

CHAPTER 14: ORGANIC GEOCHEMISTRY

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 breakdown products of dead organisms. Organic substances may be either water insoluble or water soluble. Rain typically contains about 1 $\mu\text{g}/\text{l}$ dissolved organic carbon (DOC), the ocean around 0.5 mg/l DOC, and soils up to 250 mg/l. In general, insoluble 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) 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. In the final section of this chapter we examine the processes by which sedimentary organic matter evolves into important energy and chemical resources such as coal, gas, and oil.

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 (deoxyribonucleic acid), which is the blueprint for synthesis of proteins that carry out various intracellular functions, and all use ATP (adenosine 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

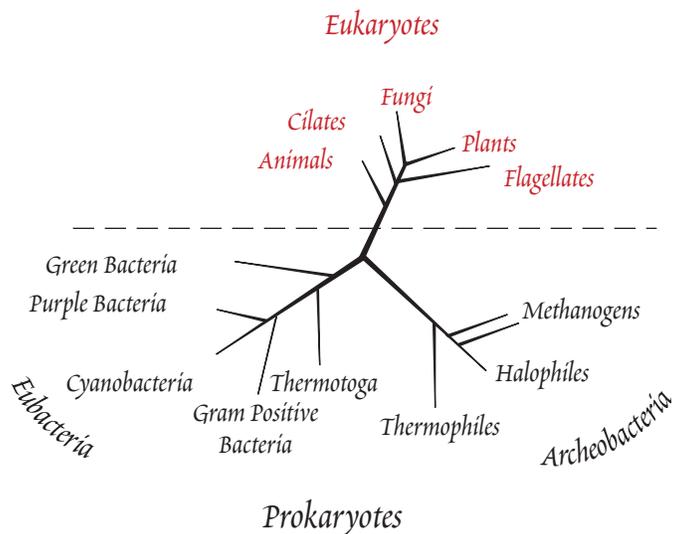


Figure 14.1. Phylogenetic relationships among organisms. The eubacteria and the archeobacteria constitute the prokaryotes; all other organisms are eukaryotes.

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

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still find any one of several in biological textbooks. Figure 14.1 presents a simplified version of the Woese system, based on ribosomal RNA sequencing, which has now achieved wide acceptance. It divides organisms into three kingdoms: *archeobacteria*, *eubacteria*, and *eukaryotes*. Two of these kingdoms consist only of bacteria; 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.

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 bacteria, 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. Bacteria 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 bacteria reduce sulfate, others oxidize sulfide, some produce methane, others 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.

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

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inorganic compounds as well, for example, quartz and tridymite or graphite and diamond, but isomers, i.e., compositionally identical but structur-

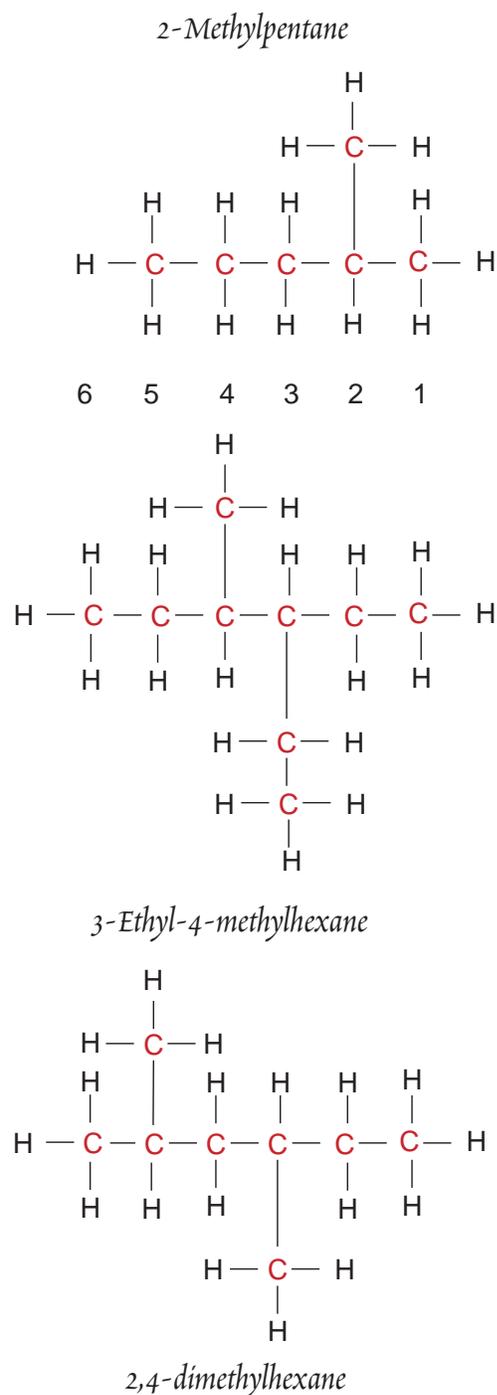
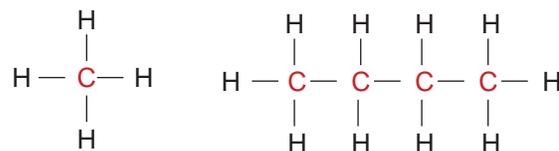
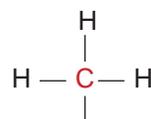


Figure 14.3. Some simple and branched hydrocarbon chains.

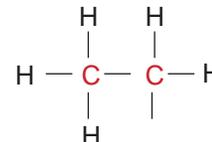


n-Methane



Methyl

n-Butane



Ethyl

Figure 14.2. Simple *n*-alkanes or chain hydrocarbons. The suffix “-ane” is used for to refer to molecules and the suffix “-yl” is used to refer to equivalent radicals formed by removing a hydrogen.

ally 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 is 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 5.3), so in the interest of clarity, we will not discuss it further.

HYDROCARBONS

Hydrocarbons are the simplest group of organic compounds in that they consist only of 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, which consist of a straight or branched chain of

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carbon and hydrogen atoms. These compounds are also called *paraffins*, or *alkanes*. If they are unbranched, they are called *normal* or *n-alkanes*. Individual compounds are given names with a prefix indicating the number of CH_x ($x = 2, 3$) groups present and an ending "-ane". The simplest such molecule is *methane*, CH_4 . Ethane consists of 2 CH groups, propane three, and butane four. Beyond that, the root of 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). Some simple alkanes are illustrated in Figure 14.2.

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 14.3). If more than one secondary group is attached, the groups are listed in alphabetical order, for example, 3-ethyl-4-methylhexane shown in Figure 14.3. 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 14.3.

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) of the double bond, for example, 2-butene, shown in Figure 14.4. If there are more than 2 double bonds the ending becomes "-adiene", "-atriene", etc. Generic names are *alkene*, *alkadiene*, etc. Triple carbon bonds are also possible, in which case the suffix becomes "yne" for a single triple bond. Acetylene* (Figure 14.4) 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., $-\text{C}=\text{C}-\text{C}=\text{C}-\text{C}-$.

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 carbon atoms lying in a single plane (Figure 14.5). Compounds based on this structure are particularly

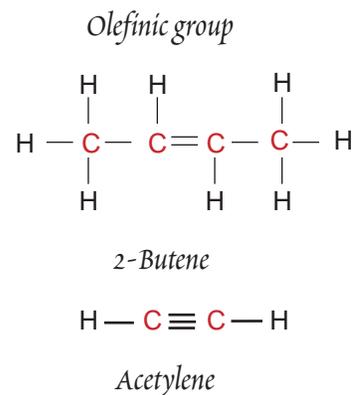


Figure 14.4. Some simple doubly and triply-bonded hydrocarbons.

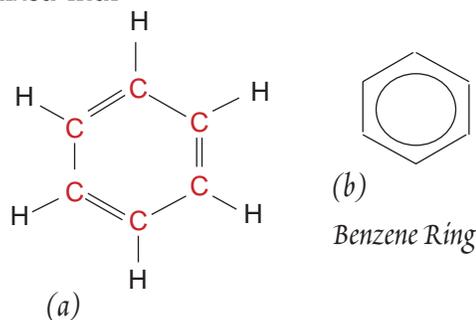


Figure 14.5. Two illustrations of the benzene ring, the foundation of aromatic hydrocarbons. In (b) the C and H atoms have been removed for clarity. Since all carbon-carbon bonds in the benzene ring are equivalent, (b) is actually a better representation than (a).

* 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.

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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*.

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 14.6. 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 CH₂O. They are either aliphatic or cyclic hydrocarbons in which a number of the hydrogens has been replaced by OH. The carbonyl group (C=O) forms aldehydes when the "R" in Figure 14.6 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 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 a *hydroxy acid* (for example, salicylic acid illustrated in Figure 14.7). 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.

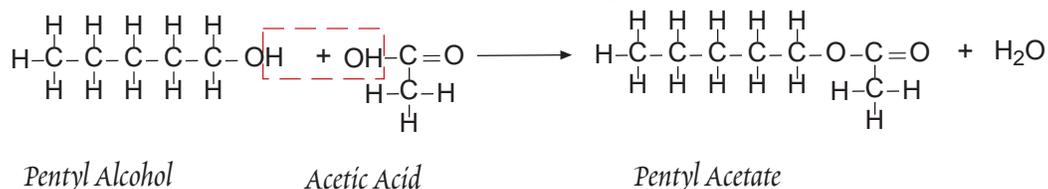
| Group | Name | Resulting Compound |
|------------------------------|----------|--|
| — OH | Hydroxyl | Phenols (Aromatics) Alcohols (Aliphatics) |
| — O — | Oxo | Esters |
| R—C=O | Carbonyl | Aldehydes Ketones, Quinones |
| —C=O OH | Carboxyl | Carboxylic Acid |
| —NH ₂ | Amino | Amines |
| —C=O NH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

Figure 14.6. Important functional groups found in organic compounds.

[†] 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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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 14.7 illustrates a few of the important compounds formed by replacement of hydrogen in basic hydrocarbons by one or more of these functional groups.

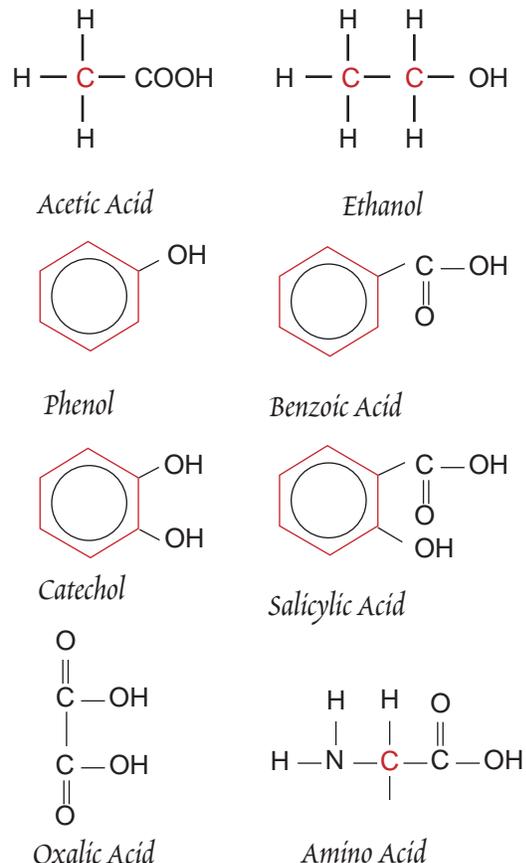


Figure 14.7. Some examples of compounds formed by substituting functional groups for hydrogen in basic hydrocarbon structures.

