily aliphatic whereas soil humic substances are primarily aromatic. This observation in itself does not exclude derivation of aquatic humic substances from soil (since leaching may preferentially remove aliphatic-rich molecules), but the difference is con-

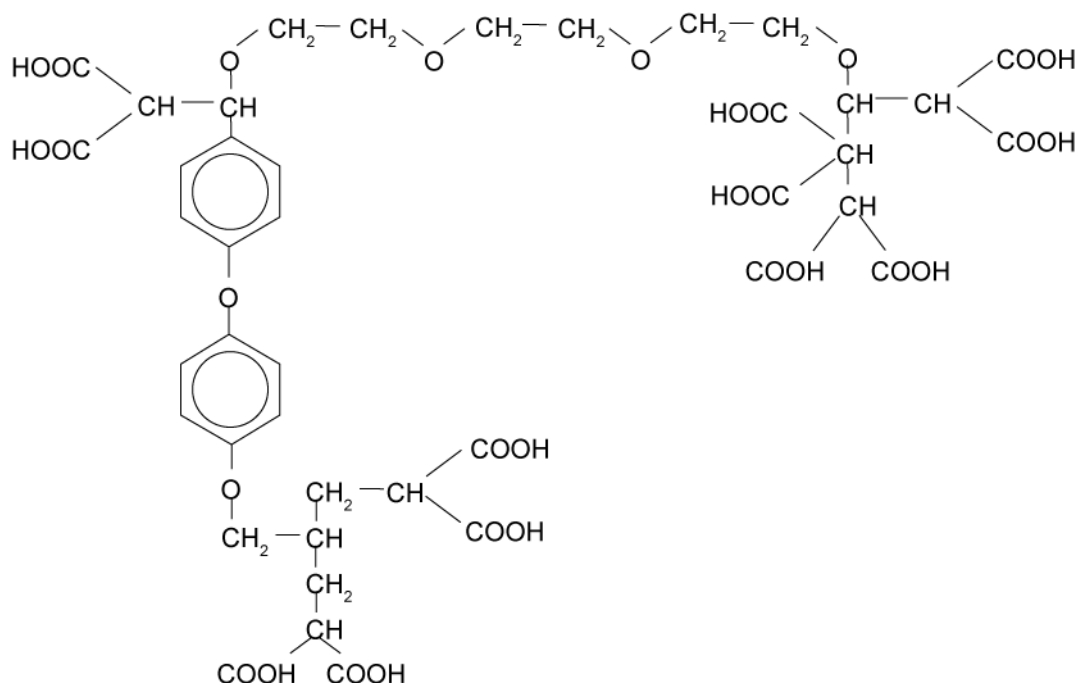


Figure 12.21. Hypothetical structure of aquatic fulvic acid. After Bergmann (1978).

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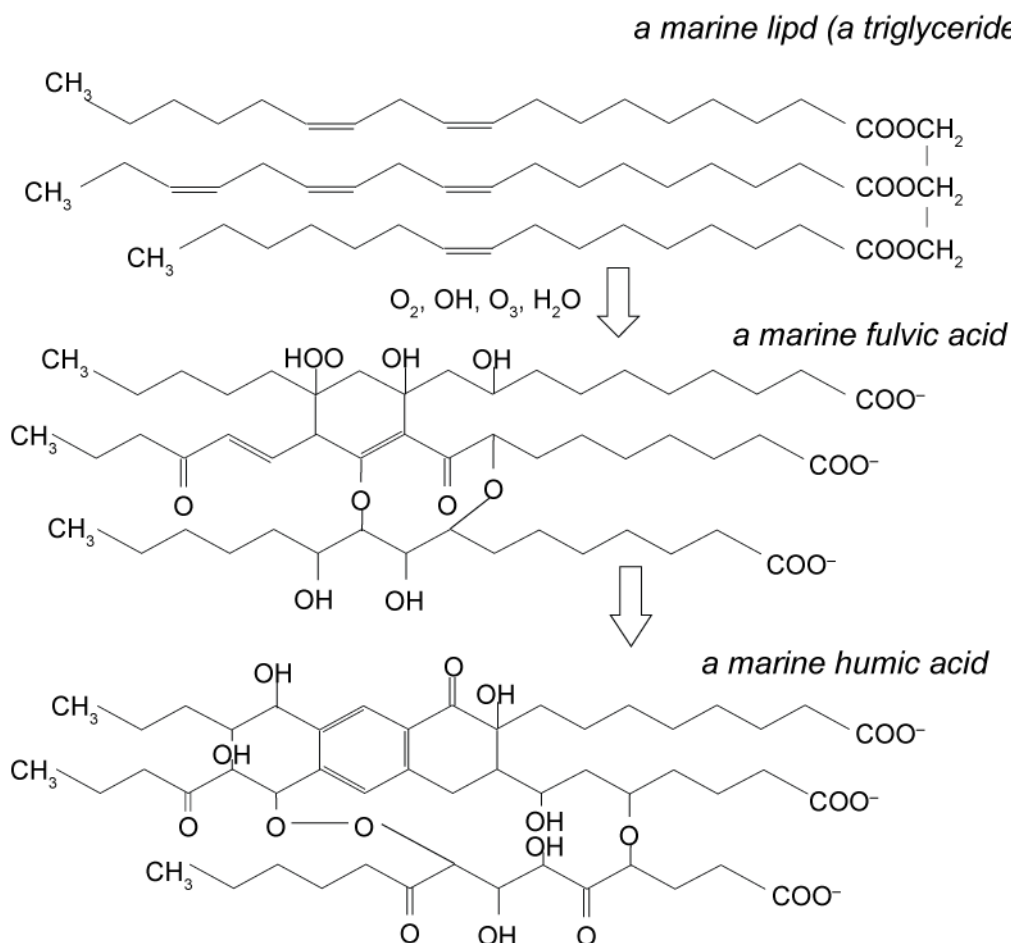


Figure 12.22. Possible mechanism for generation of marine fulvic and humic acids from triglycerides. After Harvey and Moran (1985).

sistent with soil humic substances being derived primarily from higher plants (which are rich in aromatic molecules such as lignin and tannins), and aquatic humic substances being derived primarily from algae and zooplankton (which are poor in aromatic molecules). An additional question is the degree to which humic substances are composed of partially degraded macromolecules or are condensed from simpler fragments. The latter view is supported by several observations. One is that clay particles, metal oxides, and metal cations all can promote polymerization of organic molecules. Bacteria, or enzymes released by them, have also been shown to promote condensation and polymerization of organic molecules. Hydrophilic acids may be precursors of the more complex fulvic and humic acids. As we noted, soil humic substances are highly aromatic, and this suggests that lignins and tannins derived from higher plants are important contributors to soil humic substances. Lignins and tannins are relatively resistant to decomposition, although they are probably modified to some degree by decomposers before incorporation in humic molecules. Molecular by-products of decomposers and their remains as well as waxes from higher plants are probably the primary contributors to the aliphatic components of soil humic substances (Killops and Killops, 2005).

Marine fulvic acids may arise by autoxidative cross-linking of polyunsaturated lipids, perhaps catalyzed by light and transition metals (Harvey and Moran, 1985). Olefinic carbons (i.e., those doubly bonded to other carbons) may be particularly susceptible to autoxidation. Figure 12.22 illustrates this process. A number of laboratory experiments have demonstrated the plausibility of production of marine humic substances in this manner. In this model of humic substance generation, aromatic units in

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marine humic acid arise from cross-linking of fatty acid chains. Another possibility is that aromatic units in marine humic acids are derived from terrestrial sources: degradation products of lignin and tannin washed into the sea. Most likely, however, terrestrial material is only a locally important contributor to marine humic substances.

12.5.2 Organic Matter in Soils

Organic matter can constitute a third or more of the mass of poorly drained

soils, though fractions from 6% to 10% are more common in well-drained soils. Concentrations of organic matter are highest in the surface layers (O and A) and low in the deeper layers (C). In the soil solution, a range of 2 to 30 mg/l DOC is common (Thurman, 1985). Soil organic matter, collectively called *humus*, includes biomolecules as well as humic substances. Biomolecules can be released from dead cells, excreted from living ones, or leached from foliage and rinsed into the soil by rain (i.e., throughfall). In addition, soil organic matter includes a variety of substances, called *exudates*, released by macro- and microorganisms expressly to breakdown both organic and inorganic components in soils so that they may be assimilated. Among other reasons, the exudates are necessary because many biomolecules are too large to pass through microbe cell walls. Among the most important of the exudates are simple carboxylic acids such as acetic and oxalic acid (Fig. 12.06), formic acid (HCOOH), tartaric acid (2,3-dihydroxybutanedioic acid: $\text{COOH}(\text{CH}(\text{OH}))_2\text{COOH}$) and citric acid, and a variety of phenolic acids. The OH groups of phenols may also dissociate, and hence these compounds also contribute to soil acidity and rock weathering, though less so than the carboxylic acids. These simple organic acids are commonly present in relatively high concentrations around plant roots in soils, though on average their concentration is less than 1mM in the soil solution (Drever and Vance, 1994). Because of the presence of both these simple acids and the more complex fulvic and humic acids, most soils are slightly acidic. These acids contribute both directly (through surface complexation reactions) and indirectly (as proton donors, as by increasing the solubility of cations through complex formation) to weathering of rocks, although the overall extent to which weathering is accelerated by plants is unclear. As most biomolecules are readily metabolized by bacteria, their residence time in the soil is likely to be quite short, a matter of days or less. Concentrations of these molecules are maintained by continuous production by the biota. In contrast, the residence time of refractory humic substances in soils can be as long as thousands of years.

The definition of soil humic substances differs slightly from that of aquatic and marine humic substances. Soil humic substances are divided into *fulvic acid*, *humic acid*, and *humins* based on their solubility. By definition, the organic material that remains insoluble when 500 mol/m³ NaOH is added to soil is called humin. The material dissolved by this procedure may be separated into fulvic and humic acids by adjusting the pH to 1 by addition of HCl: the material precipitated at that point is *humic acid*, that remaining in solution is *fulvic acid* (the procedure for separating fulvic and humic acid is the same for aquatic and marine humic substances).

As was the case for aquatic humic substances, there is a systematic compositional difference between soil humic and fulvic acids; indeed the compositional differences between fulvic and humic acid ap-

Table 12.06. Composition of Soil Humic and Fulvic Acids

	Humic Acid		Fulvic Acid	
	Mean	Range	Mean	Range
Elemental Comp.	wt %			
C	56.	53-59	45.7	40.7-50.6
H	4.6	3.0-6.5	5.4	3.8-7.0
N	3.2	0.8-5.5	2.1	0.9-3.3
O	35.5	32.-38.5	44.8	39.-50.
S	0.8	0.1-1.5	1.9	0.1-3.6
Functional Groups	meq/g			
Total Acidic Groups	5.6-8.9			6.4-12.2
Carboxyl	3.6	1.5-6.0	8.2	5.2-11.2
Phenolic OH	3.1	2.1-5.7	3.0	0.3-5.7
Alcoholic OH		0.2-4.9		2.6-9.5
Quinoid/keto C=O		0.1-5.6		0.3-3.1
Methyloxy OCH ₃		2.1-5.7	3.0	0.3-5.7

After Schnitzler (1978).

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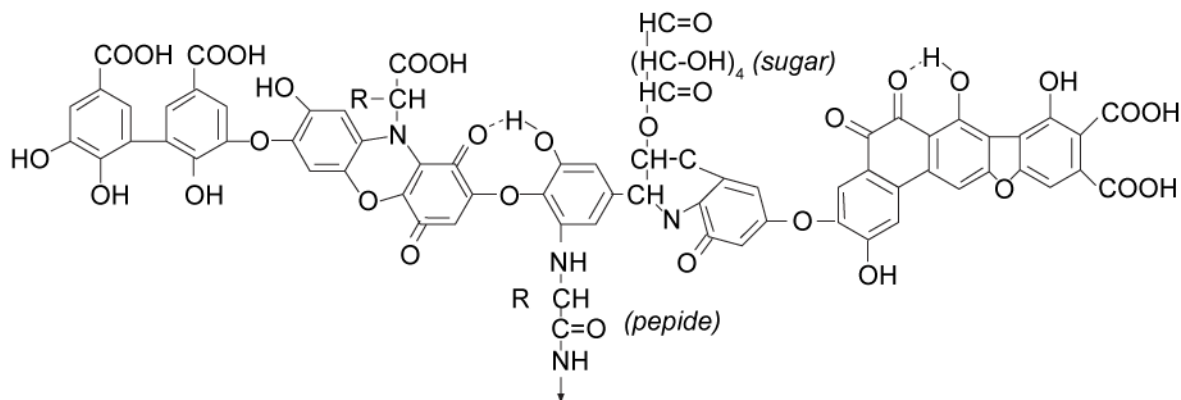


Figure 12.23. Possible structure of soil humic acid. Dashed lines represent hydrogen bonds. After Stevenson (1982).

pears greater in soils than in water. As is summarized in Table 12.06, humic acid is richer in carbon and poorer in oxygen and sulfur than fulvic acid, and poorer in hydrogen and richer in nitrogen as well. The higher content of polar groups such as carboxyl accounts for the higher solubility of fulvic acid. Soil fulvic acids tend to have molecular weights $<2 \times 10^3$, while the molecular weight of soil humic acids can exceed 10^6 .

Based on these compositions, the approximate chemical formula for average humic acid is $C_{187}H_{189}O_{89}N_9S$ and that of fulvic acid is $C_{68}H_{91}O_{48}N_3S$. Compared to the composition of living organisms, humic and fulvic acids have substantially lower ratios of hydrogen, oxygen, and nitrogen to carbon. Since humic substances are ultimately derived from biomolecules, this indicates that H, O, and N are lost in the humification process. Humins, the insoluble organic matter in soil, tends to be even richer in carbon and nitrogen and poorer in sulfur than either fulvic or humic acid. From these formulas we can deduce that there is a substantial degree of unsaturation (i.e., double carbon bonding) in humic substances, which partially accounts for their stability and biologically refractory nature. Stevenson and Vance (1989) estimated the average content of functional groups in soil humic and fulvic acids as 7.2 and 10.3 meq/g respectively. One possible structure for soil humic acid is illustrated in Figure 12.24.

The origin of soil humus is not precisely known. The relatively high proportion of aromatic units suggests the most important contributors to humic substances are lignins and tannins. As we noted earlier, these are polyaromatic substances that are quite refractory in a biological sense. These are partially degraded by soil microbes. Monomer or smaller polymer units may then condense, perhaps catalyzed by clays, metal ions, or bacteria. To this basic structure other components, which include amino acids, carbohydrates, and alkanes derived from fatty acids may be attached. Soil microbes are probably the primary contributors of these units.

As we found in Chapter 13, organic compounds, particularly carboxylic acids such as oxalic acid, in soils play an important role in podzolization; i.e., the depletion of Fe and Al in the upper soil horizons and their enrichment in lower horizons. This occurs as a result of the ability of carboxylic acids to form soluble complexes with Fe and Al. Fe and Al carboxylate complexes form in the upper soil layers, where organic acid concentrations are high, then are carried to deeper levels by water flow. At deeper levels, bacteria oxidize the carboxylate, and the Fe and Al precipitate as hydroxides. We examine metal-organic complexation further in the following section.

12.6 CHEMICAL PROPERTIES OF ORGANIC MOLECULES

12.6.1 Acid-Base Properties

As we noted above, the carboxyl group can dissociate to give up a hydrogen atom:

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(we use R here as a general representation for the remainder of the molecule). Like other acids, organic acids will increasingly dissociate as pH increases. As for other reactions, we can write an equilibrium constant expression:

$$K_a = \frac{a_{\text{H}^+} a_{\text{RCOO}^-}}{a_{\text{RCOOH}}} \quad 12.03$$

The equilibrium constant is commonly reported as pK_a , which, analogous to pH, is the negative of the logarithm of the equilibrium constant. The Henderson-Hasselback equation relates pK_a , activity quotient, and pH:

$$\text{pK}_a = -\log K_a = -\frac{a_{\text{RCOO}^-}}{a_{\text{RCOOH}}} - \text{pH} \quad 12.04$$

Expressed in this way, the pK_a is the pH where half of the acid molecules are dissociated and half undissociated. Most carboxylic acids have pK_a values between 1 to 5, which is below the pH of most streams and lakes, and similar to or lower than the pH range of soils (generally 3 to 8). Thus carboxylic acids will be dissociated in most environments. As we have seen, carboxylic acids (both simple and as functional groups on humic substances) are important components of dissolved and soil organic matter. The effect of increasing concentrations of organic molecules will thus be to increase the concentration of protons, lowering the pH of natural waters.

The OH groups of phenols can also dissociate and hence contribute to solution or soil acidity. Phenols are, however, much weaker acids than carboxylic acids. One measure of this is the pK_a . Whereas the pK_a values of carboxylic acids are typically 3 or so, pK_a for phenols are more typically 8. Thus at pH typical of most natural waters and soils, phenols will be only partially dissociated or not dissociated.