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 neutral. 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 14.8. 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.

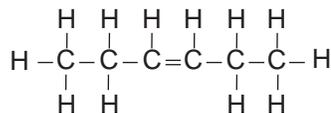
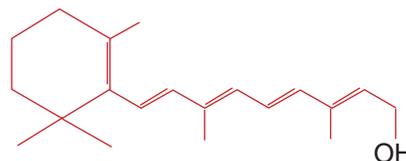
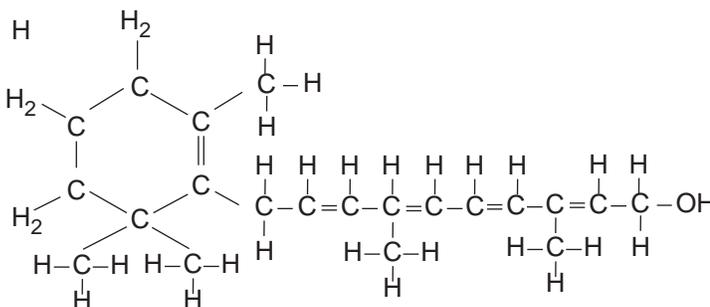
[†] Such a reaction, in which two molecules combine to form a larger molecule with the elimination of a small molecule (H₂O in this case), is called a condensation reaction or simply *condensation*. The reverse of this reaction is termed *hydrolysis*.

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SHORT-HAND NOTATIONS of ORGANIC MOLECULES

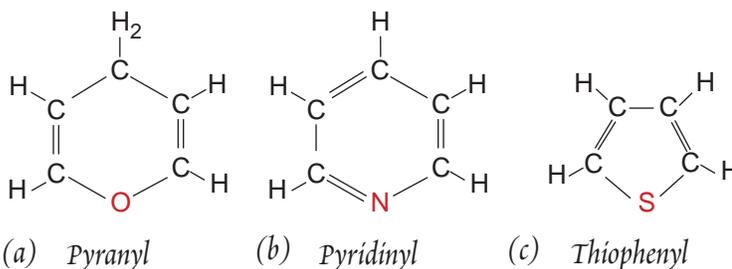
For both aliphatic and cyclic molecules, the number of carbons in the ring or chain is commonly denoted with C followed by a subscript corresponding to the number of carbons, e.g., C₆ for hexane. It is often convenient to use this notation in condensed structural formulae of long-chained aliphatic compounds. The basic repeating unit of such chains is CH₂. The number of repetitions can be expressed by enclosing the CH₂ in parentheses followed by a subscript indicating the number or repetitions, for example (CH₂)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 CH₃(CH₂)₁₆C(O)OH. If a double carbon bond occurs, this is designated by CH=CH inserted at the appropriate place. Thus palmitoleic acid, a common unsaturated fatty acid with the formula CH₃(CH₂)₅CH=CH(CH₂)₇C(O)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 CH₂ unit, and a second (CH₂)_n follows, *n* indicating the number of subsequent repetitions. Thus the formula for 3-methylhexane would be CH₃(CH₂)₂(CH₃)(CH₂)₂CH₃.

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 14.5). As in this illustration, carbons and hydrogens bonded to them are often omitted from representations of organic

(a) 3-*n*-hexene

(b) Retinol (Vitamin A)

Figure 14.9. 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.



(a) Pyranyl (b) Pyridinyl (c) Thiophenyl

Figure 14.8. 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; names of the resulting compounds are (a) pyran, (b) pyridine, and (c) thiophene.

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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 14.9. 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.

Biologically Important Organic Compounds

Obviously, life is 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 daltons. 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.

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 chemo-

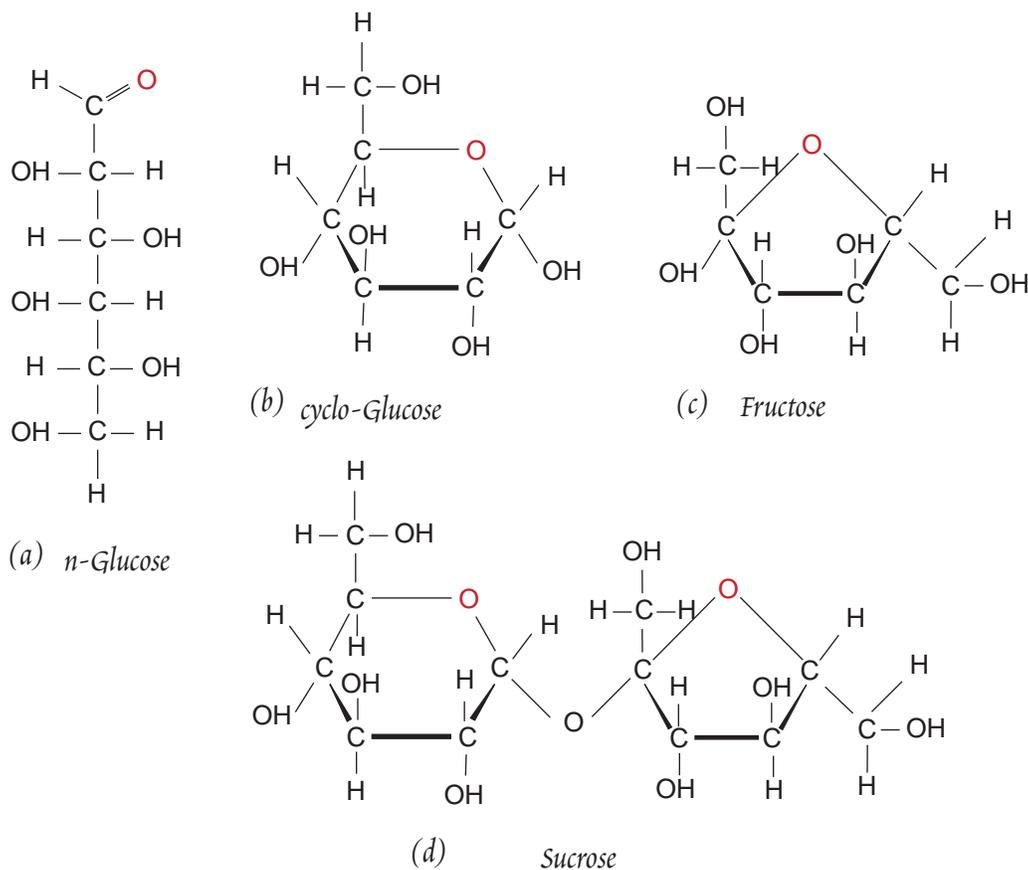


Figure 14.10. Some simple sugars. (a) linear glucose, (b) cyclic glucose, (c) fructose, and (d) sucrose, a disaccharide formed by condensation of glucose and fructose.

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synthesis rather than photosynthesis, but carbohydrate is also the immediate product of chemosynthesis. Thus carbohydrates may be regarded the fundamental substance of life.

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 $C_6H_{12}O_6$. Both can exist as straight chains or cyclic structures (Figure 14.10), though the cyclic structures predominate. Glucose and fructose are examples of *monosaccharides*, the mono-prefix indicating they consist of single chains or 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 $(C_6H_{10}O_5)_n$ 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 $(C_6H_{10}O_5)_n$ 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 daltons. Glycogen, a polysaccharide used for energy storage in animals, is closely related 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.

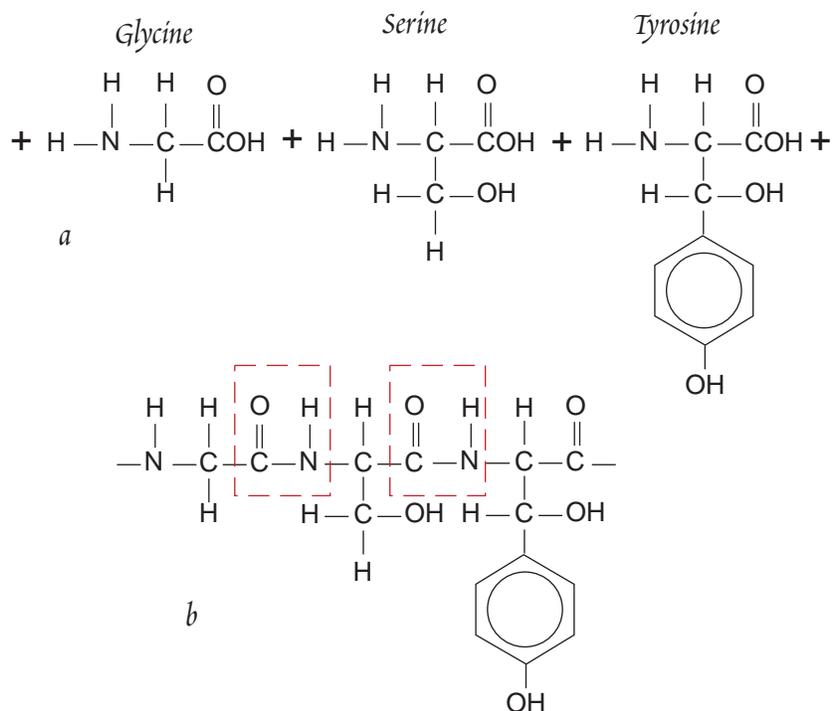


Figure 14.11. (a) Three of the twenty common amino acids that can combine to form proteins. (b) Peptide segment consisting of glycine, serine and tyrosine bound by peptide linkages (dashed boxes). Peptide linkage occurs between amine and carboxyl groups with the elimination of H_2O .