In contrast to carboxyl and phenol groups, nitrogen-containing groups, such as amino groups, are basic as they tend to bind free protons. By analogy to pK_a , defined above, we can define a pK_b , which is the pH will half the molecules or groups will be protonated and half unprotonated. Aliphatic amines are the most strongly basic, with typical pK_b values of 10 to 12. At pH values below this, they will be protonated. Thus in most natural waters and soils they will bear a positive charge and behave as cations. Because particle surfaces are typically negatively charged, these organic

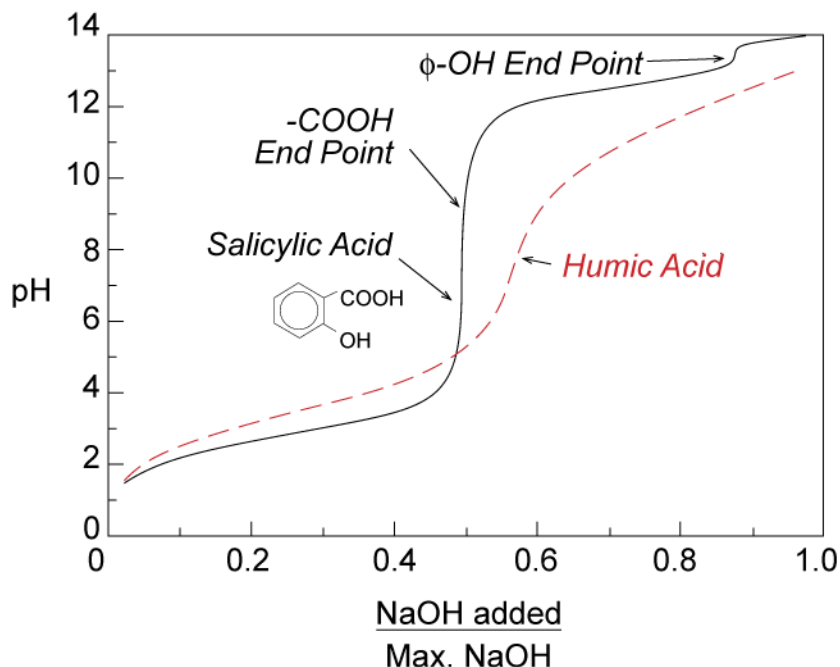


Figure 12.24. Comparison of titration curves of salicylic and humic acid. The salicylic acid shows two end-points, corresponding to its carboxyl and phenol functional groups. The humic acid shows a smeared out titration curves corresponding to a continuously changed pK_a . After Morel (1983).

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cations are readily bound to particle surfaces and removed from solution. Aromatic amines are typically weaker bases, with pK_b values around 4 to 6. They will be protonated only in acidic waters and soils.

As we have seen, humic and fulvic acids are generally the most abundant organic substances in natural waters and soils. They often contribute significantly to the acidity of waters and soils. Under some circumstances, such as lowland tropical rivers, swamps, etc., they are the principle negative ions present. They typically contain 10^{-2} eq/g ionizable acid groups per weight of organic carbon. Carboxyl groups are most common, but other functional groups are also present. As a result, humic substances cannot be characterized by a single pK_a . Their titrations curves (Figure 12.24) typically have a “smeared out” appearance, a result both of the variety of functional groups present, and electrostatic interactions between these groups.

12.6.2 Complexation

Another important geochemical property of organic molecules is their ability to form complexes with metals, especially transition metals and aluminum. Complexation between metal ions and organic anions is similar, for the most part, to complexation between metals and inorganic anions. One important difference

is that many organic compounds have more than one site that can bind to the metal. Compounds having this property are referred to as *multidentate*. Complex formation with multidentate ligands is called *chelation*, and the complexes formed are called *chelates*. A simple example is the oxalate ion, $(COO)_2^{2-}$, which consists of 2 carboxyl groups (Figure 12.07) and is *bidentate*. Citric acid and glutamic acid (an amino acid) are tridentate ligands (although the amino group will not dissociate and take on a positive charge, it nevertheless has an electron pair available to share). A second important difference is that organic functional groups are only weakly acidic, meaning they have a high affinity for protons and are often only partially dissociated at the pH of natural waters. As a result, metal-organic complexation is strongly pH dependent.

A metal-oxalate complex results in the formation of a ring (Figure 12.25), with the two oxygens that are singly bonded to carbon each binding to the metal. In the oxalate complex, the ring has five members; a 6-member ring would be formed in a metal-malonate; 7 member rings are formed by phthalate or succinate chelates. A metal glycine complex forms 2 rings on opposing sides of the metal (Figure 12.26). Salicylate is an-

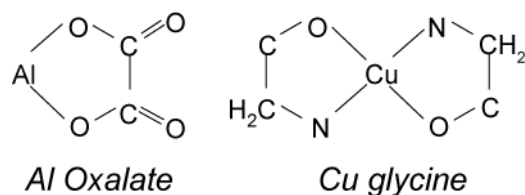


Figure 12.25. Examples of rings formed by chelates.

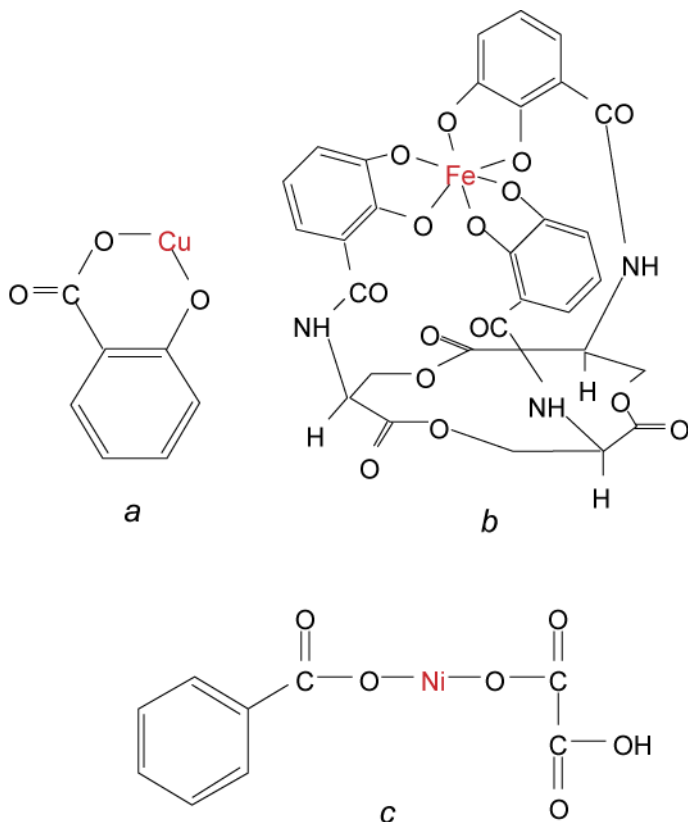


Figure 12.26. a. Copper salicylate complex. The Cu ion is bound to both the carboxylic and phenol groups. b. Enterobactin, a natural iron chelating agent. c. Ni complexed by separate benzoate and acetate groups.

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other example of a bidentate ion (Figure 12.26a). In this case, the binding sites are formed by two different functional groups: carboxyl and hydroxyl. Not all organic anions are multidentate, of course. Benzoate, acetate, and phenol are examples of unidentate organic anions. It is also possible for a single metal ion to bind to more than one organic ligand, as illustrated in Figure 12.26c.

Multidentate ions can very strongly bind trace metals. A few natural chelators that are specific for Fe have been characterized. One, endobactin, is illustrated in Figure 12.26b. These Fe specific chelators may have stability 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 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 12.07 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 valence state of the metal, the stronger the complex. Thus in Table 12.07, 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), $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}$.

It is the functional groups of organic molecules that are primarily responsible for metal ion complexation. Amines, azo compounds (compounds containing a $-\text{N}=\text{N}-$ 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 Fig. 12.15).

Table 12.07. 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 $\text{NH}_2\text{CH}_2(\text{COO})^-$

² $(\text{HOOC})(\text{CH}_2)_2\text{CHNH}_2\text{COO}^-$

³ $\text{C}_2\text{H}_5\text{COO}^-$

⁴ $(\text{HOOC})\text{CH}_2\text{C}(\text{OH})(\text{COOH})\text{CH}_2\text{COO}^-$

⁵ $\text{CH}_3\text{CH}_2\text{COO}^-$

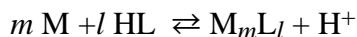
⁶ $\text{HOC}_6\text{H}_4\text{COO}^-$

From Morel and Hering (1993).

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Multidentate complexes are generally more stable than corresponding unidentate ones. We can see this in Table 12.07, 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 from 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:



the equilibrium constant for this reaction is then:

$$K = \frac{[M_m L_l] a_{H^+}}{[M]^m [HL]^l} \quad 12.05$$

$$\text{or in log form:} \quad \log K = \log[M_m L_l] - m \log[M] - l \log[L] - \text{pH} \quad 12.06$$

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 12.07. 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 complexing metals. A variety of experiments suggest the majority, 50 to 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 12.07, we would expect humic substances to strongly complex 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 the 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 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., Hofmann et al., 2007, Ellwood, 2004). In some cases, more than

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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., Barr and Croot, 2001). 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 desferrioxamine B, are produced by organisms to acquire essential trace metals such as Fe. They may produce others 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 12.02 demonstrates that glycine, a common amino acid, and citrate, a common hydroxycarboxylic acid, and salicylate, a 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 12.01), 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 the drawing the conclusion that organic trace metal complexes are inevitably insignificant. We considered only 3 species in this example, and while they strongly bind copper, all are at fairly low concentration. Other organic anions, particularly including

Example 12.01. Speciation of Organic Ligands in Fresh Water

Using the stability constants in Table 12.07, and the calculated free ion activities for major cations in Example 6.07, 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:

$$\Sigma L = L^- + HL + AL + BL + CL + \dots \quad 12.07$$

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:

$$[ML] = \beta \times [M] \times [L^-] \quad 12.08$$

where $[ML]$, $[M]$, and $[L^-]$ are the concentrations of the complex, free metal ion or proton, and free ligand respectively. Substituting 12.08 into 12.07, we have:

$$\Sigma L = [L^-] + \beta_{HL} [H] [L^-] + \beta_{AL} [A] [L^-] + \beta_{BL} [B] [L^-] + \dots \quad 12.09$$

Rearranging, we have:

$$[L^-] = \frac{\Sigma L}{1 + \beta_{AL} [A] + \beta_{BL} [B] + \dots} \quad 14.10$$

Since the concentrations of the organic ligands are much lower than 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 12.08. The result is shown in the adjacent table. We see that at the pH of this example (8), glycine and salicylate are essentially 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^{-09}	1.82×10^{-14}

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humates, are often present a sufficient concentration to complex a significant fraction of some trace metals. Problem 12.05 and 12.06 at the end of this chapter illustrates 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 pre-

Example 12.02. Speciation of Cu in Fresh Water

Use the adjacent stability constants as well as those for glycine, citrate, and salicylate in Table 12.07 to calculate the speciation of Cu in the water sample analysis in Example 6.07, assuming $\Sigma\text{Cu} = 10^{-9}$ M. Use the calculated free ion concentrations of anions in Examples 6.07 and 12.01.

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 that 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 12.01; that is we write a conservation equation for copper:

$$\Sigma\text{Cu} = [\text{Cu}^{2+}] + [\text{CuOH}^+] + [\text{Cu(OH)}_2] + [\text{CuCl}^+] + [\text{CuCO}_3] + [\text{CuSO}_4] + [\text{CuGly}] + [\text{CuCit}] + [\text{CuSal}] \quad 12.11$$

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

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

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

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

We can then calculate the concentrations of the individual species using 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.

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 6.07. 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.

Cu Stability Constants

	log β
CuOH^+	6.3
Cu(OH)_2	11.8
CuCl^+	0.5
CuCO_3	6.7
CuSO_4	2.4

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%
CuCO_3	5.97×10^{-10}	59.69%
CuSO_4	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%
Cu^{2+}	1.06×10^{-10}	10.63%

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sent 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 and other that the electrostatic charge on 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 the attraction of metal ions for it. As a result, 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 onto 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 adsorbent. The adsorption partition coefficient, K_p , is defined as:

$$K_p = \frac{\text{moles sorbate} / \text{mass solid}}{\text{moles solute} / \text{volume solution}} \quad 12.14$$

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 (Fig. 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 or-

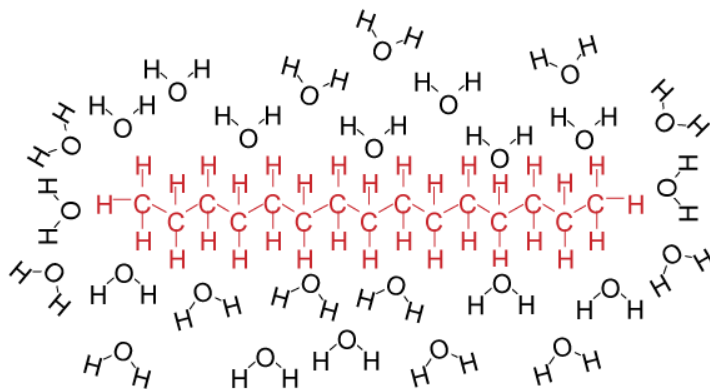


Figure 12.27. Disruption of water molecules by a large nonpolar organic molecule, in this case a C₁₅ n-alkane.

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ganic molecules. The adsorption coefficient for hydrophobic substances on 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:

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

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

$$K_{om} = K_p/f_{OC} \quad 12.17$$

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 as DDT and PCB's (polychlorinated biphenols). It is easy to understand why this should be so: the larger the molecule, the greater volume of water whose structure is disrupted. In addition, and 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.

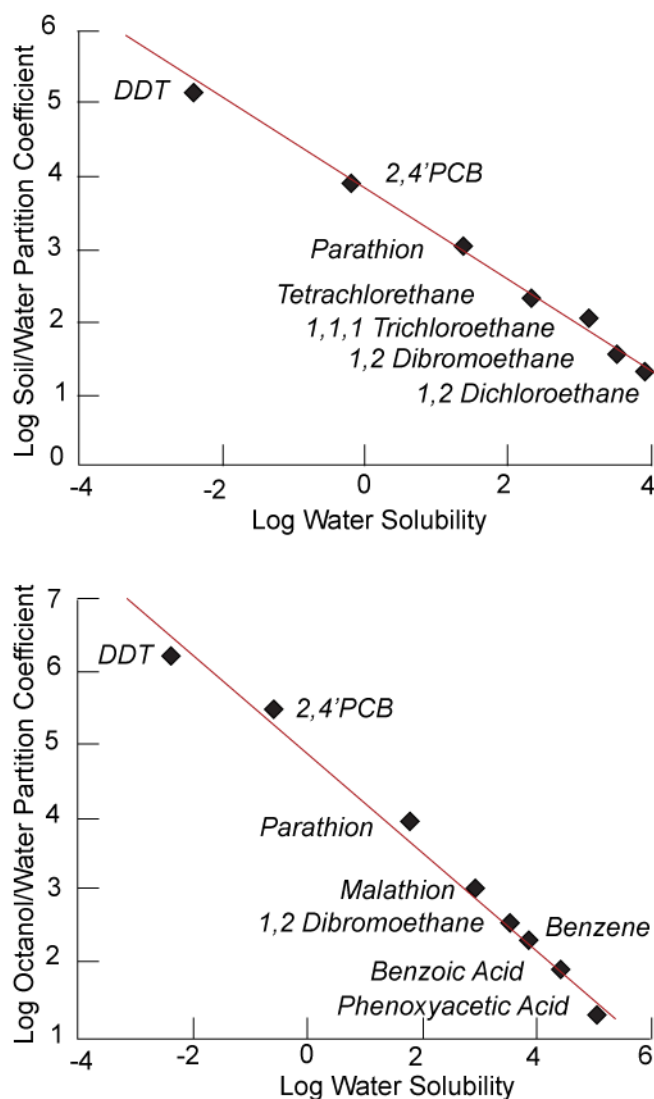


Figure 12.28. (a) Soil/water adsorption partition coefficients for a variety of organic compounds as a function of water solubility determined by Chiou et al. (1979). (b) Octanol/water partition coefficients as a function of water solubility of organic compounds determined by Chiou et al. (1979).

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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 of 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 non-polar part. Such molecules are called *amphipatic*. A good example is fatty acids, which, as we have seen, consist of hydrocarbon chains with a carboxyl groups 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*:



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:



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 there is which a direct bond between the acid functional group and the metal, can occur:



For cationic functional groups, such as quarternized nitrogen, *cation ion exchange* reactions such as:



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, e.g., 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:

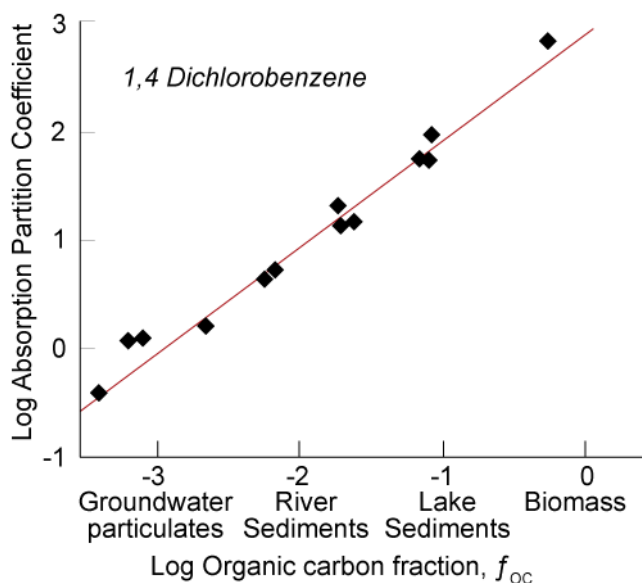


Figure 12.29. Adsorption partition coefficient for 1,4 dichlorobenzene plotted as a function of fraction of organic carbon in the solid absorbent. Other hydrophobic molecules show similar relationships. After Schwarzenbach and Westall (1980).

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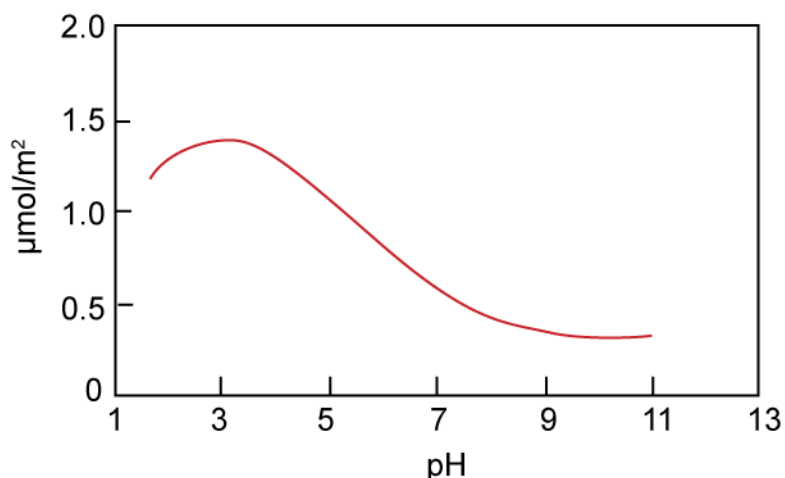


Figure 12.30. Adsorption of humic acid on $\delta\text{-Al}_2\text{O}_3$ as a function of pH. After Stumm (1992).