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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 14.7). The simplest amino acids are *glycine*, which consists of the amino acid group with a hydrogen at the free position (Figure 14.11), and *alanine*, which has CH_3 at the free position. Amino acids may be characterized as either 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

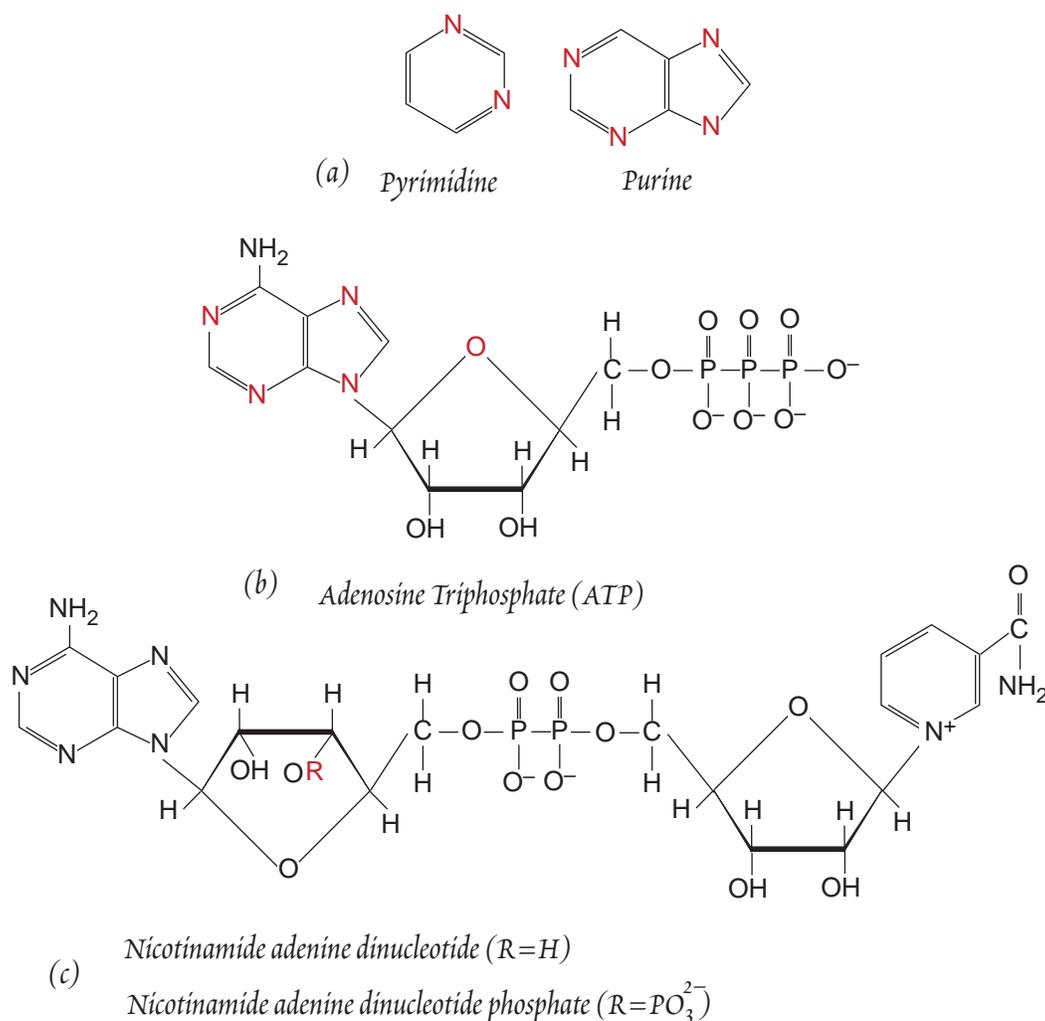


Figure 14.12. (a) The structure of pyrimidine and purine groups, essential components of nucleotides. (b) Structure of the nucleotide adenosine triphosphate (ATP). (c) Structure of NAD or nicotinamide adenine dinucleotide (when the radical labelled R is H) and NADP or nicotinamide adenine dinucleotide phosphate (when R is phosphate).

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Figure 14.11. 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 is 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 (e.g., tendons) 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 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 14.12). The nucleotides adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADP), illustrated in Figure 14.11, 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.

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 14.7b) 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.

Lipids

Unlike carbohydrates and proteins, *lipids* are defined not by their composition and structure, but by their behavior: lipids are those 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 14.13). 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.

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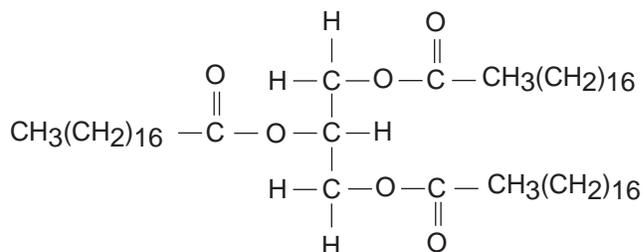


Figure 14.13. A triglyceride fat formed from the alcohol glycerol and three molecules of stearic acid.

cause 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 14.14).

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 or acyclic, saturated or unsaturated. 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 are derivatives of *phytol*, a diterpenoid that forms part of chlorophyll-a, a key compound in photosynthesis. During diagenesis, phytol is converted to *phytane* (Figure 14.14c and 14.14d) through the loss of

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 be-

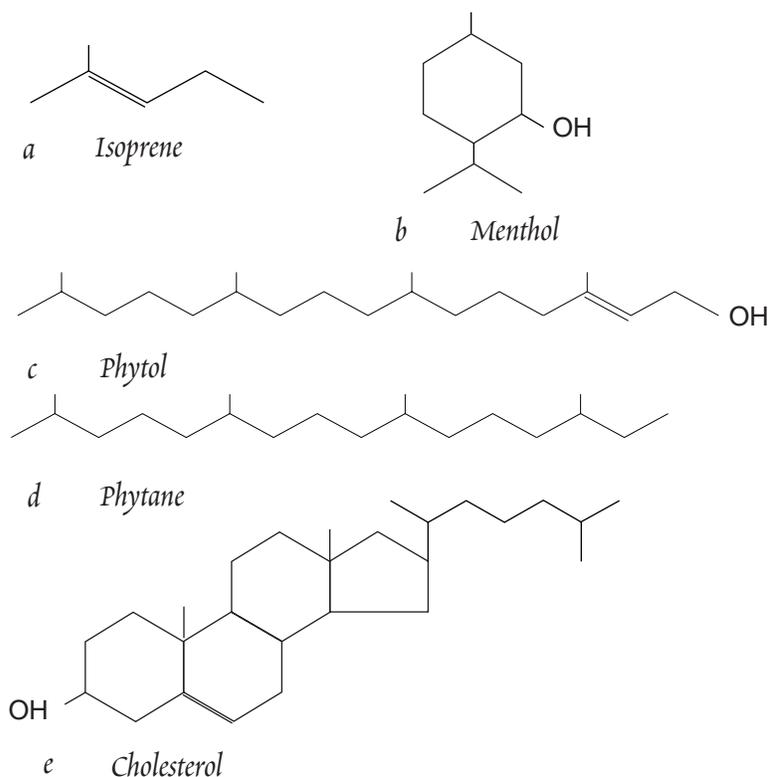


Figure 14.14. Terpenoids. a. Isoprene, the building block of all terpenoids. b. Menthol, a simple cyclic monoterpene. c. Phytol, an acyclic diterpenene. d. Phytane, an acyclic diterpenane derived from phytol. e., Cholesterol, illustrating the ring system shared by all steroids. The carbon atoms at the apices of the phenols and the hydrogens bound to them are not shown.

* *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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the OH functional group and hydrogenization (loss of the C-double bond). Another important isoprenoid is squalene, a triterpenoid (C₃₀H₅₀). 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* 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. A few terpenoids are illustrated in Figure 14.14.

Like proteins, lipids play a variety of roles in life. Phospholipids are the primary constituents of cell membranes. Fats and oils serve to store energy. Lipids include pigments that are essential in photosynthesis in plants (e.g., chlorophyll) and vitamin A production in mammals (e.g., carotenoids). Other lipids form protective barriers (e.g., cutin), 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*.

LIGNIN AND TANNINS

Lignin is another important structural material in higher plants. 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, which do not produce lignin, lignin is a much less important contributor to marine organic carbon.

Tannins 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.

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 H₂S or other reduced species, to synthesize organic compounds in a process called chemosynthesis.

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 be 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

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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 oxygen, 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. 14.15), 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 are strongly absorb light in the red and blue parts of the visible spectrum (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 14.16) 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 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

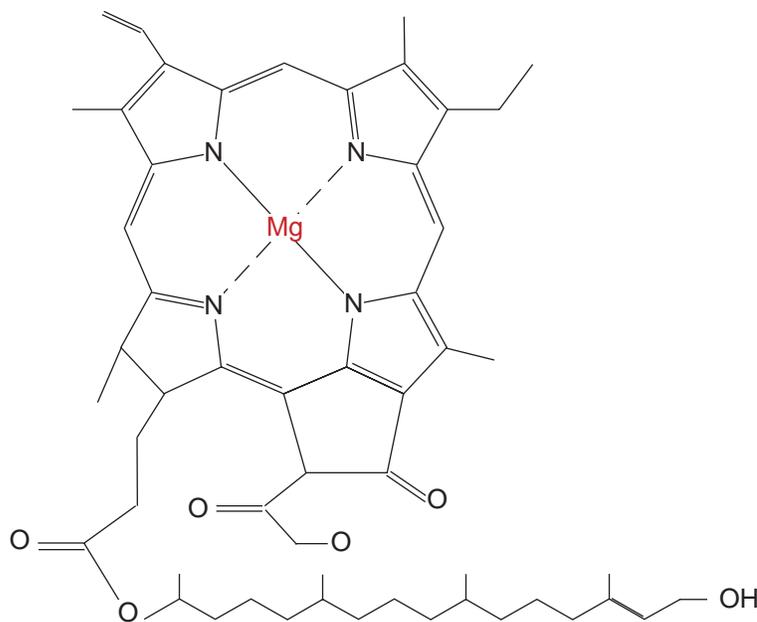


Figure 14.15. Structure of chlorophyll-a. The linear chain is a phytol unit.