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: non-polar parts may be adsorbed through the mechanisms just

described. 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 the availability of hydrogen ions in solution will affect the charge on a solid surface in contrast 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 pH's 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 acids 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 plays 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) lowering the pH of solution (Drever and Vance, 1994; Bennett and Casey, 1994), and (4) 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).

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Furrer and Stumm (1986) investigated the effect of a variety of simple organic acids on dissolution of δ - Al_2O_3 and demonstrated a first order dependence of the dissolution rate on the surface concentration of organic complexes, i.e.:

$$\mathcal{R} = k [\text{S}\equiv\text{L}]$$

where $[\text{S}\equiv\text{L}]$ 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 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 oxalic acid, a dicarboxylic acid (Figure 12.07), 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 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.

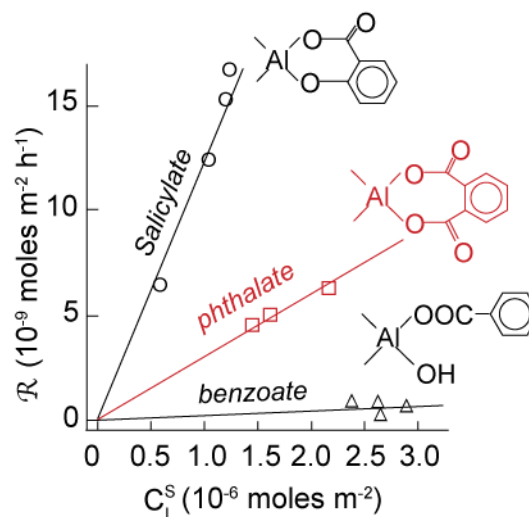


Figure 12.31. Rate of ligand-promoted dissolution of δ - Al_2O_3 as a function of organic ligand surface concentration. Chelates forming 5- and 6-member rings, such as those formed by salicylate, produced faster dissolution than 7-member rings, such as those formed by phthalate. Unidentate ligands, such as benzoate, have only a small effect on dissolution rate. From Furrer and Stumm (1986).

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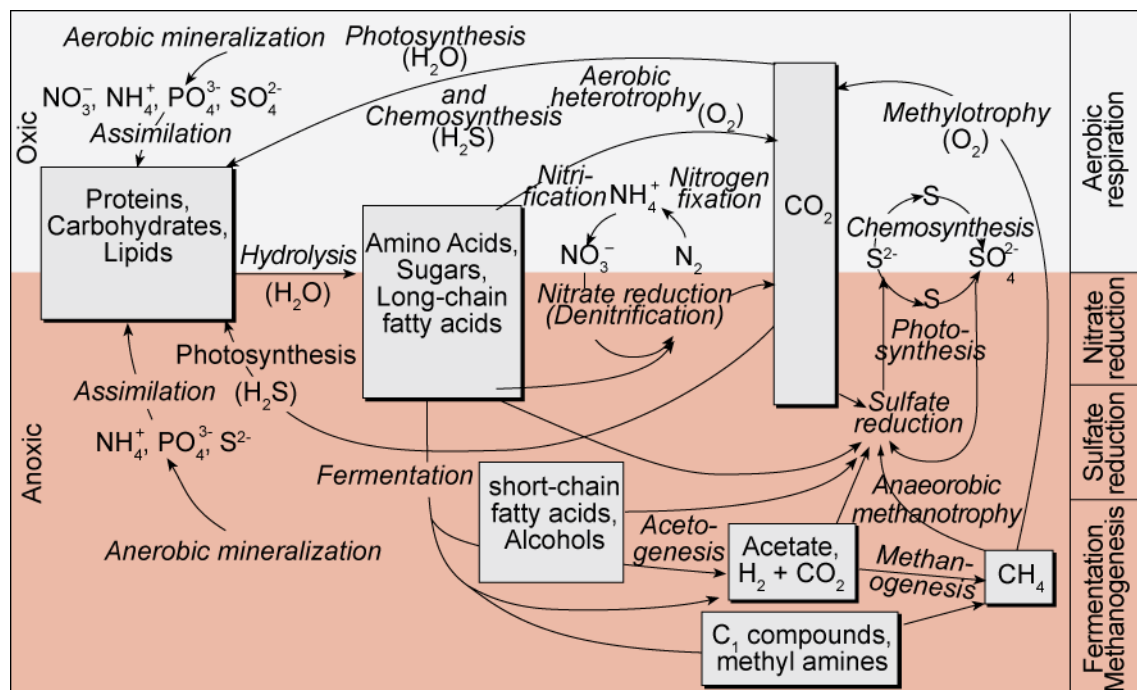


Figure 12.32. Role bacteria in the cycling of carbon, nitrogen, and sulfur between inorganic and various organic forms. After Killops and Killops (2005).

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 through 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

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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 argues 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 exceed 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) point out that sediments accumulating in oxic and anoxic basins have similar organic carbon contents and argue that the primary control is primary production in surface waters. They also argue that 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) point out 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 organic matter upward toward more oxygen-rich layers. They argue 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 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

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source of electron acceptors (oxidants) is used rather than an external source. An example familiar to brewers and vintners is the fermentation of glucose to alcohol:



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 pe. We can predict the order of the use of these oxidants from the ΔG of the redox reactions involved, shown in Table 12.08. 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 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 methyltrophic (methane-oxidizing) 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 1 or 2 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

Table 12.08 Free Energy Changes for Bacterial Reactions

Reaction	ΔG (kJ/mol CH_2O)
$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_{2(\text{aq})} + \text{H}_2\text{O}$	-493
$5\text{CH}_2\text{O} + 4\text{NO}_3^- \rightarrow 2\text{N}_2 + 4\text{HCO}_3^- + \text{CO}_{2(\text{aq})} + 3\text{H}_2\text{O}$	-472
$\text{CH}_2\text{O} + 3\text{CO}_{2(\text{aq})} + \text{H}_2\text{O} + 2\text{MnO}_2 \rightarrow 2\text{Mn}^{2+} + 4\text{HCO}_3^-$	-348
$^+3\text{CH}_2\text{O} + 4\text{H}^+ + 2\text{N}_2 + 3\text{H}_2\text{O} \rightarrow 3\text{CO}_{2(\text{aq})} + 4\text{NH}_4^+$	-125
$\text{CH}_2\text{O} + 7\text{CO}_{2(\text{aq})} + 4\text{Fe}(\text{OH})_3 \rightarrow 4\text{Fe}^{2+} + 8\text{HCO}_3^- + 3\text{H}_2\text{O}$	-103
$2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-$	-99
$2\text{CH}_2\text{O} \rightarrow \text{CH}_4 + \text{CO}_{2(\text{aq})}$	-88
$^+3\text{CH}_2\text{O} + 2\text{N}_2 + 7\text{H}_2\text{O} \rightarrow 3\text{CO}_{2(\text{aq})} + 4\text{NH}_4(\text{OH})$	-54

Modified from Berner (1981).

[†]Because the speciation of ammonia is pH dependent, the ΔG of the nitrogen fixation reaction depends strongly on pH.

[§] 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.

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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 onto 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.

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 originates from plants, 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, curatans, 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. 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

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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 ($>45^\circ$) moors and bogs. These moors 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, amides, and hydroxy, are preferentially removed from their parent molecules.
- Loss of functional groups such as COOH and OH 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 to their saturated equivalents due to hydrogenation of double carbon bonds.
- Aliphatic compounds decrease in abundance compared to 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, addition of 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 soluble organic matter, called *bitumen*. Kerogen, an inhomogeneous macromolecular aggregate, constitutes 90 percent 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,

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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*. Kerogen derived principally from the remains of higher plants is rich in aromatic compounds, sometimes called *humic kerogen*, 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 10Å. 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 bacterial decomposition contribute to kerogen formation, resistant biomolecules, such as tannins, cutins, polyterpenoids, algaenans, etc. 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 rarer 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 12.33) and origin. The *inertite* group consists of carbonized remains formed by rapid oxidation under aerobic conditions. One mechanism by which inertite forms is probably wild fires in peat-producing environments[†]. Inertite may include the carbonized remains of just about anything: woody tissue, fungi, spores, cuticles, resins, algae, etc. 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

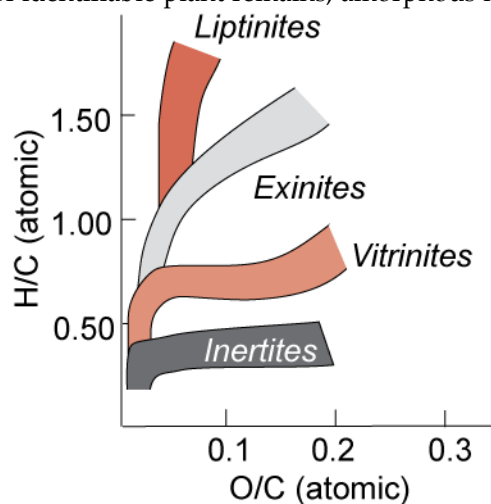


Figure 12.33. Compositional difference between kerogen maceral groups liptinite, exinite, vitrinite, and inertite. A plot of the H/C ratio vs. the O/C ratio such as this is commonly called a *van Krevelen diagram*. Modified from Tissot and Welte (1984).

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

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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 12.34). *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 U.S. is a good example. *Type II* kerogen, the most common type, has intermediate H/C (~ 1.25) and O/C (< 2.0) ratios. It is derived primarily from planktonic and bacterial remains deposited in marine environments (though remains of high 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 (< 0.3). It is rich in aromatic 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 12.33 and 12.34 shows that *Type I* kerogen is related to *liptinite* macerals, *Type II* to *exinites*, and *Type III* to *vitrinite*. High sulfur *Type II* 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 to 5 percent of the total organic carbon (the remainder being kerogen), though this figure is occasionally higher. During subsequent thermal evolution, however, the fraction of bitumens increases at the expense of kerogen (see below). Bitumen consists primarily of 2 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 link 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 $\sim 8 - 12$ %). Both have molecular weights greater than 500 and commonly several thousand.

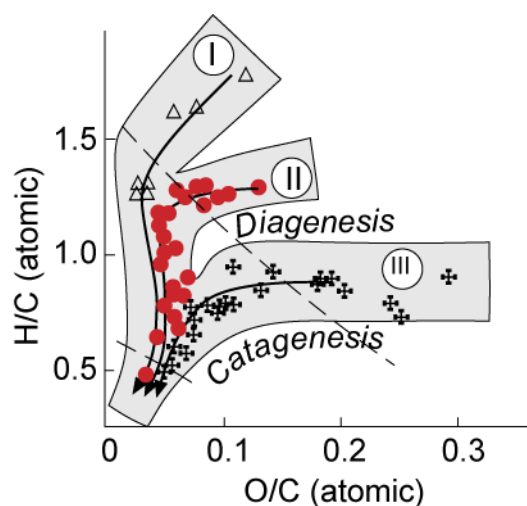


Figure 12.34. H/C and O/C ratios of the three types of Kerogen. Open triangles: *Type I*, closed red circles: *Type II*, crosses: *Type III*. Arrows show the direction of compositional evolution during diagenesis and subsequent thermal maturation (catagenesis and metagenesis). Dashed lines show boundaries between regions of diagenesis, catagenesis, and metagenesis. After Tissot and Welte (1984).

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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 CS₂ 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 C₂₅ to C₃₃, which are derived from even-carbon numbered fatty acid and alcohol components of cuticular waxes of higher plants through decarboxylation.
- C₂₂ C₁₅ and C₁₇ n-alkanes derived from hydrocarbons and corresponding fatty acids in phytoplankton.
- Isoprenoids, most notably pristane (C₁₉) and phytane (C₂₀) 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 where it was generated. In some areas there are multiple potential parents of petroleum being produced. For example, in the Gulf of Mexico, both 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 petroleum deposit form. For example, where n-alkanes longer than C₂₂ 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 C₂₈/C₂₉ 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 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 rock 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 to 150° C are reached, a complex mixture of hydrocarbons, *petroleum*, is produced, along with less amounts of asphaltene 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*.

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One of the principal effects of diagenesis is the condensation of the complex macromolecules from simpler ones. During catagenesis, this process is reversed as kerogen disproportionates 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 12.34.

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, i.e., 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 to that of a calibrated standard using a microscope photometer. Vitrinite reflectance increases from about 0.2% in recent sedimentary organic matter to 4% or

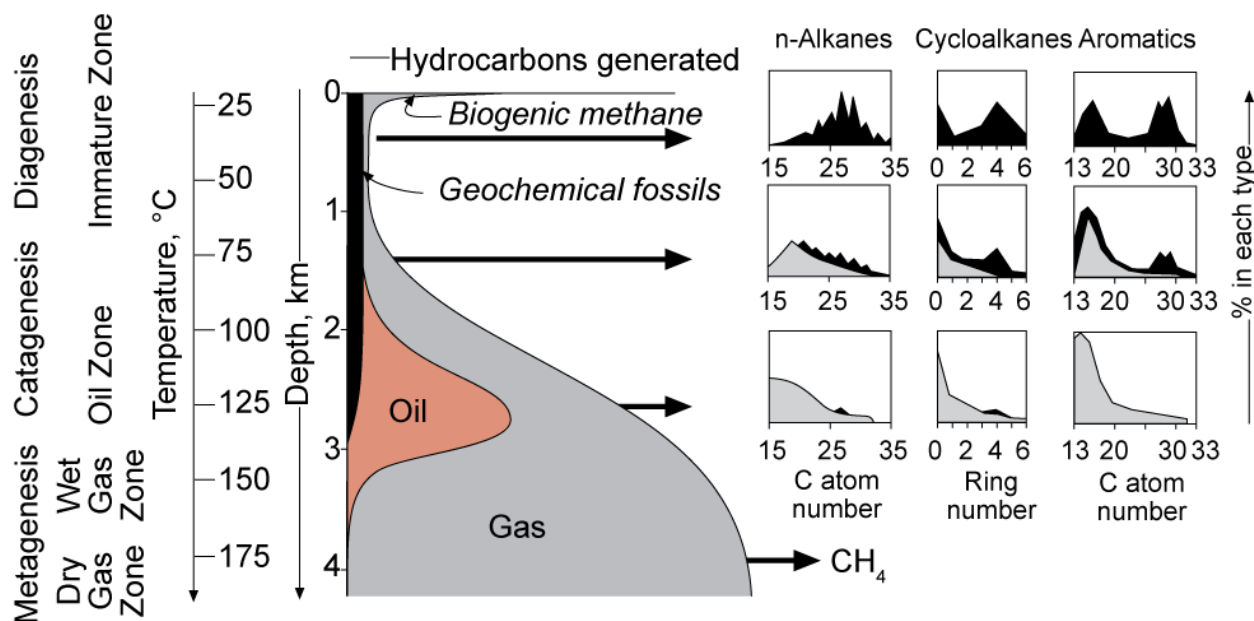


Figure 12.35. General scheme for hydrocarbon generation as a function of depth and temperature. Composition of the hydrocarbons generated is shown in the graphs to the right. Temperature and depth scales assume a geothermal gradient of 40° C per km. After Tissot and Welte (1984).

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more in over-mature kerogen. In the oil-generating stage of catagenesis, vitrinite reflectance is typically in the range of 0.6 to 1.3%.

Figure 12.35 summarizes the generation of oil and gas as a function of temperature. During catagenesis, heteroatom 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, a process called *cracking*. Carbon-carbon bonds in the center 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, $\sim C_{35}H_{54}$. This decreases to less than $C_{10}H_{18}$ at 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 to 180°C , is called the “wet gas zone”. At higher temperatures, the liquid hydrocarbons are completely eliminated by C-C bond breaking. 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 to 10° increase in temperature. Because of this, catagenesis depends on 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) geothermal gradient. The burial rate primarily on rate at which the sedimentary basin subsides. The geothermal gradient at the surface of the Earth varies widely, from $10^\circ/\text{km}$ to $80^\circ/\text{km}$ 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 to $50^\circ\text{C}/\text{km}$ 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. The temperature required for the onset of petroleum generation varies inversely with time. For example, this threshold is about 60°C in Lower Jurassic sediments of the Paris Basin, but is 115° in Mio-Pliocene sediments of the Los Angeles Basin. The temperature and depth scales in Figure 12.35 correspond to a relatively high geothermal gradient ($40^\circ\text{C}/\text{km}$). Reaction rates also depend on the type of kerogen involved. Labile reactive kerogen (Type I) reacts at relatively low temperatures; refractory Type III can require substantially higher temperatures for petroleum generation (as high as 250°C). Since long aliphatic chains are unstable at these temperatures, the principal product of Type III kerogen is methane.

12.7.3.2 Migration and Post-Generation Compositional Evolution

Most petroleum source rocks are fine-grained. Subjected to the pressure of burial, their porosities are typically quite low; hence liquid and gaseous hydrocarbons are expelled once the source rock becomes saturated. Being less dense than rock, as well as water, petroleum and gas tend to migrate upward. The mechanisms of migration of hydrocarbons are not fully understood, but probably involve both passage

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through microfractures and diffusion through the kerogen matrix. Migration will continue until the petroleum reaches an impermeable barrier, a "trap", or the surface. From the standpoint of economic recovery, the ideal situation is a trap, such as a clay-rich sediment, overlying a porous and permeable "reservoir" rock such as sandstone. Expulsion efficiencies vary with kerogen type. In Type I kerogen, nearly all the oil can be expelled from the source rock. In Type III kerogen and coal, however, most or all of the oil may remain trapped in the source rock and be ultimately cracked to gas.