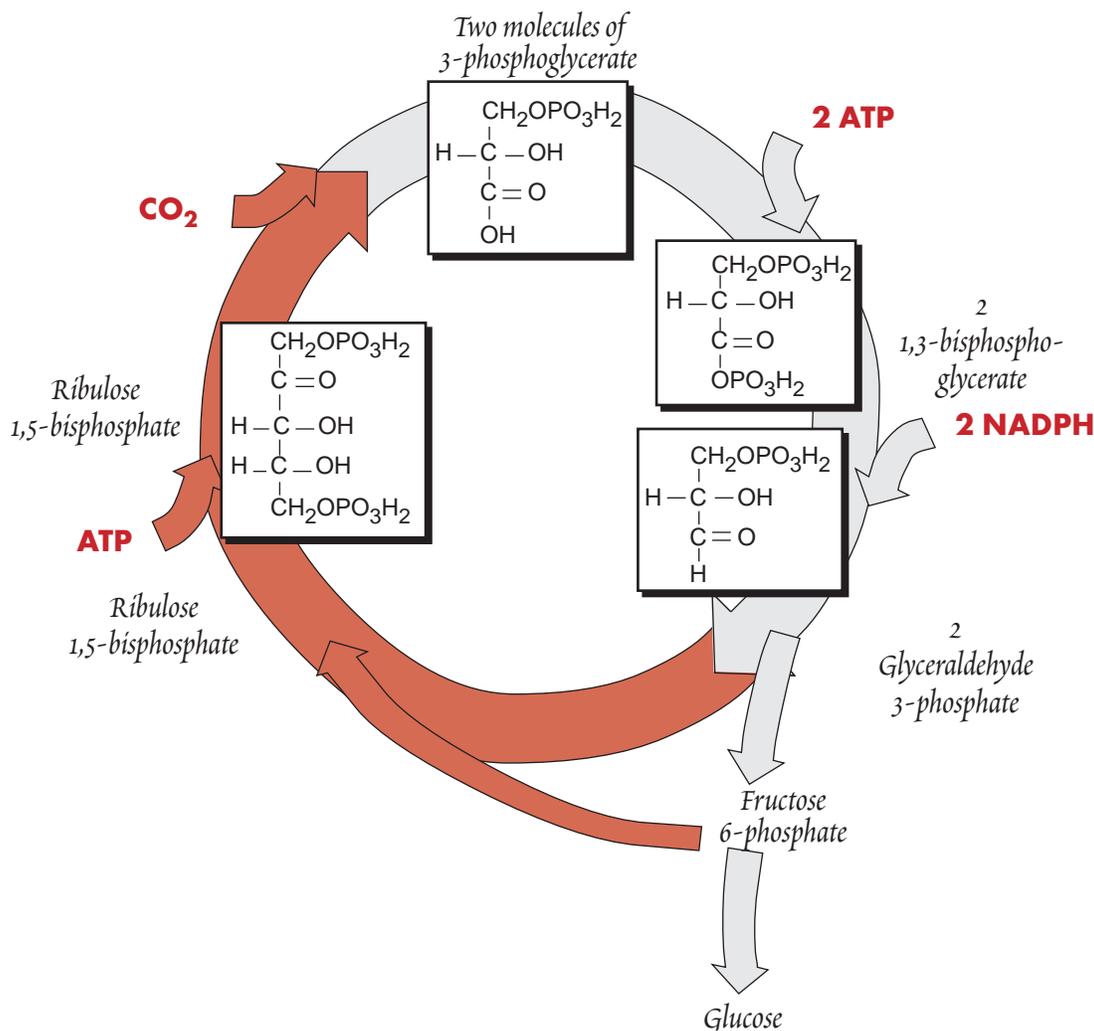


Figure 14.16. The Calvin cycle of dark reactions for the production of glucose in C_3 plants.

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. 14.17). 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 con-

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centrations 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‰, where as 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. Though they require reduced species for energy, chemosynthetic bacteria are aerobic. Thus they live at boundaries between oxic and anoxic conditions.

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 ($\text{CH}_3\text{COCO}_2\text{H}$) 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 process results in a net production of 2 ATP molecules per glucose molecule (and an additional energy gain of 80kJ/mole).

[‡] 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.

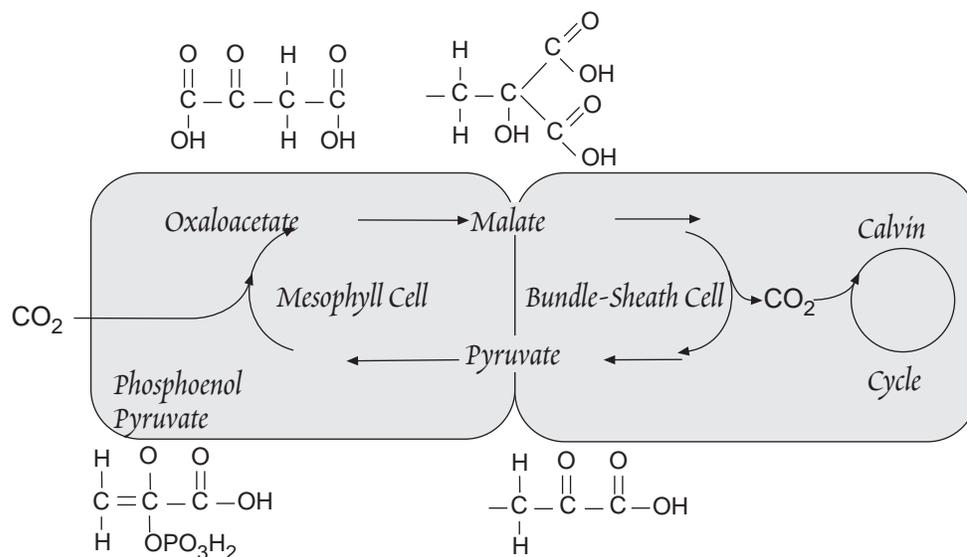


Figure 14.17. The Hatch-Slack photosynthetic cycle utilized by C_4 plants.

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Glycolysis does not release CO₂. 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 14.18), or alternatively the *Citric Acid Cycle* (in con-

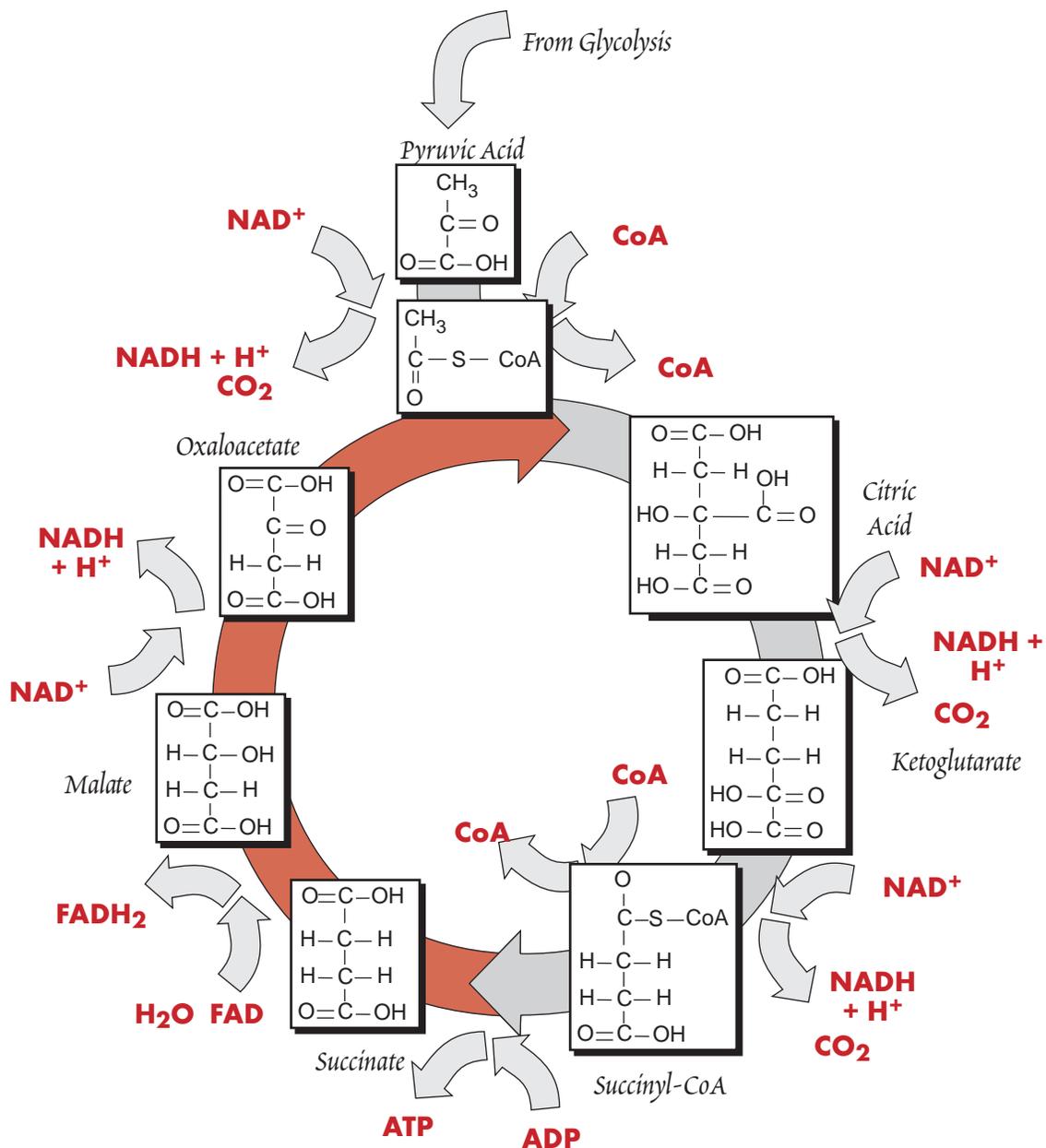


Figure 14.18. Illustration of the Krebs, or Citric Acid, Cycle, in which organic matter is oxidized by organisms to produce energy in the form of ATP. New pyruvate enters the cycle at the top, where one carbon removed from the structure. The remaining two carbons join with a four carbon oxaloacetate chain from a previous cycle to form citric acid, from which 2 additional carbons are successively stripped.

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trast, 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.

ORGANIC MATTER IN NATURAL WATERS AND SOILS

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 *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 0.45μ , corresponding to molecular weights greater than about 10,000. They may be specifically referred to as colloidal organic matter (COM). Figure 14.19 illustrates the range in concentrations of dissolved and particulate organic carbon. Groundwater and seawater typically have the lowest organic carbon concentrations, while wet-

*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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land 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; though the concentration is generally less 1 mg/l or less, 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 organisms 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 most natural waters, as Figure 14.20 illustrates.

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

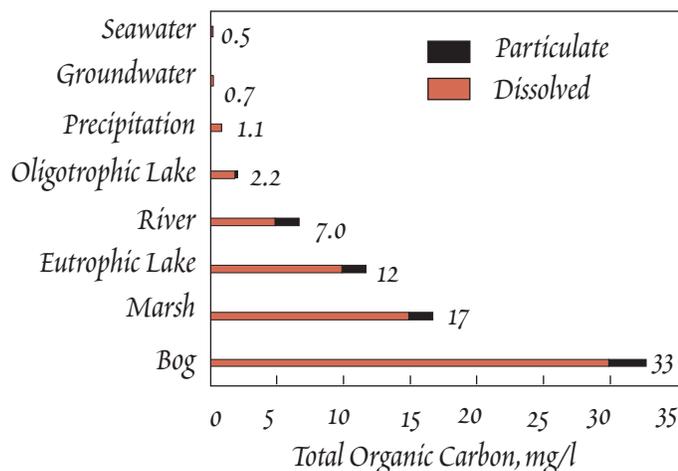


Figure 14.19. Average concentration of dissolved, particulate, and total organic carbon in various natural waters. From Thurman (1985).