The quantity and quality of the petroleum generated depends largely on the type of organic matter. Since petroleum tends to migrate out of the source rock as it is created, it is difficult to judge the amount of petroleum generated from field studies. However, both mass balance calculations on natural depth sequences and laboratory pyrolysis experiments on immature kerogen give some indication of the petroleum generation potential (Tissot and Welte, 1984, Rullkötter, 1993). Type I kerogen yields up to 80% light hydrocarbons upon pyrolysis. Mass balance studies of Type II kerogen indicate a hydrocarbon generation potential of up to 60%. Type III kerogens yield much less hydrocarbon upon pyrolysis (<15%).

Chemical changes may occur in several ways during and after migration. Fractionation during migration can occur as a result of the differing diffusivity and viscosity of hydrocarbons: light hydrocarbons are more diffusive and less viscous than heavy ones. As a result, they will migrate more readily and the hydrocarbons in a reservoir are often enriched in the light fraction compared to the source rock. Asphaltenes are insoluble in light hydrocarbons and may precipitate as a consequence of this process. Polar constituents in oil, asphaltenes and resins, may be absorbed by mineral surfaces and are less readily expelled from the source rock, resulting in a depletion in these components in oil in reservoir rocks compared to source rock bitumen. The more water-soluble components of petroleum may dissolve in water, either flowing through a reservoir or encountered by migrating petroleum. This process,

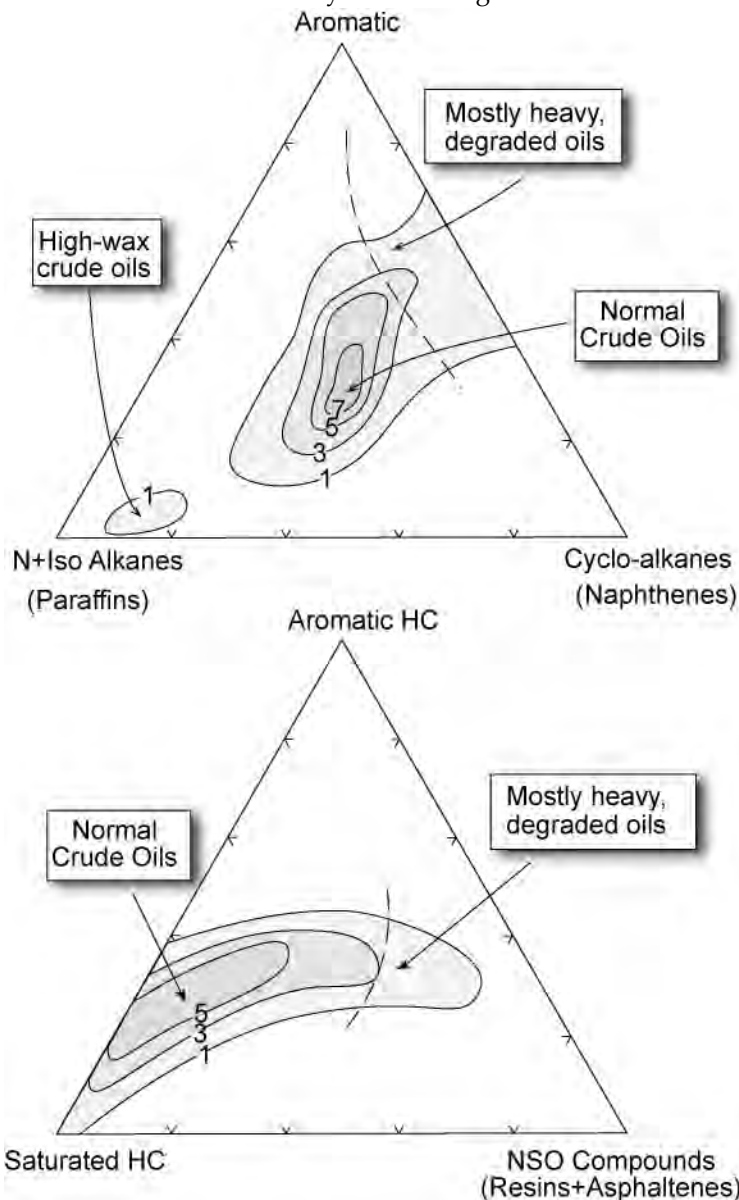


Figure 12.36. Ternary diagrams representing the composition of crude oils. (a) Isofrequency contours of hydrocarbons boiling above 210°C in 541 crude oils divided between aromatics, cyclic-, and n- and isoalkanes. (b) Isofrequency contours of saturated hydrocarbons, aromatic hydrocarbons, and NSO compounds (wt percent in the fraction boiling above 210° C) in 636 crude oils. After Tissot and Welte (1984).

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called *water washing*, will deplete the petroleum in these water-soluble components. Aerobic bacteria encountered by petroleum can metabolize petroleum components, a process called *biodegradation*. Long, unbranched alkyl chains are preferentially attacked, followed by branched chains, cycloalkanes, and acyclic isoprenoids. Aromatic steroids are the least affected. Finally, further thermal evolution can occur after migration, resulting in an increase in methane and aromatic components at the expense of aliphatic chains.

12.7.3.3 Composition of Crude Oils

Figure 12.36 summarizes the compositions of crude oils. Average “producible” crude oils contain 57% aliphatic hydrocarbons (with a slight dominance of acyclic over cyclic), 29% aromatic hydrocarbons, and 14% resins and asphaltenes. On an elemental basis, it consists approximately of 82-87% C, 12-15% H, 0.1-5% each of S and O, and 0.1-1.5% N. On an atomic basis, this corresponds to a C:H:S:O:N ratio of 100:190:2.5:4:1.5. An average, crude oil consists of 57% aliphatic hydrocarbons, 29% aromatic hydrocarbons, and 14% resins and asphaltenes. The distribution of n-alkanes differs widely between various types of crudes as may be seen Figure 12.36. Among cycloalkanes, those with 2 to 4 rings generally predominate. Alkylated compounds dominate the aromatic fraction; those with one to three additional carbons are most common. Aromatics decrease in abundance with increasing number of rings, so that benzene derivatives (one ring) are most common, followed by naphthalenes (two rings), etc. Molecules containing both saturated and unsaturated rings (naphthoaromatics) are also present, typically in an abundance of 5 wt. %. Upon primary distillation, typical crude oil yields 27 volume percent gasoline (C_4 - C_{10} compounds), 13% kerosene (C_{11} - C_{13}), 12% diesel fuel (C_{14} - C_{18}), 10% heavy gas oils (e.g., heating oil) (C_{19} - C_{25}), and 20% lubricating oil (C_{26} - C_{40}) (Royal Dutch Shell, 1983). The ratio of these products can be changed by further refining processes such as solvent extraction, thermal cracking, catalytic cracking, etc., so that, for example, the gasoline yield can be as high as 50%.

12.7.4 Compositional Evolution of Coal

Coal, as we noted earlier, forms from organic-rich sediments typically deposited in swamps. Coal evolution is a process of selective preservation of some resistant organic remains, which generally constitute a minor fraction of the original mass, followed by minor reorganization of the biopolymers that survive (Hatcher and Clifford, 1997). Two types of coals are recognized: sapropelic and humic. Humic

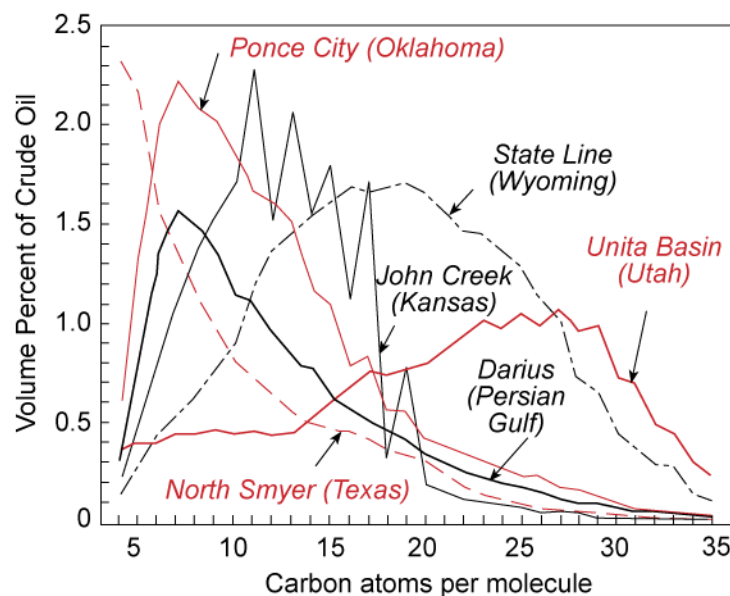


Figure 12.37. Distribution of n-alkanes in different crude oils. After Tissot and Welte (1984).

coals are by far the most common. They are bright, usually stratified, rich in aromatics and composed primarily of the remains of higher plants. Less common sapropelic coals are dull, rarely stratified, and derived from lipid-rich organic matter such as the remains of algae (boghead coals or torbanites) or spores (cannel coals). The primary maceral group of humic coals is vitrinite, while that of sapropelic coals is exinite.

The evolution of coal, illustrated in Figures 12.38 and 12.39, is generally broken into two phases: *peatification* and *coalification*. Coalification is subdivided into *biochemical* and *geochemical* stages. Together, peatification and the biochemical stage of coalification are equivalent to di-

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agenesis, while the geochemical stage of coalification is comparable to catagenesis. During peatification, bacterial and fungal attack results in depolymerization and removal of functional groups from the original biomolecules (Figure 12.39). This process is begun by aerobic organisms and continued by anaerobic bacteria once conditions become reducing. This is accompanied by the evolution of various gases (e.g., CO_2 , NH_3 , N_2 , CH_4 , H_2O) and condensation of the degradation products into humic substances. As in diagenesis, the concentrations of the most labile components decrease, while those of more refractory ones increase. The latter include lignins and tannins, and lipids derived from leaves, spores, pollen, fruit, and resin. Another important process during peatification is compaction and expulsion of water.

During biochemical coalification, continued loss of functional groups drives the O/C ratio to lower values with only a slight decrease in H/C ratio. Remaining labile components are metabolized and refractory material continues to condense to aromatic-dominated structures (Figure 12.39). The final product of the diagenetic phase is *brown coal*, which contains 50-60% C and 5-7% H. This material may be accompanied by a small bitumen fraction, derived primarily from lipid components.

Temperature and pressure increase with burial and this initiates the geochemical stage of coalification. Coal at this stage contains 1-2% N and generally less than 1% S. Continued compaction results

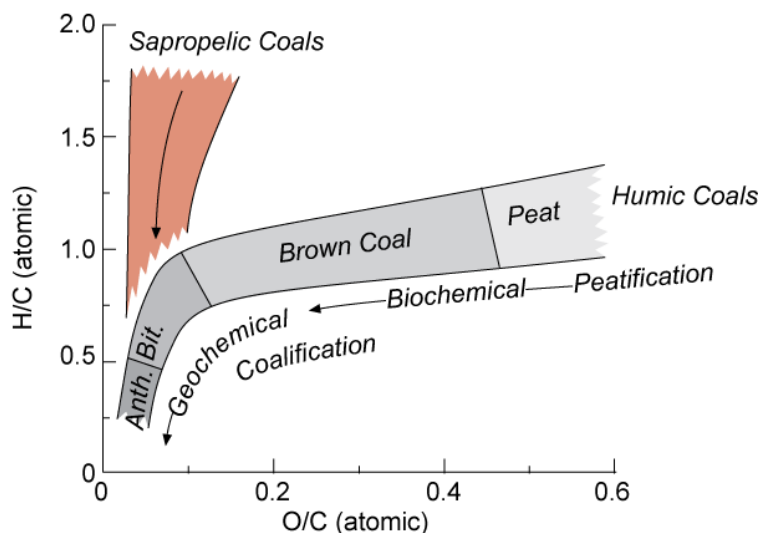


Figure 12.38. Chemical evolution of coals. After Killops and Killops (2005).

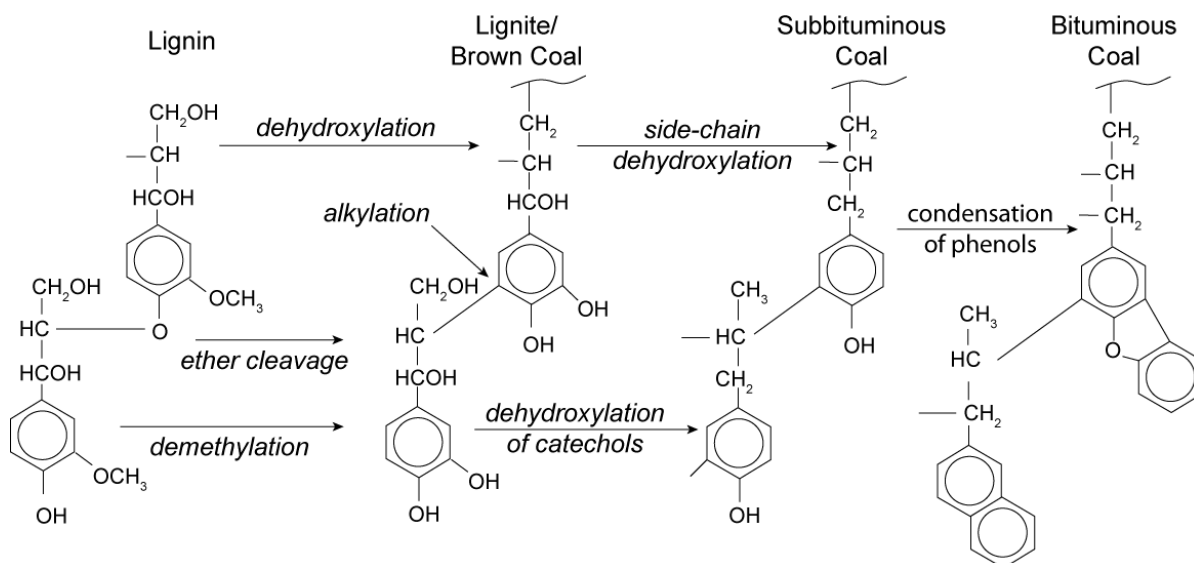


Figure 12.39. Chemical evolution of lignite to coal. After Hatcher and Clifford (1997).

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in a continued decrease in the water present. Loss of functional groups produces further reduces the O/C ratio with only minor decrease in the H/C ratio. By the time the O/C ratio reaches 0.1, most of the functional groups have been lost. The resulting material is now called *bituminous coal*, which requires temperatures in the range of 40 to 100° C. Bituminous coal has a fairly bright appearance and contains 75% or more C and the water content less than 10%. At this point, vitrinite reflectance reached 0.5% and 70% or more the carbon is in aromatic. During peatification and the early stages of coalification, CO₂ and H₂O are the primary volatile species produced.

With further heating, aromatization of cycloalkyl structures becomes the dominant process, releasing methane. Aromatization and loss of methane reduce the H/C ratio, which decreases rapidly upon further heating. In the temperature range of 100 to 150° C, *anthracite* is formed as the H/C ratio decreases below 0.5%. Anthracite is characterized by vitrinite reflectance of >2.5% and a carbon content of greater than 90%. Ninety percent or more of this carbon is in aromatic structures. As in kerogen, these aromatic structures initially take the form of randomly ordered nuclei. During the geochemical stage of coalification, these nuclei become increasingly ordered, so that by the anthracite stage, they are arranged as approximately parallel sheets, progressing toward the arrangement in graphite.

12.8 ISOTOPE COMPOSITION OF HYDROCARBONS

12.8.1 Bulk Isotopic Composition

The isotopic composition of sedimentary organic matter and its derivatives, such as coal and oil, depend on (1) the isotopic composition of the originally deposited organic matter and (2) isotopic fractionations occurring during diagenesis and subsequent thermal evolution. The ultimate source of carbon in sedimentary organic matter is atmospheric CO₂ or marine HCO₃⁻. The $\delta^{13}\text{C}_{\text{PDB}}$ value of the former is about -7‰, while the $\delta^{13}\text{C}_{\text{PDB}}$ in average surface ocean water is +2.2‰ (both of which vary somewhat). As we found in Chapter 9, isotopic fractionation during photosynthesis results in organic carbon being substantially lighter (lower $\delta^{13}\text{C}$) than either atmospheric or dissolved CO₂. Terrestrial C₃ plants typically have $\delta^{13}\text{C}$ of -25 to -30‰, C₄ plants have $\delta^{13}\text{C}$ of -10 to -15‰, while marine plants are somewhat more variable in isotopic composition (-5 to -30‰), though most have isotopic compositions of -20 to -28‰, i.e., slightly heavier than terrestrial C₃ plants. There is some further fractionation of carbon isotopes as other organic molecules are synthesized, with lipids being isotopically lighter than carbohydrates and proteins. While these differences are small compared with the fractionation during photosynthesis, they do appear to persist through diagenesis.

Most living organisms have $\delta\text{D}_{\text{SMOW}}$ in the range of -60 to -150‰. Within this range, hydrogen isotope ratios vary due to hydrogen isotope fractionation in the hydrologic cycle (Chapter 9). Terrestrial plants tend to be more deuterium depleted than marine ones, and terrestrial plants from cold climates are particularly depleted. Lipids are depleted in δD relative to bulk organic matter by 60‰ or more. Most kerogen, coal, and oil show about the same range in δD as do organisms. As might be expected, however, lipid-rich kerogen and oil can have substantially lower δD .

The situation with nitrogen isotopes is similar: nitrogen isotope ratios in sedimentary organic matter generally reflect that of the biomass from which it is derived, with terrestrial plants having slightly lower average $\delta^{15}\text{N}_{\text{ATM}}$ than marine plankton (Fogel and Cifuentes, 1993). $\delta^{15}\text{N}$ generally decreases somewhat during diagenesis due to bacterial utilization of short chain peptides following peptide bond hydrolysis (Macko, et al., 1993). In contrast, sulfur bound in organic matter is more likely to have been derived from inorganic forms of sulfur, in seawater this is ultimately sulfate, which in the modern ocean has $\delta^{34}\text{S}$ of +20. As we found in Chapter 9, there is typically a large negative fractionation during bacterial sulfate reduction; consequently, modern marine kerogen typically has a $\delta^{34}\text{S}$ of around -10. The exact values depend in part on the extent to which the system was open or closed during reduction: the later case resulting in more limited fractionation. Sulfur isotope ratios are little affected by catagenesis and migration, and thus are sometimes used to correlate oils with their source rocks.