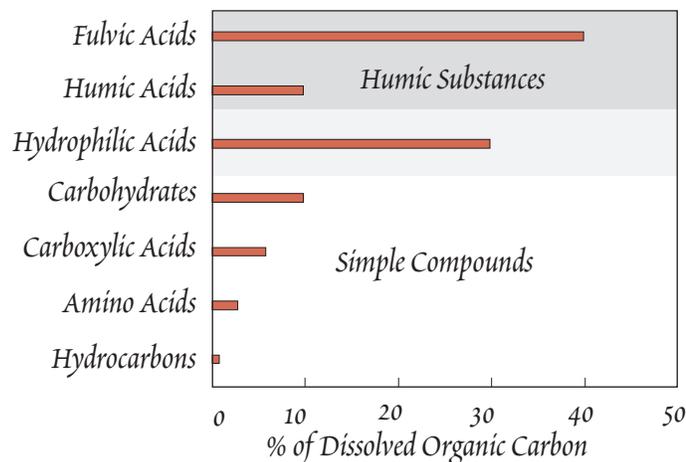


Figure 14.20. Components of dissolved organic carbon in typical river water. After Thurman (1985).

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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 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 14.1

TABLE 14.1. 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).

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 14.21 summarizes the concentrations of carbohydrates in various natural waters. As this Figure shows, polysaccharides are the most abundant carbohydrates, fol-

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lowed 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 $\mu\text{g}/\text{l}$ 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, i.e., pollutants, will be dealt with in a subsequent chapter.

Of the volatile hydrocarbons, methane is by far the most abundant. Some methane can be produced 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 14.2. The solubility of methane in water is 800 $\mu\text{g}/\text{l}$ (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 (pentadecane 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 phytoplank-

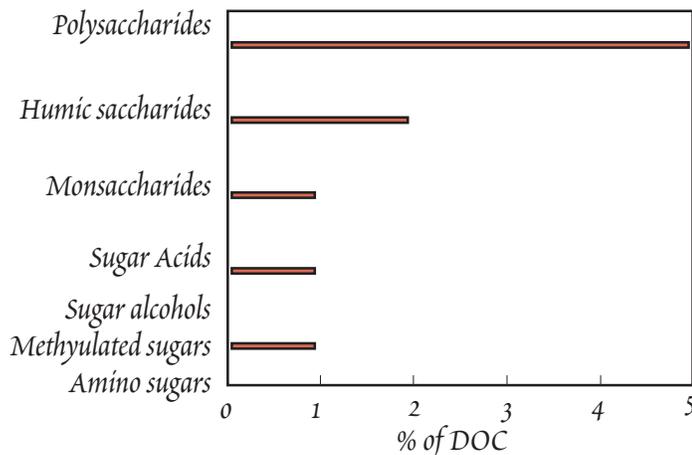


Figure 14.21. Abundances of dissolved carbohydrates in seawater as a percentage of total dissolved organic carbon. After Thurman (1985).

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ton. 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.

HUMIC SUBSTANCES

Humic substances are high molecular weight (> 500 daltons) 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. Although their molecular structures remain poorly known, the chemical composition and functional groups of humic substances are well characterized. The most important of these are carboxyl, 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.

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.

The concentration ranges of humic substances are given in Table 14.3. 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 14.4 compares the compositions of humic and fulvic acids from several envi-

TABLE 14.2. 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).

TABLE 14.3. 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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ronments. Humic acid is usually richer in carbon and poorer in oxygen than fulvic acid; it is also on average poorer in hydrogen and richer in nitrogen. 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 daltons) than humic acid (>2000 daltons). In addition, fulvic acid has a higher content of carboxyl acid groups than does hu-

mic acid, while humic acid is richer in phenolic groups (Table 14.5). 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 only in trace 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 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 14.22 illustrates one proposed hypothetical structure of aquatic fulvic acid. This molecule has a molecular weight of about 1000 daltons. Marine humic acids appear to have even a smaller proportion of aromatic carbon, and marine fulvic acids have essentially none. Since aromatic structures are far more common in terrestrial plants than

Table 14.4. 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 14.5 Functional Groups in Dissolved Fulvic and Humic Acids

| | Carboxyl | 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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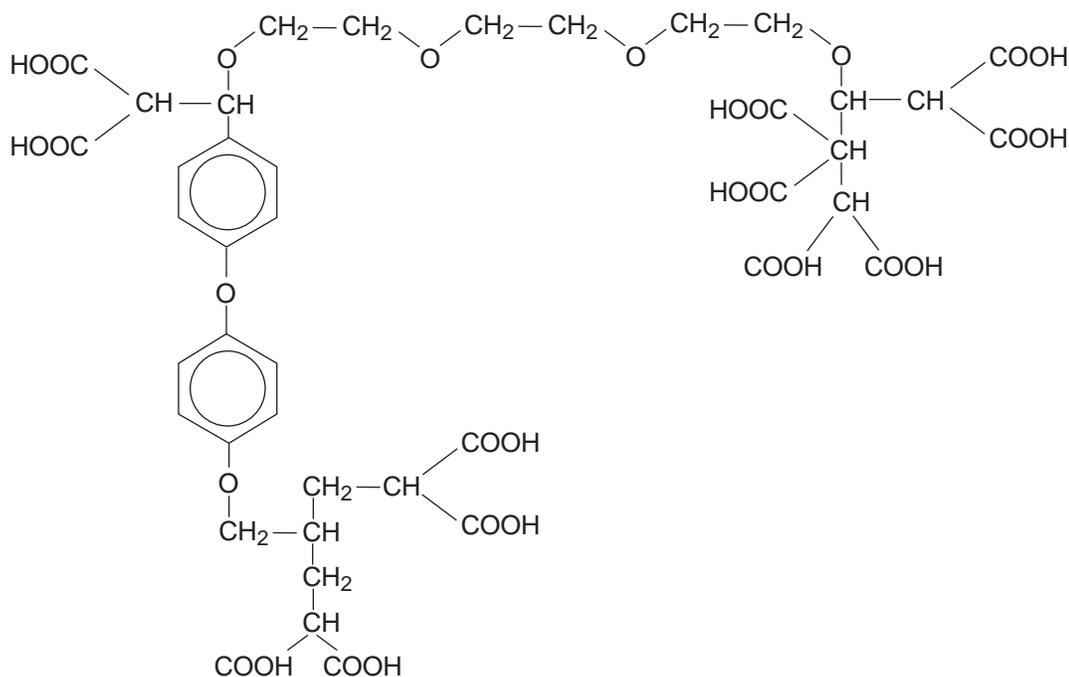


Figure 14.22. Hypothetical structure of aquatic fulvic acid. After Bergmann (1978).

marine ones, this is not surprising.

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 alkalenes, 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 consistent 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-prod-

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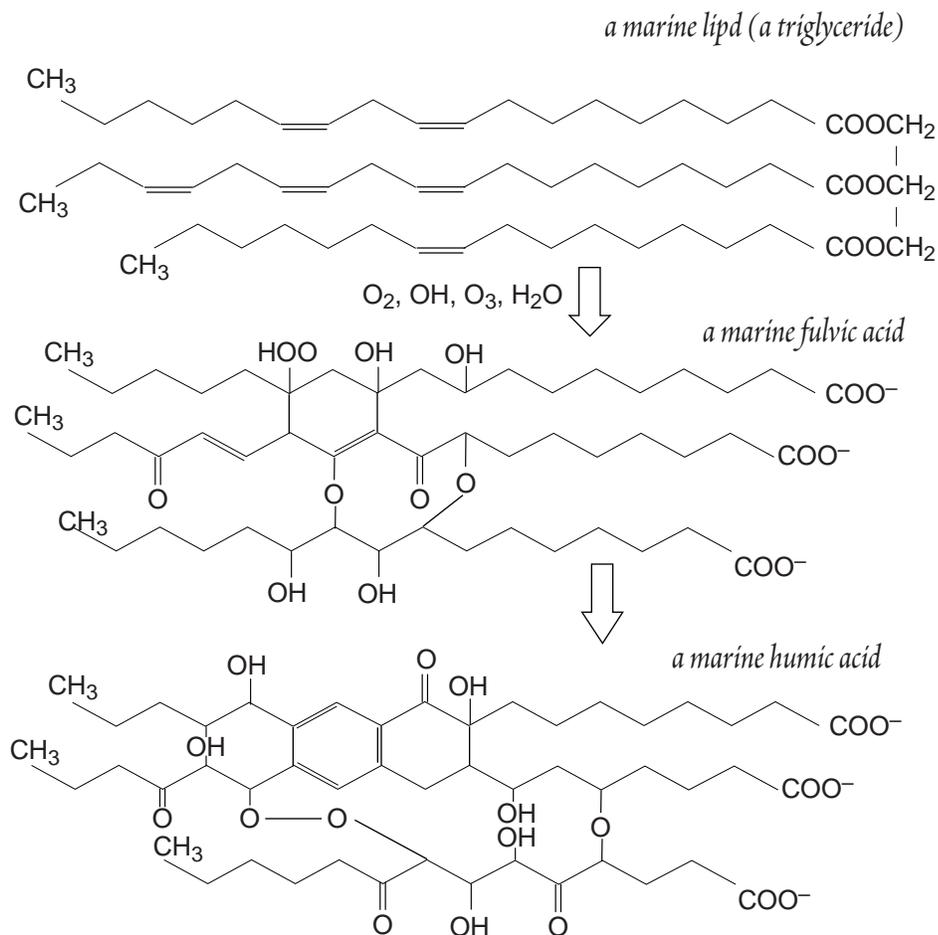


Figure 14.23. Possible mechanism for generation of marine fulvic and humic acids from triglycerides. After Harvey and Boran (1985).

ucts 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, 1993).

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 14.23 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 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.

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), as we saw in Chapter 13. 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

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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 the most important of the exudates are simple carboxylic acids such as acetic and oxalic acid (Fig. 14.6), formic acid (HCOOH), tartaric acid (2,3,-dihydroxybutanedioic acid: COOH(CH(OH))₂COOH) 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, though, as we found in Chapter 13, 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 can 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 *humic acid* 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 appears greater in soils than in water. As is summarized in Table 14.6, 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 <2×10³, while the molecular weight of soil humic acids can exceed 10⁶.