For the most part, isotopic fractionation of carbon during diagenesis of organic matter is small. As a result, the $\delta^{13}\text{C}$ of sedimentary organic matter is typically within a few permil of the $\delta^{13}\text{C}$ of the biomass

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from which it is derived. Sedimentary organic matter and humic substances in soil and water tend to be slightly more depleted (by 2 to 3 per mil) in ^{13}C than the organisms from which they are derived, though cases where the opposite is true have been observed. There are several possible causes for this (reviewed in Tissot and Welte, 1984, Hoefs, 1987, and Macko et al., 1993). First, functional groups, such as carboxyl, tend to be relatively ^{13}C rich. Loss of functional groups during diagenesis or condensation of humic substances will drive the residual organic carbon to lower $\delta^{13}\text{C}$. Second, there appears

to be a kinetic fractionation involved in condensation of humic substances and kerogen-like molecules. Third, preferential remineralization of proteins and carbohydrates leaves a lipid-rich residue, which will be isotopically light.

Fractionation of carbon isotope ratios during thermal evolution through the oil generation stage is drives kerogen toward higher $\delta^{13}\text{C}$ values, but the difference is small. In immature kerogen, bitumens are depleted in $\delta^{13}\text{C}$ compared to kerogen, but this difference decreases with increasing maturity (Schoell, 1984). Sofer (1984) found that $\delta^{13}\text{C}$ of the oils are within 2‰ of the isotopic composition its source kerogen. Conkright and Sackett (1992) found that $\delta^{13}\text{C}$ of organic carbon in sediment cores from DSDP (Deep Sea Drilling Project) Site 368 near the Canary Islands decreased with proximity to an intrusive diabase sill by 2 to 3‰. They attributed the decrease to thermal maturation and loss of isotopically light methane caused by heating from the sill.

There can be significant fractionation of carbon and hydrogen isotopes in the generation of methane. As Figure 12.40 shows, methane produced by methanogenic bacteria, called “biogenic methane” during diagenesis is highly depleted in ^{13}C . Methane produced during catagenesis, termed “thermogenic methane” is depleted in both ^{13}C and deuterium compared to associated oil and kerogen. These fractionations reflect the lower strength of ^{12}C – ^{12}C bonds compared to ^{13}C – ^{12}C bonds and therefore the greater ease with which the former are broken. As the metagenesis stage is entered, however, the isotope fractionation between methane and residual kerogen decreases and the isotopic composition methane generated during this stage approaches that of kerogen. This is just what we would expect from both the inverse relationship between the fractionation factor and temperature and the decreasing fractionation as reactions proceed to completion (see Chapter 9).

Methane in mid-ocean ridge hydrothermal vent fluids has systematically higher $\delta^{13}\text{C}$ (-15 to -20‰) than biogenic and thermogenic methane derived from sedimentary organic matter (Schanks et al., 1995), demonstrating its abiogenic origin. The isotopic fractionation between methane and CO_2 in these fluids suggests equilibration at temperatures in the range of 600 to 800° C (Whelan and Craig, 1983).

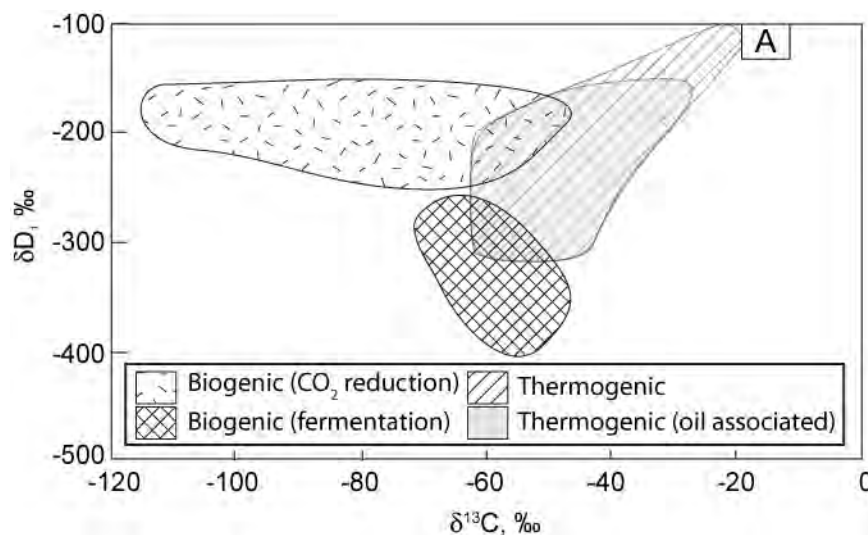


Figure 12.40. Isotopic composition of methane from various sources. “Biogenic” methane is methane produced by methanogens during diagenesis, “Oil Associated” is methane associated with oil, “A” is the composition of abiogenic methane from mid-ocean ridge hydrothermal systems. Modified from Schoell (1984) and Whiticar (1990).

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12.8.2 Compound-Specific Isotopic Analysis

Because the isotopic composition of oil is similar to that of its parent kerogen, isotope ratios are a widely used exploration tool the petroleum industry. Isotope ratios of bulk organic matter is, however, a tool of rather limited usefulness. For example, bulk isotopic analysis cannot be used to discriminate between depositional environments, as the isotopic differences between marine and terrestrial organic matter are neither sufficiently large nor sufficiently systematic. A far more powerful tool emerges through isotopic analysis of specific compounds, particularly biomarkers discussed in section 12.7.2.3. Compound specific isotopic analysis has proved useful not only in petroleum exploration, but in environmental and paleontological research. For example, the carbon isotopic distinctions between C_3 , C_4 , and marine biomass (Figure 9.18) is retained in derivative n-alkanes in sedimentary matter. Based on isotopic analysis of C_{29} n-alkanes derived from leaf waxes in sediment cores from Central American lakes, Huang et al. (2001) showed that over the last 27000 years, ratio of C_4 to C_3 plants in the region depended on climate. As the last glacial period ended, conditions in the region became more arid, the proportion of C_4 plant-derived alkanes has increased. Isotopic composition of specific components of petroleum gases, e.g., methane, ethane, propane, can be related to specific classes of kerogen and to correlate these gases with their source rocks (Killops and Killops, 2005).

Isotopic analysis of C_{37} alkadienone (i.e., a 37-long hydrocarbon chain including a ketone bond and two unsaturated carbons) in marine sediments has proved to be useful in reconstructing variations in atmospheric CO_2 . This molecule is a component of cell membranes of a specific group of haptophyte algae (e.g., coccolithophorids such as *Emiliania huxleyi*), and is particularly resistant to diagenetic change (indeed, it survives in petroleum). The idea behind this approach is that lower atmospheric CO_2 levels should result in greater isotopic fractionation between atmospheric CO_2 and organic matter produced by photosynthesis, Δ . This is true because isotopic fractionation during photosynthesis (section

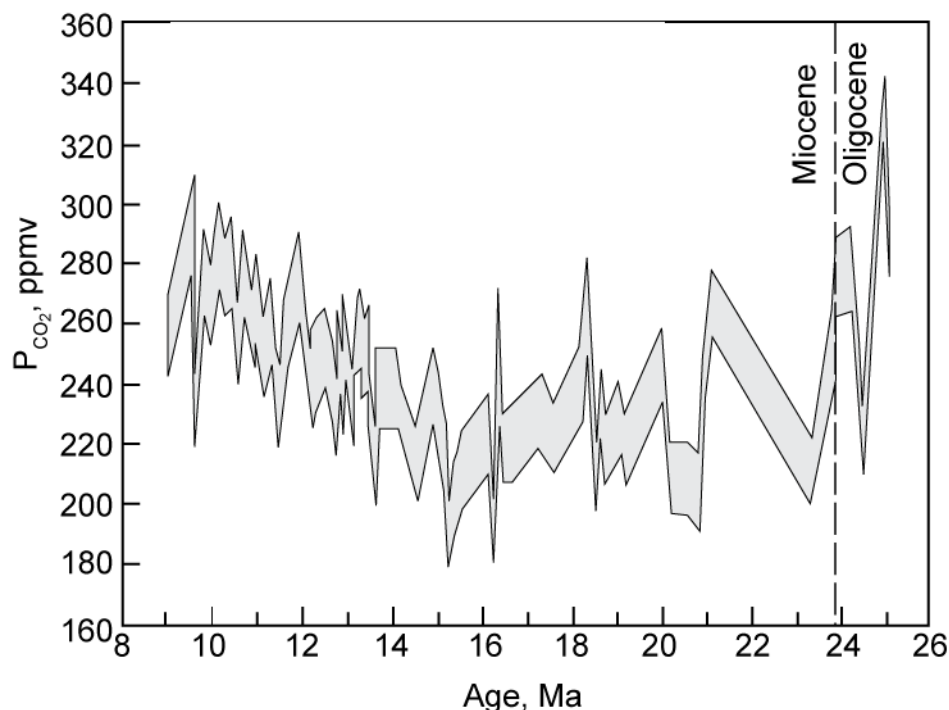


Figure 10.41. Atmospheric CO_2 concentration during the Miocene calculated from the difference between $\delta^{13}C$ in C_{37} diunsaturated alkenones and carbonate in sediments from DSDP site 588 by Pagani et al. (1999). Grey area falls between maximum and minimum values calculated using different assumptions.

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9.5.1) depends on the extent to which intracellular CO_2 is fixed into organic matter. When CO_2 is abundant, photosynthesis ^{12}C is selectively fixed and the fractionation is large. When CO_2 is less abundant, photosynthesis is less selective, proportionally more ^{13}C is fixed into organic matter, and the fractionation is smaller. Pagani et al. (1999) analyzed $\delta^{13}\text{C}$ in C_{37} alkadienone and in carbonate shell of planktonic foraminifera in Tertiary marine sediments, the latter being a measure of dissolved inorganic CO_2 (which, as we saw in Chapter 6, is primarily in the form of bicarbonate). Relating the difference between the two requires overcoming two complications. The first is that the fractionation will also depend on the photosynthesis rate: at high rates, there will be a draw down of intracellular CO_2 and the fractionation will be small even if extra-cellular CO_2 is abundant. Pagani (1999) essentially finessed this issue by focusing on sediments from areas of the ocean where photosynthesis is limited by nutrient abundance (oligotrophic regions); in other words, they assumed a constant photosynthesis rate. The second complication is that marine phytoplankton draw CO_2 from the ocean, not the atmosphere; so one final factor is the relationship between CO_2 in ocean surface waters. In oligotrophic open ocean surface waters, this should depend only on the solubility of CO_2 in water, which depends, effectively, only on temperature. Combining paleotemperature estimates based on $\delta^{18}\text{O}$ (discussed in Chapter 9), and $[\text{CO}_2]_{\text{aq}}$ estimated from the fractionation between C_{37} alkadienone and carbonates in the same sediments, they estimated atmospheric CO_2 through most of the Miocene and late Oligocene (Figure 12.41). The results were surprising because they showed that CO_2 has been near its pre-industrial modern level throughout most of the Miocene. Thus the cooling that occurred in the late Miocene was not due to decreasing atmospheric CO_2 as was widely suspected. P_{CO_2} does appear to have declined sharply at the Oligocene-Miocene boundary, coinciding with a known glacial event, but otherwise there is relationship to apparent climate change over this period. There is generally good agreement between this method of estimating atmospheric CO_2 concentrations and estimates based boron isotopic measurements in foraminiferal shells discussed in Chapter 9.

12.9 THE CARBON CYCLE AND CLIMATE

In 1896, Svante Arrhenius (whom we met in Chapter 5 in connection with his contribution to kinetic theory) published a paper in which he suggested that the concentration of atmospheric CO_2 might be increasing as a result of the extensive burning of coal that began with the industrial revolution. Taking note of the way in which CO_2 absorbs infrared radiation, he supposed that increasing atmospheric CO_2 variations would result in warming of the Earth's surface temperature. Arrhenius thus provided the first warning that burning of fossil fuels would result in greenhouse-driven climate change as well as the key to understanding how climate has evolved over the entirety of Earth's history. In this final section, we will have space only to briefly review greenhouse climate theory and carbon geochemistry. There are of course, many books that cover this topic in much greater depth.

12.9.1 Greenhouse Energy Balance

A greenhouse remains warm because visible light from the Sun is readily transmitted through glass. That electromagnetic energy is adsorbed by the ground and objects within the greenhouse and is converted to thermal motion of atoms and molecules: heat. As a consequence of that heat, the atoms radiate electromagnetic radiation. The wavelength emitted by those atoms is in the infrared in accordance with Wein's Law, which states that the wavelength of maximum spectral emittance of black body radiation is inversely related to temperature. Glass, however, absorbs much of that infrared radiation rather than transmitting it. The glass then re-emits radiation, about half of which is directed downward back into the greenhouse. This effectively traps energy in the greenhouse and it warms. As it does, it emits radiation more intensely (according to Stephan's Law, the intensity of black body radiation is proportional to the fourth power of temperature) until an equilibrium sets in such that as much radiative energy escapes the greenhouse as arrives from Sun.

The Earth atmosphere works much in the same way. Visible light from the Sun is largely passes through the atmosphere and is adsorbed by the Earth's surface, which then radiates in the infrared. That radiation is adsorbed when its frequency matches a resonance of the vibrational frequency of the

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bonds in a particular molecule. The principal gases in the modern Earth's atmosphere, N_2 , O_2 , and Ar, are monatomic or symmetric diatomic molecules which do not absorb in the infrared part of the spectrum. However, certain trace gases in the atmosphere, notably H_2O , CO_2 , CH_4 , and N_2O , strongly absorb certain wavelengths of infrared radiation. CO_2 , CH_4 , and N_2O absorb at different frequencies and thus each independently affects the atmospheric energy balance. However, the absorption bands of H_2O and CO_2 do overlap somewhat. Because relatively small amounts of these gases can absorb a large fraction of the radiation at specific frequencies, the effect of these gases on atmospheric energy balance does not scale linearly with their concentrations, but rather with the log of their concentrations. Thus, for example, small changes in the abundance CH_4 have a much greater affect on the energy balance than do small changes in more abundance CO_2 , even though CO_2 absorbs at frequencies close to the Earth's maximum spectral emittance and is thus inherently a more effective greenhouse gas than CH_4 , which adsorbs on the edge of the Earth's spectrum.

The combined effect of these gases is to absorb much of the infrared radiated by the Earth's surface and to raise the average temperature of the Earth's surface from 254 K (-19°C) to 286 K ($+13^\circ\text{C}$). H_2O is the most powerful of the greenhouse gases, because it absorbs over a relatively wide range of frequencies and because its concentration is relatively high (its atmospheric concentration can be up to 4% on a very hot, humid day in the tropics). However, the residence time of water in the atmosphere is quite short, so that its effect alone can only be limited. Its concentration in the atmosphere is strongly related to temperature and at 254 K, the atmosphere would contain very little water. Water thus merely amplifies the effect of the primary greenhouse gases, CO_2 , CH_4 , and N_2O : warmer temperatures lead to more evaporation and more humid air and a stronger greenhouse effect which leads to warmer temperatures, etc. Variations in atmospheric H_2O are important in short-term, local variations in temperature (this is why, for example, nights in humid regions are warm and nights in arid ones are cold). On long time scales, however, variations in the concentration of CO_2 and the other greenhouse gases control climate. Variations in atmospheric greenhouse gas concentrations are a result of how carbon is cycled between the atmosphere and other reservoirs and how the Earth and life have evolved over the last 4.5 Ga. We consider these in the following sections.

12.9.2 The Exogenous Carbon Cycle

We'll adopt (and anglify) the French word "*exogène*" to refer to the Earth's surface, including the atmosphere, biosphere, hydrosphere, cryosphere, soil, and reactive, unlithified sediments. Carbon in the exogene cycles between a variety of forms, of which organic carbon is one. This carbon cycle is illustrated in Figure 12.42. Roughly 110 gigatons (Gt) of carbon are fixed into organic carbon by photosynthesis of terrestrial plants every year. About half of this, around 50 Gt, is quickly returned to the atmosphere through respiration of plants or animals feeding on them, while the other half flows into a reservoir of non-living organic carbon that includes leaf litter, dead trees, peat, and soil organic matter. The mass of this reservoir is approximately steady-state, so that roughly this same amount is oxidized to CO_2 every year. The non-living organic carbon reservoir contains more than twice as much carbon as the terrestrial biota (more than 99% of which is plants), and more carbon than is present in the atmosphere and biota combined. Atmospheric CO_2 also readily exchanges with dissolved forms of carbon in the ocean, with roughly 90 Gt of CO_2 dissolving in the ocean and a similar amount exsolving out every year. The marine dissolved carbon reservoir, about 98% of which is HCO_3^- , contains roughly 50 times as much carbon as does the atmosphere. Carbon is cycled far more rapidly between organic and inorganic forms in the marine environment: net primary production (photosynthesis minus respiration) of marine phytoplankton is roughly 40 Gt, about 80% of terrestrial net primary production, even though the marine biosphere is 200 times smaller than the terrestrial one. Only the surface layer of the ocean, roughly the upper 200 m, exchanges readily with the atmosphere. The deep ocean, which contains the bulk of the dissolved carbon, is isolated from the atmosphere. Carbon flows into that reservoir either through downwelling of surface waters, which occurs mostly near the poles, or through falling organic remains such as dead organisms and fecal pellets. Nearly all of that falling organic matter is remineralized to HCO_3^- before reaching the sediment. The process by which carbon moves from the atmosphere into the

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marine biota via photosynthesis and from there into the deep ocean through sinking organic particles and then into dissolved CO_2 is known as the *biologic pump*. In addition, carbonate shells of planktonic organisms, most notably coccolithophorids and foraminifera, also fall through the water column to the deep water. Those shells falling below about 4000 m largely redissolve as water at this depth becomes strongly corrosive. One reason it is corrosive is that its pH is lower. As a consequence, dissolved CO_2 concentrations are significantly higher in the deep ocean than in surface waters (Figure 9.15). This deep water CO_2 eventually returns to the surface through upwelling and mixing, but the process is slow. The average ventilation time of the ocean, i.e., the average time deep water spends out of contact with the atmosphere, is about 1500 years based on ^{14}C analysis. Thus the biologic pump acts to sequester CO_2 from the atmosphere and maintains atmospheric CO_2 levels some 150 to 200 ppm lower than it would be otherwise (Falkowski et al., 2000).