Based on these compositions, the approximate chemical formula for average humic acid is C₁₈₇H₁₈₉O₈₉N₉S and that of fulvic acid is C₆₈H₉₁O₄₈N₃S. Compared to the composition of living organisms, humic and fulvic acid 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. Humin, the insoluble organic matter in soil, tends to be even

Table 14.6. Composition of Soil Humic and Fulvic Acids

| Elemental Comp. | Humic Acid | | Fulvic Acid | |
|----------------------------|------------|----------|-------------|-----------|
| | Mean | Range | Mean | Range |
| | 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 |
| | meq/g | | | |
| Functional Groups | | | | |
| Total Acidic Groups | 5.6-8.9 | | 6.4-14.2 | |
| 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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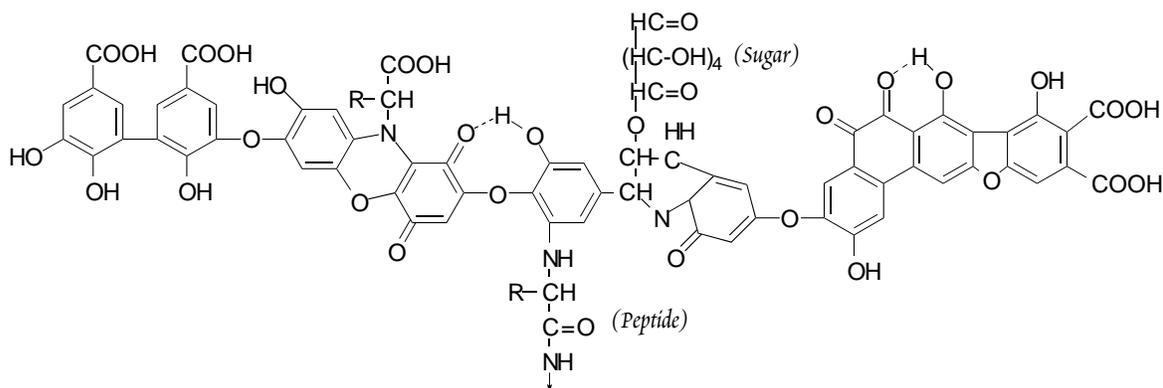


Figure 14.24. Possible structure of soil humic acid. After Stevenson (1982).

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 14.24.

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, the carboxylate is oxidized by bacteria, and the Fe and Al precipitate as hydroxides. We examine metal-organic complexation further in the following section.

CHEMICAL PROPERTIES OF ORGANIC MOLECULES

Acid-Base Properties

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



(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:

$$K_a = \frac{a_{\text{H}^+} a_{\text{RCOO}^-}}{a_{\text{RCOOH}}} \quad 14.3$$

The equilibrium constant is commonly reported as $\text{p}K_a$, which, analogous to pH, is the negative of the logarithm of the equilibrium constant. The Henderson-Hasselback equation relates $\text{p}K_a$, activity quotient, and pH:

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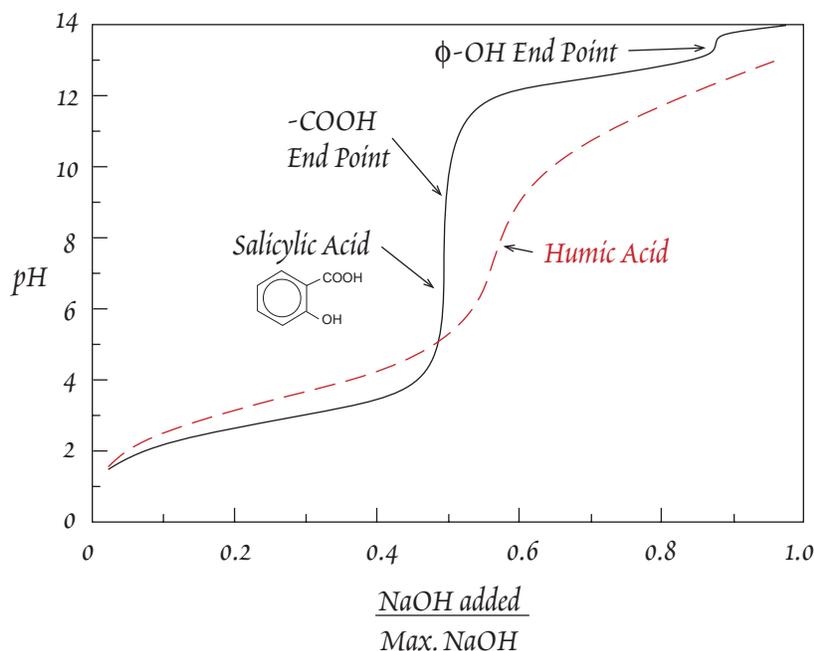
$$\text{pK}_a = -\log K_a = -\frac{a_{\text{RCOO}^-}}{a_{\text{RCOOH}}} - \text{pH} \quad 14.4$$

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 have the strongest basicity, 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 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 titration curves (Figure 14.25) typically have a "smeared out" appearance, a result both of the variety of functional groups present, and electrostatic interactions between these groups.



COMPLEXATION

Another important geochemical property of organic molecules is their ability to form complexes with metals,

Figure 14.25. 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 . From Morel (1983).

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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, $(\text{COO})_2^{2-}$, which consists of 2 carboxyl groups (Figure 14.7) 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 14.26), 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 14.26). Salicylate is another example of a bidentate ion (Figure 14.27a). 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.

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 14.27b. These Fe specific chelators may have stability constants in excess of 10^{30} , so they are indeed very strong chelators. However, they are at sufficiently low concentration that they usually do not play a significant role in trace metal chemistry. However, they may do so in special circumstances such as plankton blooms. It is also possible for a single metal ion to bind to more than one organic ligand, as illustrated in Figure 14.27c.

Just as for inorganic metal-ligand complexes, we can define stability constants (β) and apparent stability constants (β^*) for metal-organic ligand complexes. Table 14.7 lists some examples of stability constants for metal-organic complexes that we might expect to find in natural waters. Several generalizations may be made. First, as we saw for inorganic lig-

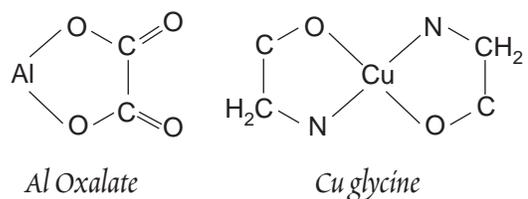


Figure 14.26. Examples of rings formed by chelates.

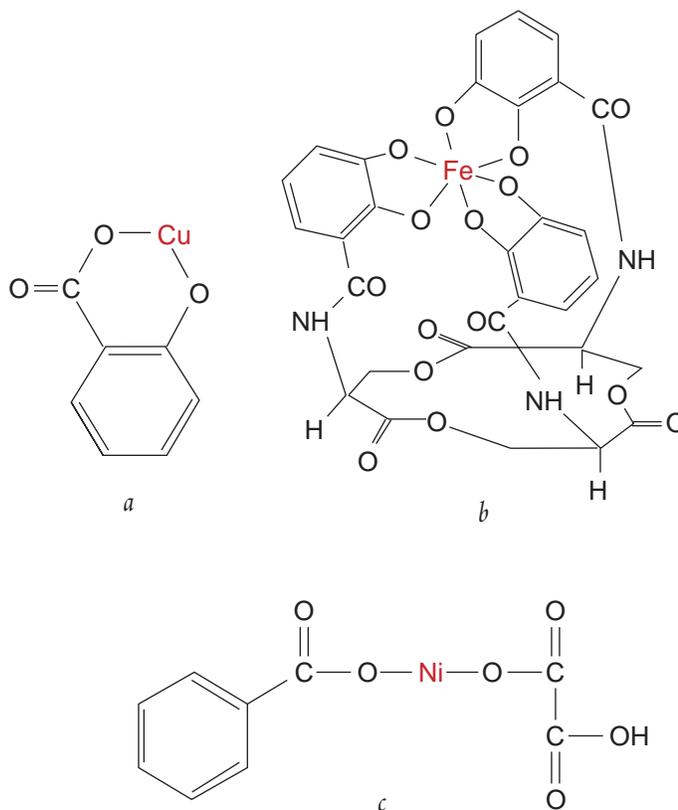


Figure 14.27. a. Copper salicylate complex. The Cu ion is bound to both the carboxylic and phenol groups. b. Enterobactin, a natural iron chelating agent. c. Ni complexed by separate benzoate and acetate groups.

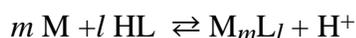
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ands, the higher valence state of the metal, the stronger the complex. Thus in Table 14.7, Fe^{3+} forms stronger complexes with all listed ligands than does Fe^{2+} . Second, there is high degree of correlation between the equilibrium constants of all organic ligands for a given metal. For the divalent metals, stability of metal-organic complexes follows the Irving-Williams series (Chapter 6), $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+}$.

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. 14.15).

Multidentate complexes are generally more stable than corresponding unidentate ones. We can see this in Table 14.7, where the stability constants for citrate, with 3 carboxyl binding sites are higher than those for acetate, with one carboxyl binding site. Another interesting property of multidentate ligands is that the degree of complexation decreases less strongly with dilution than from monodentate complexes.

As was the case for inorganic complexes, the stability of metal-organic complexes are 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:

$$K = \frac{[\text{M}_m\text{L}_l][a_{\text{H}^+}]}{[\text{M}]^m[\text{HL}]^l} \quad 14.5$$

or in log form: $\log K = \log [\text{M}_m\text{L}_l] - m \log [\text{M}] - l \log [\text{HL}] - \text{pH} \quad 14.6$

Table 14.7. Log 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 | | | 14.2 |
| 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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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 dominate 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 14.7. Nevertheless, as these examples show, these mixed complexes must often be considered in speciation calculations, particularly at high and low pH. A more complete compilation of stability constants for metal-organic complexes may be found in Morel and Hering (1993).

Humic and fulvic acids are, as we have seen, usually the most abundant dissolved organic compounds. The functional groups on these substances are capable of 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 14.7, we would expect humic substances to strongly complex trace metals. This appears to be the case, although the situation is somewhat complicated be-

EXAMPLE 14.1. SPECIATION OF ORGANIC LIGANDS IN FRESH WATER

Using the stability constants in Table 14.7, and the calculated free ion activities for major cations in Example 6.7, 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:

$$\Sigma L = L^- + HL + AL + BL + CL + \dots \quad 14.7$$

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

$$[ML] = \beta \times [M] \times [L^-] \quad 14.8$$

where [ML], [M], and $[L^-]$ are the concentrations of the complex, free metal ion or proton, and free ligand respectively. Substituting 14.8 into 14.7, we have:

$$\Sigma L = [L^-] + \beta_{HL} [H] [L^-] + \beta_{AL} [A] [L^-] + \beta_{BL} [B] [L^-] + \dots \quad 14.9$$

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 14.10 gives us the free ion concentration. From that, we can calculate the concentration of each of the complexes using 14.8. 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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cause 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 modelling 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 has been much debated. There is a fair body of experimental evidence to support the idea that a large fraction of at least some trace metals (e.g., Cu, Zn, Pb) in natural waters is complexed by organic compounds. This evidence consists of bioassay and electrochemical measurements that show the “reactive” concentrations (i.e., free ion) are well below total concentrations (e.g., Hering et al., 1983; Donat and Bruland, 1990). While conceding that organic ligands do indeed have a strong preference for some metals, particularly transition metals, others have argued on more theoretical grounds that in most natural waters, organic ligands complex only a small fraction of these trace metals (e.g., Nürnberg and Valenta, 1983). This argument is based on the following observations. First, concentrations of dissolved organic ligands are generally quite low. Second, the organic ligands that are present will be almost entirely complexed by the major metal ions (e.g., Ca^{2+} , Mg^{2+}) and H^+ (Example 14.1). While these complexes have lower stability constants, these ions are much more abundant. Third, trace metals will be largely complexed by the more abundant inorganic ligands. Again, while these complexes are less stable, this is more than compensated for by the much greater abundance of inorganic ligands. However, even proponents of this view concede that in certain circumstances, such as estuaries, organic-rich tropical rivers and areas of high productivity in the oceans, where water has high natural DOC concentrations or waters polluted by strong chelators such as EDTA, some trace metals will be almost completely complexed by organic ligands. In other areas, it is possible that the difference between these perspectives reflects the presence of very strong complexing agents known as siderophores, such as trihydroxamate siderophore desferrioxamine B, that are produced by organisms to (1) acquire essential trace metals, such as Fe and Zn, and (2) defend themselves against the toxicity of others, such as Cu and Pb. The distribution of these substances, which can have stability constants in excess of 10^{30} , remains poorly known.

Example 14.2 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 14.1), and therefore unavailable to bind Cu, and 95% of the citrate is complexed with Ca and Mg. Second, the greater abundance of inorganic anions such as hydroxyl and carbonate results in their dominating the speciation of Cu. However, one should avoid 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 humates, are often present a sufficient concentration to complex a significant fraction of some trace metals. Problem 14.5 and 14.6 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 present on a single molecule, each of which will have a different intrinsic stability constant and pK_a . Second, these functional groups are close enough to one and other that the electrostatic charge one site

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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 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).

EXAMPLE 14.2. SPECIATION OF CU IN FRESH WATER

Use the adjacent stability constants as well as those for glycine, citrate, and salicylate in Table 14.7 to calculate the speciation of Cu in the water sample analysis in Example 6.7, assuming $\Sigma\text{Cu} = 10^{-9}$ M. Use the calculated free ion concentrations of anions in Examples 6.7 and 14.1.

Answer: In calculating trace element speciation, it is common to assume that complexation with trace metals does not reduce the free ion concentrations of the anions. For this assumption to be valid, the free ion concentrations of the anions should greatly exceed 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 14.1; that is we write a conservation equation for copper:

$$\Sigma\text{Cu} = [\text{Cu}^{2+}] + [\text{CuOH}^+] + [\text{Cu}(\text{OH})_2] + [\text{CuCl}^+] + [\text{CuCO}_3] + [\text{CuSO}_4] + [\text{CuGly}] + [\text{CuCit}] + [\text{CuSal}] \quad 14.11$$

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

$$\text{CuCit} = \beta_{\text{CuCit}} \times [\text{Cu}^{2+}] \times [\text{Cit}] \quad 14.12$$

Substituting the mass action equations into 14.11 and solving for $[\text{Cu}^{2+}]$, we have:

$$[\text{Cu}^{2+}] = \frac{\Sigma\text{Cu}}{1 + \sum_i \beta_{\text{CuL}_i} [\text{L}_i]} \quad 14.13$$

We can then calculate the concentrations of the individual species using 14.12. 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 6.7. However, an examination of the situation reveals a

CALCULATED COPPER SPECIATION

| | Conc | % |
|--------------------------|------------------------|--------|
| CuOH^+ | 2.12×10^{-10} | 21.22% |
| $\text{Cu}(\text{OH})_2$ | 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% |

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.

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ADSORPTION PHENOMENA

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 14.28). 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 adsorbed onto nonpolar surfaces, such as those of organic solids.

Hydrophobic adsorption differs from other types of adsorption phenomena in that adsorption occurs not a result of an affinity of the surface for the solute, but because 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:

$$K_p = \frac{\text{moles sorbate/mass solid}}{\text{moles solute/volume solution}} \quad 14.14$$

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 14.29a: 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. 14.29b). Octanol is a largely nonpolar molecule, so that there is little structure or ordering of molecules in liquid octanol as there is in water. Thus there is no disruption of solvent molecules when a nonpolar solute is dissolved in octanol. The octanol/water partition coefficient is thus a measure of the "hydrophobicity" of organic molecules. The adsorption coefficient for hydrophobic substances on organic substrates may be empirically estimated by the following relationship:

$$K_{\text{om}} = b (K_{\text{O/W}})^a \quad 14.15$$

where K_{om} is the partition coefficient between organic solids and water, $K_{\text{O/W}}$ 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:

$$K_p = b f_{\text{OC}} (K_{\text{O/W}})^a \quad 14.16$$

where f_{oc} is the fraction of organic matter in the solid. Comparing 14.15 and 14.16, we see that

$$K_{\text{om}} = K_p / f_{\text{OC}} \quad 14.17$$

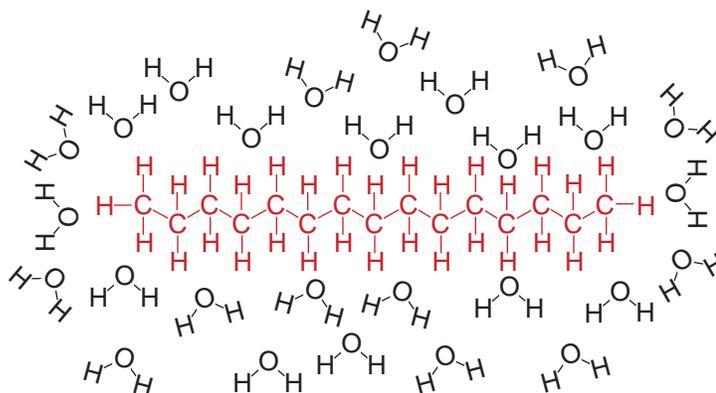


Figure 14.28. Disruption of water molecules by a large nonpolar organic molecule, in this case a C_{15} n-alkane.

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In general, the solubility of organic molecules decreases with increasing molecular weight. This observation, known as *Traube's Rule*, is apparent from Figure 14.29. 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 adsorbed and the strength of this adsorption increases with atomic weight. In part, this is true for the same reason solubility decreases: a greater volume of water is disrupted by large molecules. However, as we noted above, van der Waals interactions between the adsorbed substance and the surface also contribute to hydrophobic adsorption. These interactions increase with increasing size of the molecule. Van der Waals interactions contribute a surface binding energy of roughly 2.5 kJ/mol per CH_2 group on the surface. Clearly, the more CH_2 groups involved, the more strongly the substance will be bound to the surface. For this reason, polymers are readily adsorbed to surfaces even if the adsorption free energy per segment is small. Adsorption of large polymers can be virtually irreversible.

Hydrophobic molecules are adsorbed preferentially to organic surfaces, which are largely nonpolar, rather than inorganic ones. Thus the degree to which hydrophobic substances are absorbed will depend of the fraction of organic matter that makes up solid surfaces. This is illustrated in Figure 14.30.

OTHER ADSORPTION MECHANISMS

Many naturally occurring organic molecules contain both a polar and a non-polar part. Such molecules are called *amphipathic*. 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 acid and acetic acid) 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*:

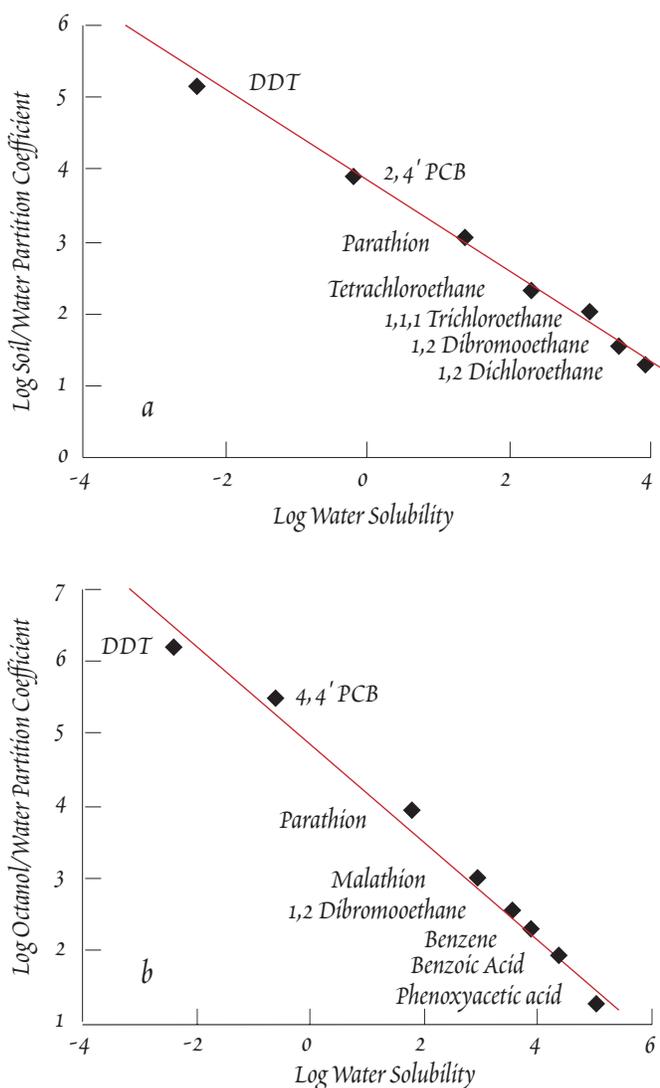


Figure 14.29. (a) Soil/water adsorption partition coefficients for a variety of organic compounds as a function of water solubility determined by Chiou et al. (1979). (b) Octanol/water partition coefficients as a function of water solubility of organic compounds determined by Chiou et al. (1979).

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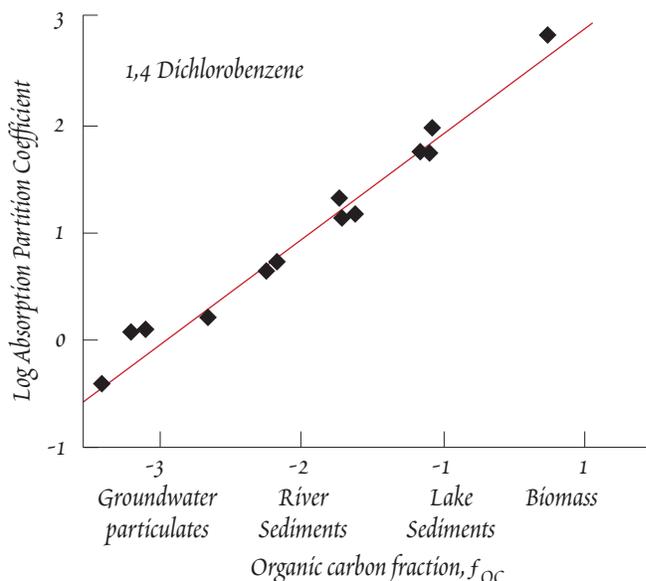


Figure 14.30. Adsorption partition coefficient for 1,4 dichlorobenzene plotted as a function of fraction of organic carbon in the solid absorbent. Other hydrophobic molecules show similar relationships. After Schwarzenbach and Westall (1980).

where an organic cation replaces a metal cation at a surface. For anionic functional groups, such as carboxylic acids, anion ion exchange can occur. This is the analogy of reaction 14.18 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:

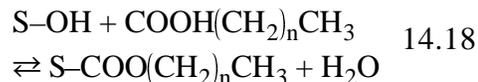


Hydrogen bonding is not restricted to acids. Organic bases, notably those containing nitrogen groups such as amines and pyridines, can also form hydrogen bonds with a hydrogen at a solid surface. Hydrogen bonding between dissolved organics and mineral surfaces is less important because the oxygens of mineral surfaces are not as electronegative as in organic compounds.