On short geological times scales, 100,000 years and less, atmospheric carbon dioxide levels are controlled by the balance of carbon fluxes into and out of the oceans and the terrestrial biosphere and soils. Over the last million years or so, these fluxes have varied in response to glacial cycles driven by Milankovitch forcing (Chapter 9), resulting in variation in atmospheric CO_2 concentrations. As Figure 12.43 shows, CO_2 varied from around 190 ppm in glacial episodes to around 280 ppm in interglacial episodes.

Glacial cycles affect CO_2 fluxes in a number of ways. The first of these is volume and temperature of the oceans. The smaller the volume of the ocean, the less CO_2 it can hold; ocean volume over the past million years or so has been controlled by waxing and waning of ice sheets. CO_2 is more soluble in water at lower temperature, so low temperatures favor a net flux of CO_2 from the atmosphere to the oceans. The affect of glacial cycles on these two factors is thus opposite. Glacial cycles also affect the

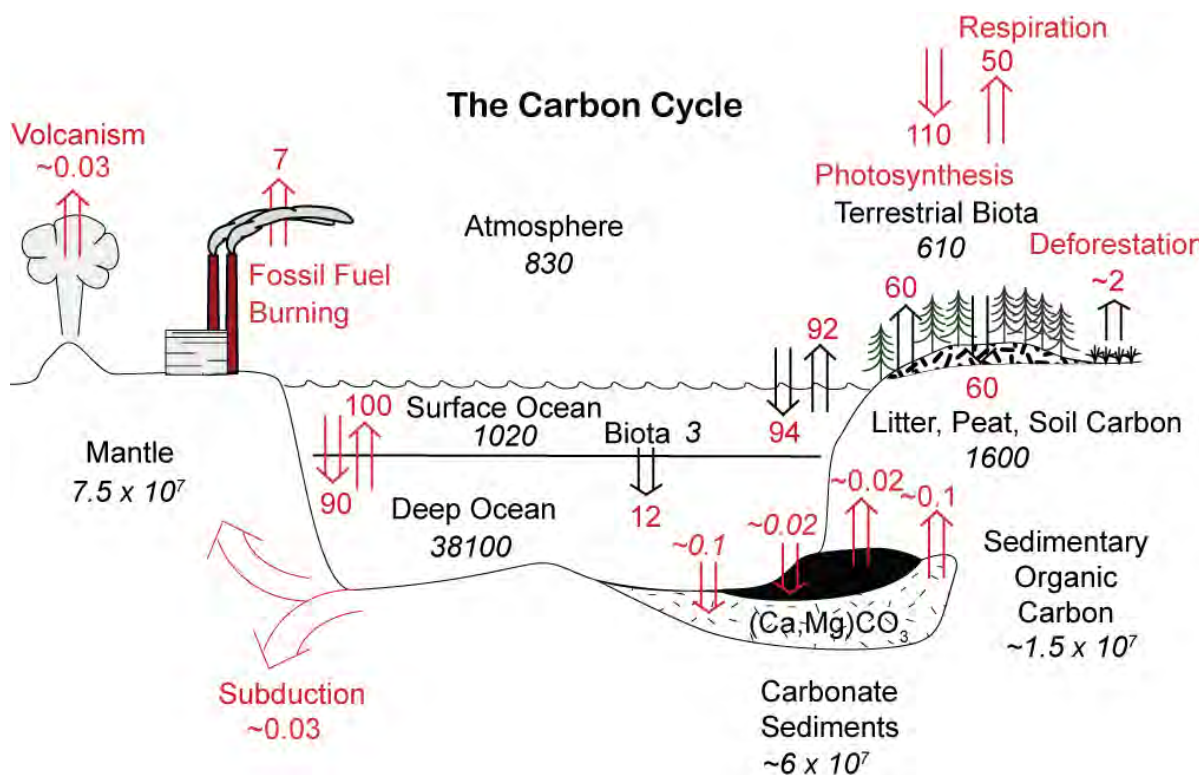


Figure 12.42. The carbon cycle. Numbers in green show the amount of carbon (in 10^{15} grams or gigatons, Gt) in the atmosphere, oceans, terrestrial biosphere, and soil (including litter, debris, etc.). Fluxes (red) between these reservoirs (arrows) are in Gt/yr. Magnitudes of reservoirs and fluxes are principally from Siegenthaler and Sarmiento (1993) and Falkowski et al. (2000).

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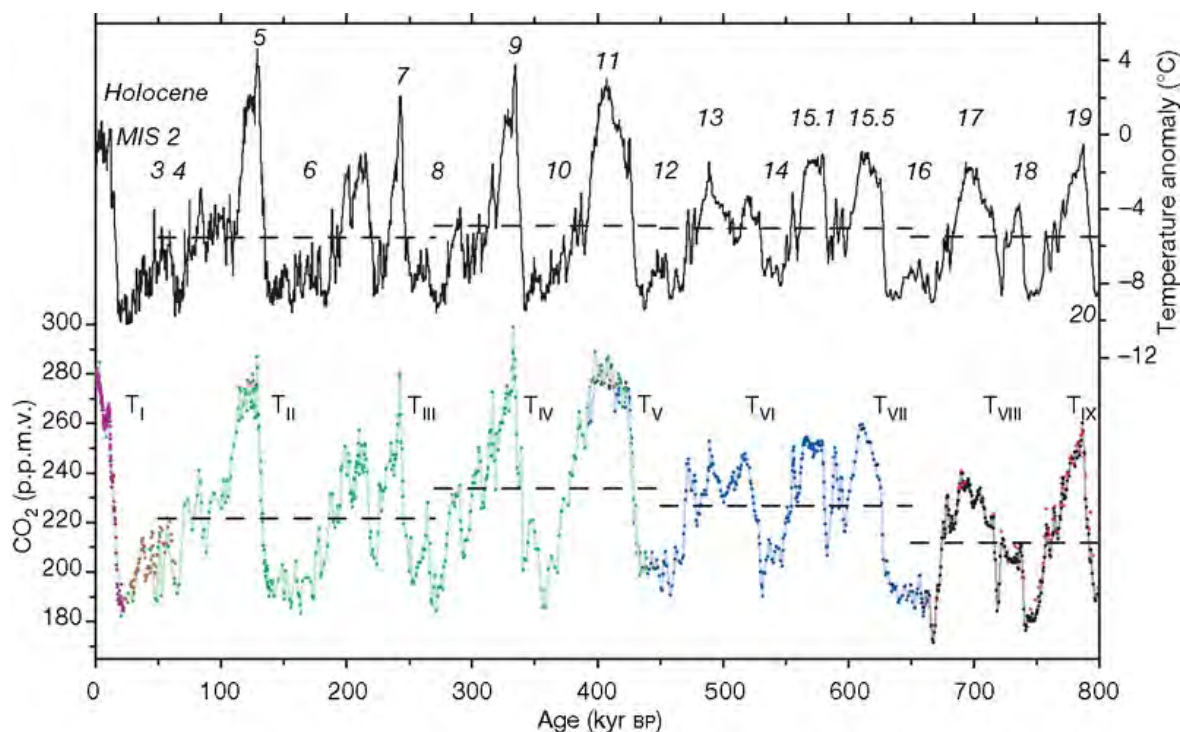


Figure 12.43. Comparison of CO₂ in bubbles (gray shows analytical uncertainties) in the EPICA ice core with temperatures calculated from δD . From Luthi et al. (2008). Numbers on the temperature plot are marine isotope stages. T_I, T_{II}, etc. on the CO₂ plot are terminations of glaciations.

terrestrial biota, but, again, with opposing affects. During glacial times, sea level drops and the area available for terrestrial vegetation expands, but expansion of glaciers also reduces this area. Precipitation patterns also changed from glacial to interglacial times and also affect the biota as the area of arid regions change. Variations in climate and the terrestrial biota in turn drive variations in the mass of carbon stored as dead organic matter in soils, forest litter and peat. Interestingly, there is no simple relationship between the mass of living carbon in a biome and the mass of dead carbon stored in soils, etc. For example, two biomes, tundra and grassland, account for only 4% of the terrestrial biomass yet account for more than a quarter of organic matter stored in soils, etc. This is because organic matter decays slowly in these environments whereas it decays quite quickly in tropical and temperate forests, which together account for over 60% of the terrestrial biomass. Thus the interaction between climate, atmospheric CO₂, and the terrestrial biomass is complex and is has not yet been fully quantified.

The most important changes in CO₂ fluxes into and out of the atmosphere in glacial-interglacial cycles appear to be those into and out of the oceans. These fluxes change response to climate-driven changes in ocean circulation, which change the ventilation time of the ocean and hence the storage of CO₂ in the deep ocean. Toggweiler et al. (2006) suggested that the key ocean circulation changes result from a climate-driven migration of the westerly winds in the Southern Ocean. In the present, interglacial climate, the most intense westerly winds are located south of the Antarctic polar front. As a result of a phenomenon called Ekman transport, these winds drive water away from Antarctica, and as a result, water rises, or "upwells" from depth, allowing CO₂ built-up in the deep ocean to vent to the atmosphere, keeping atmospheric CO₂ concentrations high. During glacial times, these westerlies shifted equatorward allowing for build-up of CO₂ in circum-Antarctic deep water. In addition, changes in the efficiency of the biological pump can affect the balance of CO₂ between ocean and atmosphere (e.g., Boyle, 1988). Most of the ocean is oligotrophic, meaning that photosynthesis is limited by the abundance of nutrients in the surface water. Hence, the rate at which biological pump works is governed by

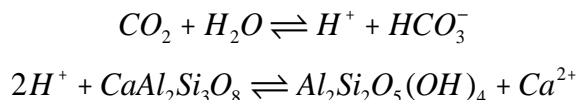
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surface water nutrients levels. These are in turn governed by factors such as the rate at which nutrients are delivered from the land, the areal extent of continental shelves where nutrients can be recycled from the ocean bottom, and return of nutrient-rich deep water to the surface by ocean circulation. Since CO_2 is a strong greenhouse gas, this shift of CO_2 between the atmosphere and the ocean serve to amplify the climate changes that produce them in the first place. In this way, the quite small changes in geographic and temporal distribution of insolation were strengthened sufficiently to produce the remarkable glacial–interglacial cycles of the Pleistocene.

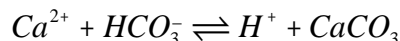
12.9.3 The Deep Carbon Cycle

Carbon at the Earth's surface is also part of a deeper, slower cycle. A small fraction of the organic carbon fixed every year is buried in sediments (Figure 12.42). Much of what is initially buried in sediment is remineralized during diagenesis, but a fraction is sequestered from the exogene for geologic times. Some fraction of this sedimentary organic carbon eventually returns to the exogene through weathering and some fraction is subducted into the mantle. Some of the subducted organic carbon is returned relatively quickly to the atmosphere through subduction-related volcanism or decarbonation during metamorphism, while some continues into the deep mantle. That too can eventually return to the atmosphere through mid-ocean ridge and mantle plume-related volcanism.

When dissolved in water, CO_2 forms carbonic acid and dissociates (Chapter 6), providing hydrogen ions that then attack silicate minerals:



Calcium released in this way are carried by rivers to the sea along with bicarbonate ions where they precipitate as calcite:



Much of the calcite redissolves in the deep water or sediment, but some is buried as part of the carbonate reservoir in Figure 12.42. The effect of silicate weathering is thus to remove CO_2 from the atmosphere. Weathering of limestone has no effect on atmospheric CO_2 , however, as carbonate ions produced in the process are also precipitated as calcite in the ocean and thus recycled carbonate back into the sedimentary carbonate reservoir. As is the case of sedimentary organic carbon, sedimentary carbonate can eventually return to the atmosphere through metamorphism or volcanism.

Together, the relative rates volcanism and metamorphism, weathering of sedimentary organic matter, weathering of silicates (and resulting burial of sedimentary carbonate), and burial of sedimentary organic matter control the amount of carbon in the oceans, atmosphere, and biosphere on long geologic time scales (more than about 1 Ma), as first noted by Berner et al. (1983). For the last few hundred million years the masses of carbon in the various reservoirs illustrated in Figure 12.42 have been approximately constant and the fluxes into and out of the exogene have been more or less at steady-state. The modifier “more or less” is important. Indeed, the GEOCARB model developed by R. A. Berner and his colleagues at Yale University over the years (e.g., Berner et al., 1983; Berner, 2006) begins with an assumption of steady-state and then uses carbon isotope variations in marine sediments as primary input to model variations in atmospheric CO_2 that result from imbalances in fluxes into and out of the exogene, i.e., deviations from steady-state. Small changes in these fluxes likely account, at least in part, for the climatic extremes that have occurred in the Phanerozoic. The Pleistocene glaciations are only the most recent example; glaciations also occurred at end of the Ordovician and in from the late Carboniferous into the Permian. In between these times, the Earth experienced warm periods, such as the Cretaceous, when the poles were ice-free and the oceans circulated in a far different manner than they did today.

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The fluxes into and out of the exosphere do not operate independently but are coupled in complex ways that result in both positive and negative feedbacks, just as is the case in the exogenous carbon cycle. These are illustrated in Figure 12.44. Just as in the exogenous cycle, these feedbacks are linked to and affect climate. In the exogenic carbon cycle, Milankovitch cycles drove variations in the system through the Pleistocene. In the deep carbon cycle, the principal external factor is tectonic activity, including continental position, uplift, volcanism, and metamorphism. Continent position and uplift directly affect global climate, but in both positive and negative ways (climate is “positive” in this scheme when it is warm and wet). Continent position and climate can both affect also ocean circulation, albeit in complex ways, which affects nutrient distribution; that, in turn, affects the marine biota and the biological pump. Volcanism, which is closely linked to tectonic activity, affects the terrestrial biota directly by supplying soil nutrients and emitting CO_2 and reduced gases to the atmosphere (the latter consuming O_2). Uplift increases erosion and weathering, which supplies nutrients to both the terrestrial and marine biota. Increasing terrestrial and marine bioproductivity results in more burial of organic matter in sediments, which draws down atmospheric CO_2 and increases atmospheric O_2 . Increasing atmospheric O_2 increases weathering of sedimentary organic carbon, while increasing CO_2 , along with organic acids produced by the terrestrial biota, increases silicate weathering. O_2 affects the biota through wildfires: fires are more likely and burn more extensively at higher O_2 levels. Increased silicate weathering decreases atmospheric CO_2 , which decreases global temperature, which decreases weathering. Climate also affects the terrestrial biota, albeit in complex ways. These complex interactions have led to variations in climate through the Phanerozoic, such as the Ordovician, Permo-Carboniferous, and Pleis-

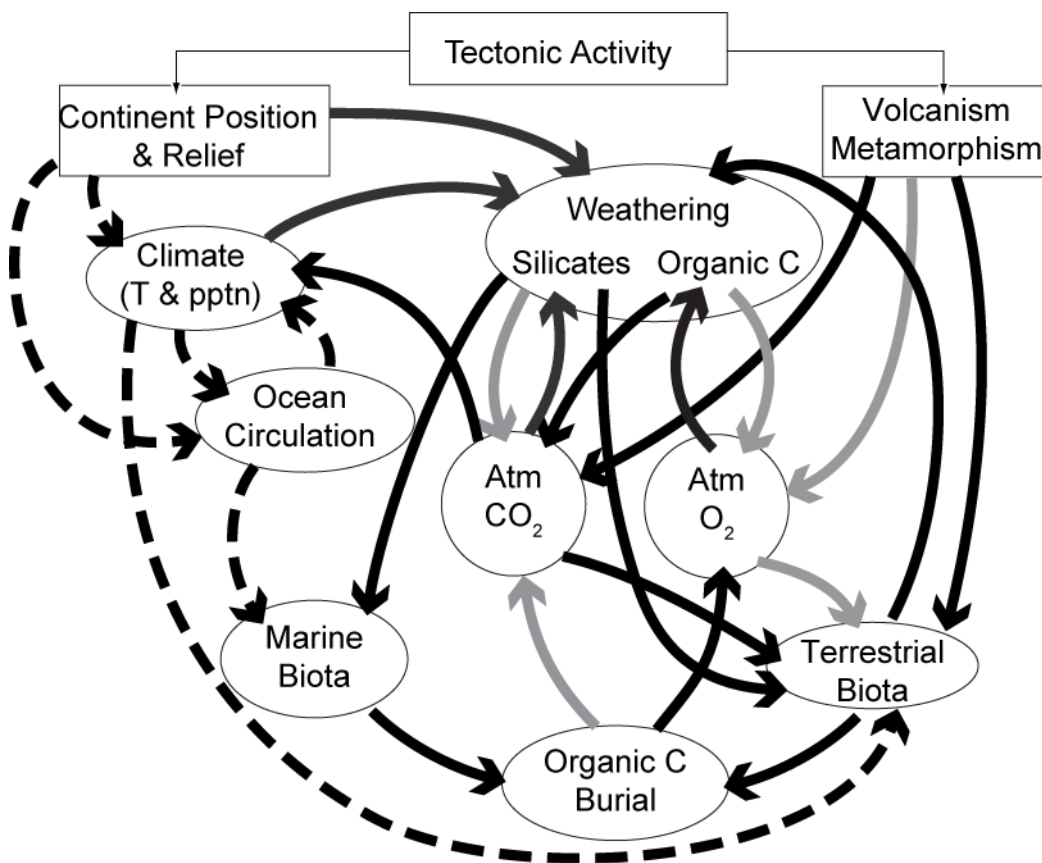


Figure 12.44. Feedback loops in the long-term carbon cycle. Black arrows represent positive feedbacks, gray arrows represent negative feedbacks, dashed arrows are complex feedbacks (can be positive or negative). After Berner (1999) and Killops and Killops (2005).

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tocene glaciations.

12.9.4 Evolutionary Changes Affecting the Carbon Cycle

Superimposed on the interactions illustrated in Figure 12.44 have been three long-term unidirectional changes that have affected the Earth, the carbon cycle, and climate.

- The first of these has been a steady increase in brightness of the Sun and, consequently, insolation. Stars grow progressively brighter over their main sequence (Figure 10.01) lifetimes. The Sun is now about 30% brighter than it was 4.5 billion years ago when it first became a main sequence star. This increase in insolation would result in surface temperature increase of nearly 22°C, all other factors being equal. Interestingly, the present mean global surface temperature is now about 13°C. This implies a mean surface temperature on the young Earth of -9°C, well below freezing, all other things being equal. Yet, liquid water appears to have been present on Earth nearly continuously since 3.8 Ga. This conundrum is known as the 'faint young Sun' paradox.
- The second change is a decline in tectonic activity. Energy to drive tectonic activity comes from two sources: radioactive decay of U, Th, and K and initial heat. The activity of these radionuclides has, of course, decreased exponentially over time. Based on the estimated abundance of radionuclides in the Earth (Table 11.03), radioactivity accounts for less than half the present heat loss from the Earth (about 45 terawatts); the remainder must reflect long-term cooling of the Earth from an initially hotter state. This long-term loss of heat and decline in radioactivity must necessarily result in long-term decline in tectonic activity, albeit not necessarily a steady one.
- The third change has been the evolution of life, which has had a profound effect on the nature of the atmosphere, and, as a result, on climate. The Earth's atmosphere in Hadean and early Archean times would have certainly been much different from the present one. Oxygen would have been absent; instead CO₂ would likely have been the dominant component, as it is in the atmospheres of Mars and Venus. It may well have been modestly reducing, with some CH₄ present. It is unclear when life, and photosynthetic life first arose, but a case can be made that photosynthetic life was present on Earth by 3.5 billion years ago, and it was almost certainly present by 2.7 Ga, based on cyanobacteria-derived biomarkers (methyl-hopanoids) in sediments of that age. Since then, photosynthesis has converted atmospheric CO₂ to organic matter, producing O₂ as a byproduct. Most of the organic matter produced by photosynthesis has simply recycled back into CO₂ through respiration, consuming the O₂ originally produced. However, some of that organic matter has been buried in sediment leading to a draw-down of atmospheric CO₂ and build-up of O₂. Indeed, there is more than 3 times as much organic carbon in sediments as needed to account for the O₂ in the atmosphere (this implies large amounts of O₂ have been consumed by oxidizing sulfur and iron). The drawdown of CO₂, and possibly methane as well, in the atmosphere has in turn affected climate. Indeed, a decrease in greenhouse gas abundances over geologic history appears to be the only way to resolve the 'faint young Sun paradox' mentioned above: higher concentrations of atmospheric CO₂ and CH₄ provided a stronger greenhouse effect keeping average surface temperatures above freezing throughout nearly all of the Precambrian. If the greenhouse effect is provided only by CO₂ (as opposed to CO₂ and CH₄), the amounts needed to offset the dimmer Sun are considerable: at the beginning of the Proterozoic (2.5 billion years ago), 100 times the present atmospheric levels of CO₂ would have been needed just to keep average surface temperature above freezing. Lower concentrations would have been needed if substantial methane were present. At the beginning of the Phanerozoic when the Sun was only 5% dimmer than at present, a CO₂ concentration some 10 times the present one would have been needed to maintain an average surface temperature similar to the modern one (assuming CH₄ concentrations similar to modern ones). While photosynthetic life was present in the oceans in Archean time, it was not until the Paleozoic that land plants evolved. The evolution of the terrestrial flora provided a new environment

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in which organic matter could be buried, namely bogs, swamps, and mires, and ultimately converted to coal. Vast deposits of coal produced during the aptly named Carboniferous period testify to the new terrestrial biota's effect on the carbon cycle. In addition, the invasion of the land by plants accelerated silicate weathering by releasing organic acids from roots. Finally, the evolution of terrestrial flora would have changed climate directly by changing the Earth's albedo (reflectivity). Deserts, sand, and soil, presumably the Precambrian land cover, reflect 25 to 30 percent of solar radiation back into space. Forests reflect only about 10 percent of that radiation. The decrease in albedo in the Paleozoic that would have resulted from the evolution of terrestrial flora would thus have effectively increased insolation and had a warming effect on climate.

12.9.5 The Carbon Cycle and Climate Through Time

Figure 12.45 shows Berner's (2006) modeled atmospheric CO_2 concentrations over the Phanerozoic. The model is based on the relationships illustrated in Figure 12.44 and the record of carbon isotope ratios in marine carbonate sediments. The latter change in response to shifts in the fluxes shown in Figure 12.44. For example, because organic carbon has low $\delta^{13}\text{C}$, an increased burial of organic carbon drives the isotopic composition of carbon in the exogene toward more positive values. Increased weathering of organic carbon would have the opposite effect. These isotopic shifts are reflected in the isotopic

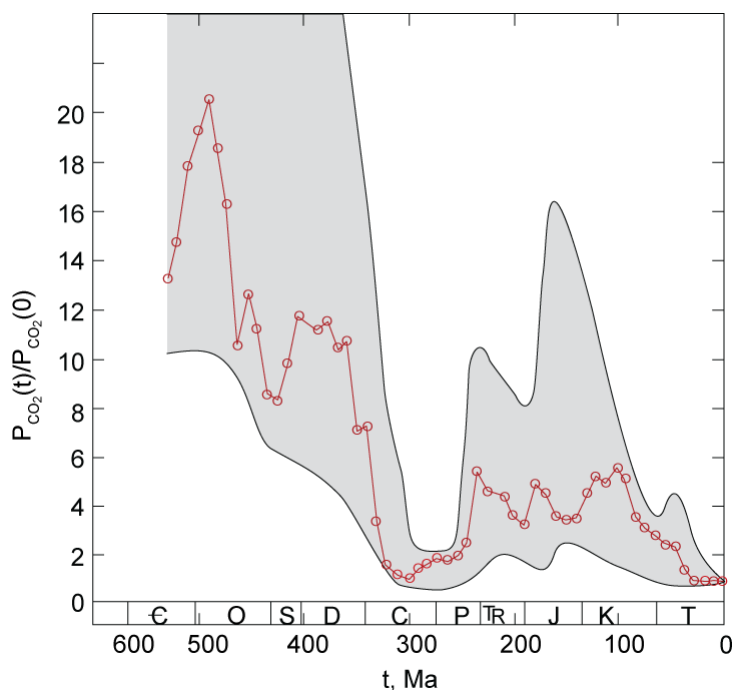


Figure 11.45. Concentration of atmospheric carbon dioxide over the Phanerozoic. Open red circles show the modeled values of Berner (2006). Errors on the model are shown as gray and are taken from Berner and Kothavala (2001).

composition of carbonates precipitated from the oceans. The overall picture suggested by this model, is one of declining atmospheric CO_2 , but if the model is correct, the decline has not been steady. A decline through the Ordovician led to a glacial epoch in the Late Ordovician-Early Silurian. The Berner model suggests this is due to silicate rock (specifically volcanics) weathering. Continental position likely also played a role, as most evidence of glaciation comes from areas positioned near the South Pole at the time. CO_2 recovered in the Silurian and Devonian, but declined again in the Carboniferous, leading to the Permo-Carboniferous glaciation. This time the cause appears to be burial of vast amounts of organic carbon in bogs, swamps, and mires that was ultimately transformed into coal. Atmospheric CO_2 recovered in the Mesozoic, but not to levels seen in the Paleozoic (remember, however, CO_2 was needed to maintain the same temperature). After reaching concentrations perhaps 5 times greater than present ones, atmospheric CO_2 declined in the late Cretaceous and early Tertiary periods. An essentially similar decline over this period is seen in the model of Hansen and Wallman (2003). Judging from CO_2 levels deduced from diunsaturated alkenones (Figure 12.41) and boron isotopes (Figure 9.46), long-term atmospheric CO_2 levels have remained low throughout the

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late Tertiary (the Neogene) into the Quaternary, although shorter term variations have occurred as a result of perturbations of the exogenous carbon cycle driven by Milankovitch cycling (Figure 12.43).

Knowing how atmospheric CO₂ and climate varied in the Precambrian is a much more difficult proposition. There is some sparse and equivocal evidence for glaciation in the late Archean, around 2.8 Ga, and strong evidence of glaciations in the Paleoproterozoic (occurring roughly between 2.4 to 2.2 Ga) and in the Neoproterozoic (occurring roughly between 0.8 to 0.6 Ga). In both the Proterozoic events, glacial sediments (diamictites) appear to have been deposited at tropical, rather than polar, latitudes, based on paleomagnetic inclinations and other geologic indicators. Other evidence, such as the presence of marine sediments above and below them, indicate that they were deposited at low elevation. Examples of glacial sediments from the Neoproterozoic are found on every continent except Antarctica. These observations suggest that these glaciations were far more severe than Phanerozoic glaciations that followed (in the Pleistocene glaciations, for example, ice sheets reached no further south than about 40° N, although mountain glaciers were, and still are, present at lower latitudes). This has given rise to the 'snowball Earth' hypothesis, glacial events so severe that oceans were entirely frozen over or nearly so (Kirschvink, 1992; Hoffman et al., 1998). The record of the Paleoproterozoic glaciation is more equivocal, but low latitude paleomagnetic inclinations in sequences in both North America and South Africa suggest the possibility that this too may have been a severe snowball-Earth-like glaciation that extended to the tropics.

The Paleoproterozoic diamictites in Huronian formation in Canada occur stratigraphically above an older conglomerate containing abundant detrital pyrite (FeS₂) and uraninite (UO₂). That reduced minerals could survive erosion, transport, and deposition suggests they were deposited in an oxygen-free atmosphere. Other examples of detrital pyrite and uraninite in Archean age sediments are relatively common but, with rare exceptions, they do not occur in sediments younger than 2.2 Ga. The Huronian diamictites are overlain by redbeds: sandstones consisting of quartz coated with hematite. The hematite is indicative of an oxidizing atmosphere. Redbeds are absent in sediments older than 2.4 Ga, but occur more or less throughout the subsequent geologic record. Detrital pyrite and uraninite and redbeds are part of a suite of evidence, including mass independent sulfur isotope fractionation discussed in section 9.7.3, that significant amounts of atmospheric O₂ first appeared 2.4 and 2.2 Ga. This period is known as the Great Oxidation Event (GOE). Oxygen levels in the atmosphere before the GOE were likely a factor of 10⁻⁵ lower than present and rose to 8 to 15% of present atmospheric levels during the GOE (e.g., Canfield, 2005; Holland, 2006). Thus the Paleoproterozoic Huronian glaciation corresponds closely in time with the appearance of atmospheric oxygen and this has led some scientists to suggest the two are related. Kasting and Ono (2006) suggest that the rise in atmospheric oxygen caused a drop in the atmospheric CH₄ (a greenhouse gas). A drop in the concentration of the latter from 10⁻³ to 10⁻⁵ would have produced a temperature decrease of 20°C, enough to trigger glaciation unless the early Proterozoic climate was much warmer than today. Alternative explanations involve pulses of mantle plume volcanism or rift-related volcanism (Melezhik, 2006; Eyles, 2008) that resulted in an increase in silicate weathering and draw-down in atmospheric CO₂.

Why did the atmosphere remain oxygen-free throughout the Archean and then rapidly increase in the Paleoproterozoic when various lines of evidence suggest oxygenic photosynthesis began at least by 2.7 Ga and possibly much earlier? One reason is that iron and sulfur in the exosphere would have been in reduced states. Before oxygen could build up in the atmosphere, the stock of reduced iron and sulfur would have to have been substantially exhausted. Indeed, the observation that post-GOE Proterozoic paleosols, like modern ones, are iron-rich (because Fe³⁺ is insoluble and cannot be leached from them) while Archean paleosols are iron-poor (because Fe²⁺ was leached) is evidence that considerable oxygen was consumed in the process of oxidizing soil Fe. Similarly, gypsum-bearing evaporites first appearing in the geologic record around the time of the GOE is evidence that oxygen was consumed in oxidizing sulfur to sulfate. Only after the stock of reduced Fe and S were oxidized could atmospheric O₂ rise. This would have taken time; just how low would have depended on the rate of oxygen production as well as the supply of reduced components to the surface by volcanism. Large variations in δ¹³C in marine carbonates deposited around this time, including excursions to values as negative as -12‰, suggest dis-

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turbances to the exogenic carbon cycle which in turn support the possibility of changes in atmospheric greenhouse gas levels. Alternatively, Kump et al. (2001) and Holland (2009), among others, have suggested that a change in the composition of volcanic gases. Although they differ in detail, both models conjecture that the mantle, and consequently volcanic gases became more oxidizing through time as a result of subduction. Thus at least in some hypotheses both the GEO and the associated Paleoproterozoic glaciations resulted from processes and changes occurring deep within the Earth rather than just the surface.

The geologic record of the Neoproterozoic glaciations is more complete and there is compelling evidence that at least two of the glaciations, the Sturtian at around 715 Ma and the Marinoan at around 635 Ma, were severe and extended into the tropics. Although there is not yet complete agreement on this point, a consensus appears to be forming that not only were the continents largely ice covered, but most or all of the ocean was frozen over by a thick layer of ice: a 'snowball Earth'. Indeed, the evidence of extensive glaciation is compelling enough that this period of the Neoproterozoic has been named the *Cryogenian*. Both are overlain by thick deposits of marine carbonates, termed 'cap carbonates' and are preceded by large negative $\delta^{13}\text{C}$ anomalies that return to positive values just before the glaciation. A possible earlier Kaigas glaciation at around 740 Ma and a later Gaskiers glaciation at around 582 Ma appear to have been less severe.

The Cryogenian glaciations followed the break-up of the Rodinia supercontinent, which began around 800 Ma. Paleomagnetic reconstructions suggest that the Rodinia was located at low latitude at the time and that the break-up proceeded longitudinally, so that the fragments remained at low latitude (in contrast to the break-up of Pangaea). Because of its size, interior regions of Rodinia would have been starved of ocean-derived moisture and weathering rates would have been slow. Weathering rates would have increased as it broke up and moisture could reach its former interior. There is reason to think that extensive volcanism would be associated with the continental rifting (as was with Pangaea), and some evidence to support that thinking. At least until the beginning of the Cryogenian, atmospheric oxygen levels were likely as low as they had been throughout the Proterozoic, less than 18% of present levels. The oceans, particularly the deep oceans were likely oxygen-poor, which may have allowed a much larger flux of CH_4 to the atmosphere. This methane would have played an important role in keeping the Earth's surface despite a dimmer Sun at the time.

These above observations play key roles in models attempting to explain the initiation of glaciation. All models involve significant disturbances to the carbon cycle and a consequent crash in greenhouse gas inventory; beyond that they differ. Godderis et al., (2011) divide the models into 3 scenarios. In the first, Pavlov et al. (2003) suggest that rising oxygen levels around this time greatly reduced the methane flux from oxygen-poor oceans. That in turn reduced the CO_2 levels in the atmosphere (because the methane eventually oxidizes to CO_2). Schrag et al. (2002) proposed the high rates of tropical weathering as Rodinia broke-up led to enhanced ocean nutrient levels and productivity and efficient burial of organic carbon. In the oxygen-poor ocean, however, much of this organic carbon would have been converted to methane and frozen into methane clathrate. In their model, the methane clathrate eventually became unstable, flooding the atmosphere with CH_4 , which soon oxidized to CO_2 (this accounts for the negative $\delta^{13}\text{C}$ in marine carbonates prior to glaciation). With the continents in the tropics, this CO_2 was quickly consumed by silicate weathering, triggering a crash in the greenhouse. The model of Donnadieu et al. (2004) is similar in many respects, but calls upon volcanic outgassing to provide an initial pulse of CO_2 , which, as in the Schrag et al. (2002) model, is consumed by silicate weathering, which is greatly enhanced in the Donnadieu model by fast amounts of young basalt exposed in the tropics. In all the models, once glaciation begins, the Earth 'whitens' and the much greater albedo provides a powerful feedback driving further cooling.

The path out of the snowball state is less controversial. With the planet completely frozen, silicate weathering stops, yet volcanism continues. Over millions of years, sufficient CO_2 builds up in the atmosphere to warm the planet so that melting begins, and decreasing albedo then provides a feedback to further warming. In addition, there would have been almost no removal of atmospheric CO_2 by photosynthesis during the snowball phase, aiding its build-up in the atmosphere. The massive amounts of

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CO₂ in the atmosphere immediately after deglaciation produce a hothouse climate that greatly accelerates silicate weathering. The consequent flux of Ca²⁺, Mg²⁺, and HCO₃⁺ to the ocean leads to massive carbonate precipitation, accounting for the cap carbonate sequences. Increases in ⁸⁷Sr/⁸⁶Sr in the Cryogenian are consistent with an enhanced flux of weathering products of the continents to the oceans, and hence are consistent with this aspect of the models.

The simple observation that photosynthesis survived the snowball Earth represents a problem for the most extreme versions of the hypothesis. If continents and oceans were thickly frozen, photosynthetic life could not have survived. One possible solution is that the oceans were not completely frozen, but climate simulations suggest that a nearly frozen Earth with open tropical seas are not stable — the oceans either freeze completely or begin to unfreeze. Another possible solution is that ice in the tropics was thin enough for sunlight to sustain at least some photosynthesis in the water below.

The termination of the Marinoan glaciation marks the beginning of the last period of the Proterozoic: the Ediacaran. Although one more, less severe, glaciation occurred in the Ediacaran, climate appears to have again stabilized. It was during the Ediacaran period that multicellular animals appear (although sponge-like fossils from the Cryogenian have now been identified). Many scientists suspect the Cryogenian glaciations set the stage for the Nature's experiments with multicellular animals in the Ediacaran and the explosion of life that saw the appearance of all animal phyla in the following Cambrian period.

12.9.6 Fossil Fuels and Anthropogenic Climate Change

Two hundred and fifty years ago humans began to replace traditional energy sources — muscle power, animal power, wind, and water — with a new energy source, coal. The coal-fired steam engine, first developed by James Watt to pump water from (ironically enough) a coal mine, was soon adapted to cut wood and stone, mill flour, spin yarn and weave fabric, provide transport, dig canals, etc. Beginning in the mid-nineteenth century, petroleum and natural gas began to supplement and partly replace coal and coal gas. The primary combustion product of all of these is, of course, CO₂. In 1896, building on an understanding of atmospheric energy balance that began with a paper written in 1827 by French mathematician Joseph Fourier, Svante Arrhenius published a paper entitled “On the influence of carbonic acid in the air upon the temperature of the ground.” In that paper, he predicted that burning of fossil fuels should lead to an increase in atmospheric CO₂ concentration, which should in turn enhance the greenhouse effect and increase global temperatures. Arrhenius thought this was a good thing because it might prevent the Earth from entering another ice age and it should enhance agricultural productivity and help to feed a growing global population. At the time, there were no systematic measurements of atmospheric CO₂ concentration and global temperature record keeping was just beginning, so the theory could not be tested.

Arrhenius's theory was largely ignored by the scientific community until the 1950's, when Hans Suess took notice of it. Suess was a nuclear chemist working on ¹⁴C dating and concerned about an apparent decrease in the specific activity[†] of ¹⁴C in the atmosphere. He suspected that increasing atmospheric CO₂ derived from fossil fuel, which would have a specific activity of 0, might be the answer. He and his colleague at the University of California San Diego, Roger Revelle, convinced another colleague, Charles Keeling, to begin measuring atmospheric CO₂ on a regular basis. Keeling soon set up a monitoring station atop Mauna Loa in Hawaii and, subsequently, one at the South Pole. Monthly measurements of atmospheric CO₂ have been made at these stations ever since; the data from Mauna Loa is shown in Figure 12.46. Superimposed on the wiggles caused by the seasonal cycle of photosynthesis in the terrestrial biosphere is a clear increase in atmospheric CO₂ from a seasonally adjusted value of 316 ppm in 1960 to 392 ppm in 2011, corresponding to an average annual increase of 1.5 ppm. The rate of rise has been increasing, however, and in the first decade of the 21st century approached 2 ppm per year. The Intergovernmental Panel on Climate Change (IPCC) estimates that the carbon emit-

[†] Recall from Chapter 8 that the specific activity is defined as the activity (decays per unit time) of ¹⁴C divided by the amount of C in grams.

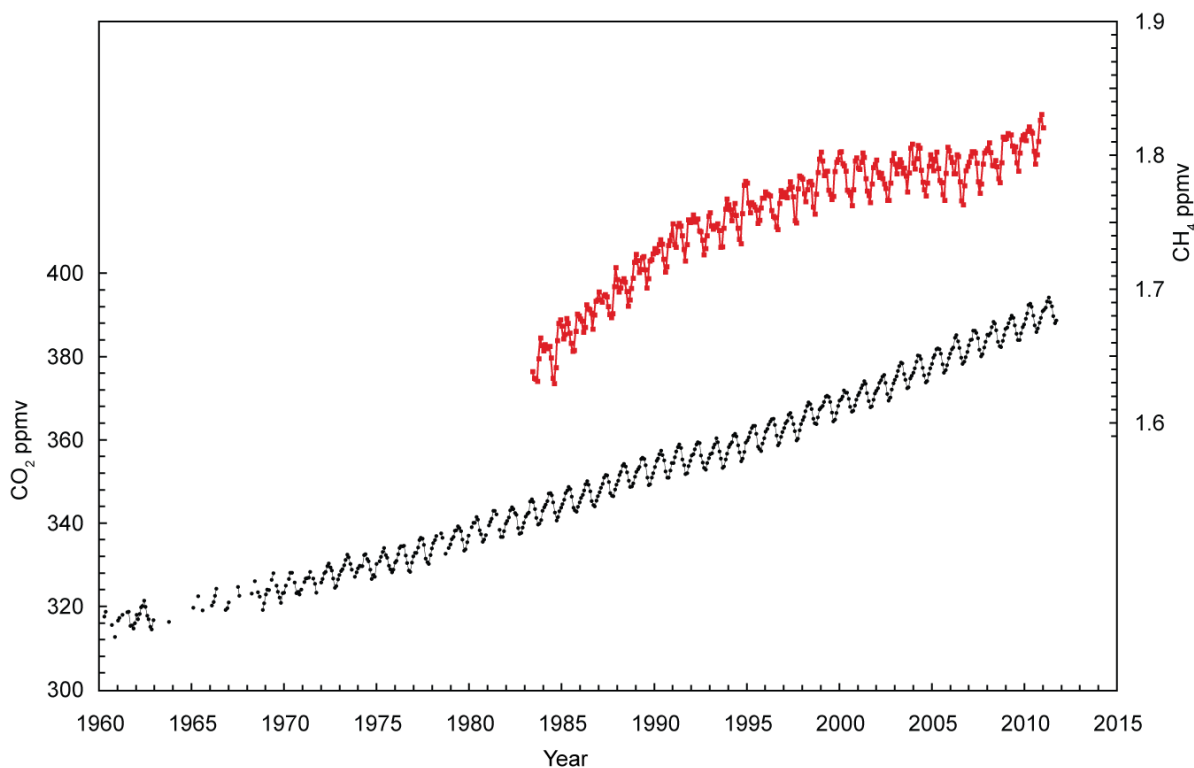


Figure 12.46. Concentrations of atmospheric CO_2 and CH_4 measured at the Scripps Institution of Oceanography Mauna Loa observatory over the last half century. Sources: Scripps CO_2 program (<http://scrippsco2.ucsd.edu>) and NOAA Earth System Research Laboratory (<http://www.esrl.noaa.gov/gmd>).

ted by fossil fuel burning increased from an average of 6.4 ± 0.4 gigatons of carbon (GtC) per year in the 1990s to 7.2 ± 3 GtC per year in 2000–2005 (Solomon et al., 2007). Thus the increase in rate of rise is consistent with the increasing rate of emissions. In addition to fossil fuel burning, the IPCC estimates that an additional 1.9 GtC per year is being added to the atmosphere through ‘land use change’ (primarily cutting of tropic forests).

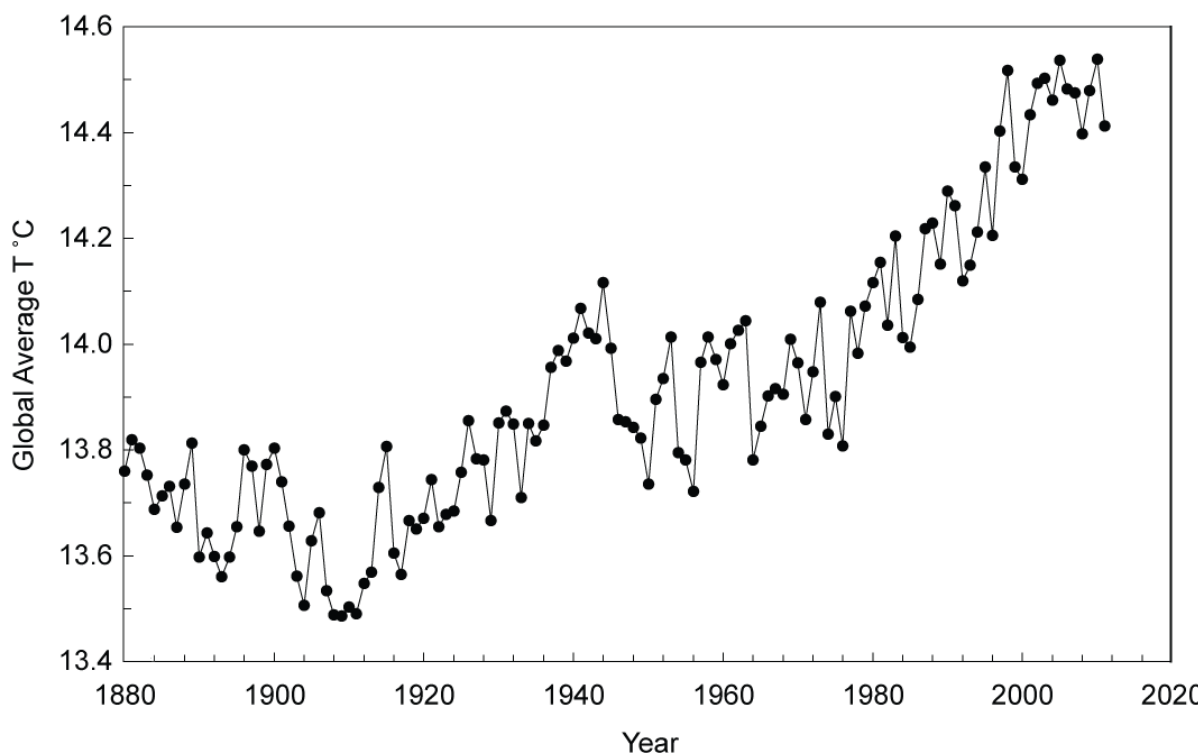
From the total emissions of around 9 GtC/yr, we would predict atmospheric CO_2 should be increasing by about 4 ppm per year, more than twice the actual rate. Put another way, the actual increase in atmospheric CO_2 is only around 4 GtC/yr. This difference reflects carbon transfer into other exogenous reservoirs shown in Figure 12.42. Various studies suggest the ocean is taking up about 2 GtC/yr. One consequence of this is ocean acidification: ocean surface pH has declined from an estimated preindustrial value of 8.17 to a present value of 8.07. The remaining 2 to 3 GtC/yr being released by fossil fuel burning and tropical deforestation is apparently being taken up by the northern hemisphere biosphere. There could be several reasons for the expansion of the northern hemisphere biosphere. First, as agriculture became more efficient in the 20th century, land cleared for agriculture has been abandoned and is returning to forest. Second, emissions from fossil fuel burning, including both CO_2 and nitrates, may be stimulating growth. Third, warming is enabling expansion of boreal forests into regions previously covered by tundra.

Figure 12.46 also shows the change in atmospheric methane concentrations. These concentrations exceed the natural range of the last 650,000 years (320 to 790 ppb) as determined from ice cores. The principle anthropogenic sources are farm animals (ruminants such as cows and sheep) and rice farm-

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ing. Other sources include landfills, sewage treatment facilities, biomass burning (incomplete burning produces methane as well as CO_2) and production and distribution of hydrocarbons (i.e., losses from oil and gas wells and distribution lines). In addition, warming may be enhancing release of methane from permafrost and methane clathrates on Arctic continental shelves.

Figure 12.47 shows annual globally averaged land and ocean surface temperatures from 1890 to 2011. It is apparent that surface temperatures have increased over the period, albeit irregularly. The net increase is about 0.75°C . Most of that change has occurred since 1960 (the same year CO_2 measurements began); indeed the rate of increase over the last 50 years (0.13°C per decade) has been more than double the average rate of increase over the last 120 years. There are numerous other indicators of changing climate as well: the average temperature of the oceans has increased to depths of at least 3000 m (the ocean has been absorbing more than 80% of the heat added to the climate system); mountain glaciers



Annual globally averaged land and ocean surface temperatures since 1890. Source: U. S. National Climate Data Center (<http://www.ncdc.noaa.gov>).

have receded and snow and ice cover has declined, as has Arctic Sea ice (the latter dramatically); the average atmospheric water vapor content has increased (in a way more or less consistent with the extra water vapor that warmer air can hold); sea level has been rising at a rate of 1.8 mm/yr over the last 50 years. As the 2007 IPCC report put it, *"warming of the climate system is unequivocal."*

In the previous sections, we saw how climate has changed over Earth's history and that these changes occurred as a result changes to the carbon cycle and atmospheric greenhouse gas concentrations. Given what Earth's history teaches us, the observed recent climate change (Figure 12.47), the observed increase in greenhouse house gas concentrations (Figure 11.46), and the known amounts of fossil fuels that have been burned, can we really question whether fossil fuel burning is leading to climate change? The 2007 IPCC report puts rather conservatively in saying; *"Most of the observed increase in global average temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic greenhouse gas concentrations."* Climate change does have some 'upside' effects, such as those noted

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by Arrhenius, but it also has downside effects and the latter are likely to outweigh the former. Furthermore, our understanding of the climate system remains quite limited. There are reasons to think that temperature increases in the future might be more rapid than the present moderate rate (as an example, CO₂ solubility decreases with temperature, so the ocean may not take up as much CO₂ in the future). We have seen that in the Pleistocene, climate swung rapidly between cold and warm states. Our understanding of the Neoproterozoic snowball Earth episodes is far more limited, but climate modeling suggests the Earth oscillated rapidly between icehouse and hothouse states.

These observations should give us pause about the world's current equivocal, even cavalier, attitude toward climate change and motivate us to move beyond fossil fuels as our principle energy source. Our fossil fuel reserves, while ultimately limited, remain vast and we could continue to rely on them through much of this century and perhaps beyond. The Saudi oil minister once observed that the Stone Age did not end because people ran out of stones. We need to find a way to move beyond the Fossil Fuel Age before we run out of fossil fuels. Promising technologies are available, many of them are either now cost effective or are approaching that point. Parts of the solution are relatively simple, such as becoming more energy efficient and replacing coal with natural gas (the latter releases only half the CO₂ per joule energy produced) while we develop true carbon-free energy sources. Other parts may require ingenuity and some short-term sacrifice in return for long-term benefit.

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Problems

- Sketch the structure of the following:
 - Citric acid: $\text{HOC}(\text{CH}_2\text{CO}_2\text{H})_2\text{CO}_2\text{H}$
 - Tartaric acid: $\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{H}$ (2,3,-dihydroxybutanedioic acid).
- Write the chemical formula and sketch the structure of 2-hydroxy-propanoic acid (lactic acid).
- Suppose you could follow the pathway of individual atoms during photosynthesis. While this is not possible, something similar can be done by isotopic labelling of water and CO_2 . If ^{18}O -labelled water is added to a suspension of photosynthesizing chloroplasts, which of the following compounds will first show enrichment in ^{18}O : ATP, NADPH, O_2 , or 3-phosphoglycerate? If you repeat the experiment with ^2H -labelled water and ^{13}C -labelled CO_2 , which of these molecules will first show enrichment in these isotopes?
- The first and second acidity constants of oxalic acid ($(\text{COOH})_2$) are $\text{pK}_{\text{a}1} = 1.23$ and $\text{pK}_{\text{a}2} = 4.19$. What is the pH of a solution formed by dissolving 1 mole of oxalic acid in 1 kg of water? If this solution is titrated with 1 M NaOH, how will pH change as a function of the amount of base added? Make a plot of pH vs. amount of base added.
- The rate of bond cleavage during the thermal maturation of kerogen approximately doubles for every 10° rise in temperature. Based on this and assuming that these reaction rates show an Arrhenius temperature dependence (equation 5.24), estimate the activation energy for these reactions.
- Astrophysicist Thomas Gold has suggested that most petroleum deposits are formed by abiogenic organic carbon (mainly in the form of methane) diffusing out of the mantle. There are few, if any, geochemists that agree. Describe at least 3 *geochemical* observations that support the "conventional" theory that petroleum is formed from sedimentary kerogen, which in turn is derived from the remains of once living organisms.

CHAPTER 12: ORGANIC GEOCHEMISTRY

7. Assume that humic acid may be modelled as consisting of two ligands: a bidentate carboxylic ligand (e.g., malonate) and a bidentate phenol one (e.g., catechol), and that the effective concentrations of these are 10^{-3} mol/g humate and 5×10^{-4} mol/g humate respectively. Using the following apparent stability constants, calculate the fraction of copper complexed if the humate concentration is 10 mg/l, the pH 8, and the total copper concentration is 10^{-8} M. Assume that copper and humate are the only species present.

Apparent stability constants:

"Malonate":	H ₂ L	pK _{a1} = 1.9
	HL ⁻	pK _{a2} = 1.9
	CuL	pK _{Cu} = 7.7
"Catechol":	H ₂ L	pK _{a1} = 6.8
	HL ⁻	pK _{a2} = 10.0
	CuL	pK _{Cu} = 17.3

8. Repeat the calculation in Problem 7 above, but for pH 5.5. At this pH, the apparent stability constants are:

"Malonate":	H ₂ L	pK _{a1} = 2.9
	HL ⁻	pK _{a2} = 2.9
	CuL	pK _{Cu} = 6.7
"Catechol":	H ₂ L	pK _{a1} = 7.8
	HL ⁻	pK _{a2} = 11.0
	CuL	pK _{Cu} = 16.3

9. The adjacent table lists organic solid/water (K_{OM}) and octanol/water (K_{OC}) partition coefficients for some non-polar compounds. Are these data consistent with equation 12.15? What values do you determine for constants a and b ? (HINT: Use linear regression.)

10. Sediment from a highly eutrophic lake was found to have an organic carbon fraction of 5.8%. Using the adsorption partition coefficient for DDT listed in problem 9, predict the concentration of DDT in the sediment if the lake water has a DDT concentration of 3 μ g/l and the sediment contains 5.8% organic matter.

	K_{OW}	K_{OM}
acetophenone	38.90	42.66
benzene	128.82	83.18
tetrachloroethylene	398.11	208.93
napthalene	2290.87	1288.25
parathion	6456.54	1148.15
pyrene	151356.12	83176.38
chlorobenzene	512.86	389.05
DDT	1548816.62	138038.43
2,4,5,2',4',5'-PCB	5248074.60	218776.16