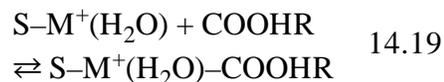
Many organic compounds will thus be subject to several types of adsorption: non-polar parts may be adsorbed to surfaces through hydrophobic bonding, while polar groups may bind through the mechanisms just described.

DEPENDENCE ON pH

Figure 14.31 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.



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 quaternized nitrogen, *cation ion exchange* reactions such as:



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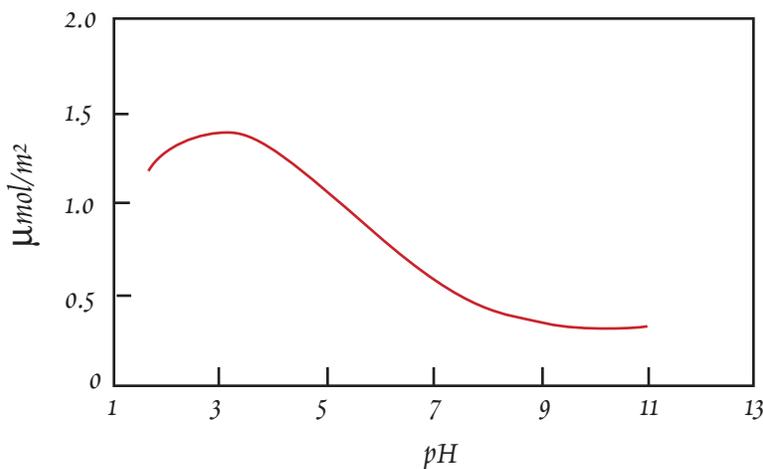


Figure 14.31. Adsorption of humic acid on δ - Al_2O_3 as a function of pH. After Stumm (1992).

the bond formed between adsorbent and adsorbate will be influenced by pH.

ROLE IN WEATHERING

In previous chapters we saw that 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, and (3) lowering the pH of solution (Drever and Vance, 1994; Bennett and Casey, 1994). In addition, organic substances serve as electron donors in the reductive dissolution of Fe and Mn oxides and hydroxides. These effects have been demonstrated in a variety of laboratory experiments (e.g., Furrer and Stumm, 1986; Zinder et al., 1986) and electron microscopy of minerals exposed to high concentrations of organic acids in both natural and laboratory situations (e.g., Bennett and Casey, 1994).

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

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

where $[\text{S}=\text{L}]$ 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

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

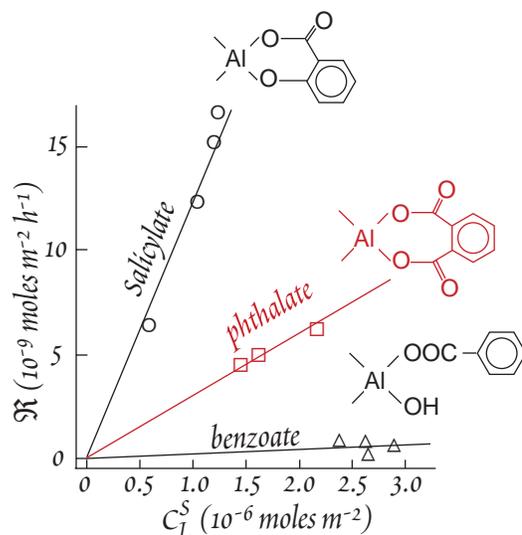


Figure 14.32. Rate of ligand-promoted dissolution of δ - Al_2O_3 as a function of surface concentration of organic ligands. Chelates forming five and six-member rings, such as those formed by salicylate, produced faster dissolution rates than 7-member rings, such as those formed by phthalate. Unidentate ligands, such as benzoate, have only a small effect on dissolution rate. From Furrer and Stumm (1986).

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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 14.32). 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. 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.

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 by respiration, a process called *rem mineralization*. Indeed, most of the organic carbon synthesized in a body of water 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 14.33.

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,

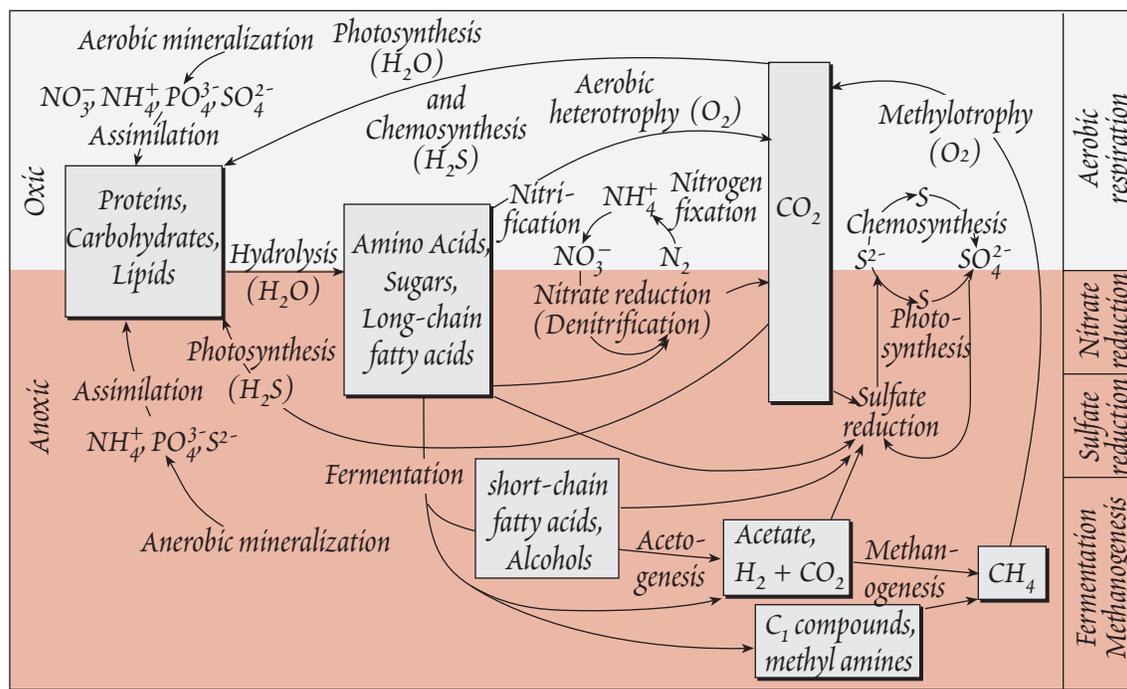


Figure 14.33. Role bacteria in the cycling of carbon, nitrogen, and sulfur between inorganic and various organic forms. After Killops and Killops (1993).

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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.

FORMATION AND DIAGENESIS OF ORGANIC-RICH SEDIMENTS*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 (we will discuss nutrient distribution and productivity in more detail in the following chapter). 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 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 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

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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. They also argue that extent of decomposition of marine organic matter is similar under oxic and anoxic conditions, though terrestrial organic matter to be degraded less by sulfate reducers. On the other hand, Killips and Killips (1993) point out 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.

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. 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 and as the organic matter is buried to progressively greater depth, it is attacked by a series of bacterial communities utilizing a progression of electron receptors (oxidants) at decreasing p_e . We can predict the order of the use of these oxidants from the ΔG of the redox reactions involved, shown in Table 14.8. Thus, moving downward in a column of accumulating sediment, we expect to see, following consumption of free oxygen, a series of zones where nitrate, Mn(IV), Fe(III), sulfate, and nitrogen reduction occur. Each of these zones will be colonized by a bacterial flora adapted for conditions in that zone[§]. Once all oxidants are consumed, respiration continues through fermentation.

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, macromolecules are broken down by consortia of bacteria. 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 CO₂. In the final step, these are converted to methane (CH₄) 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.

[§] 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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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). 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. 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. 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.

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

TABLE 14.8 FREE ENERGY CHANGES FOR BACTERIAL REACTIONS

| Reaction | ΔG (kJ/mol CH ₂ O) |
|---|---------------------------------------|
| $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_{2(\text{aq})} + \text{H}_2\text{O}$ | -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.

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

At present, the largest peat-forming environments are high-latitude (>45°) 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.

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, amigols, 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.

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- 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.

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). It is interesting that kerogen is by far the most abundant form of organic carbon on Earth; It is three orders of magnitude more abundance than coal, petroleum, and gas, and four orders of magnitude more abundant than the living biomass. Kerogen has the interesting and significant property that upon heating in the laboratory, a procedure known as *pyrolysis*, it breaks down to produce a variety of hydrocarbons similar to those found in natural petroleum. However, kerogen varies widely in its petroleum potential. Kerogen that is rich in aliphatic compounds, generally derived from aquatic and marine algae, has good petroleum potential and is called *sapropelic kerogen*. 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 appears to consist of nuclei cross-linked by chain bridges. The nuclei consist of stacks of two to four sheets of condensed aromatic rings, with roughly 10 rings per sheet, giving them a dimension of less than 10\AA . 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. It was once widely believed that kerogen, like humic substances, originated principally by condensation of low molecular weight biomolecules (amino acids, sugars, fatty acids, phenolics, etc.) produced by bacterial decomposition of more complex ones. In this view, humic substances are viewed as the precursors to kerogen. More recently, Tegelaar et al. (1989) proposed that the principal contributors to kerogen are highly resistant molecules (such as tannins, algaenans, etc.) that constitute only a

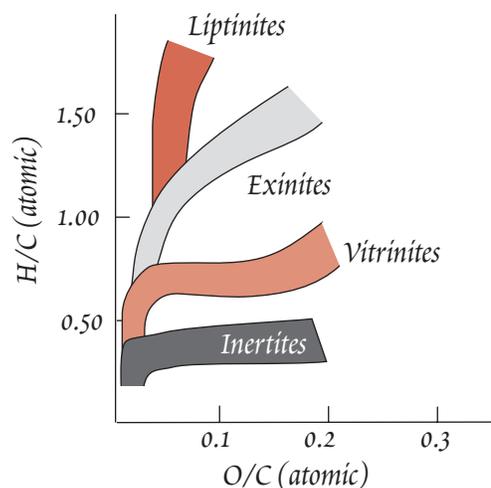


Figure 14.34. Compositional difference between kerogen maceral groups liptinite, exinite, vitrinite, and inertite. A plot of the H/C ratio vs. the O/C ratio such as this is commonly called a *van Krevelen diagram*. Modified from Tissot and Welte (1984).

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small proportion of the original organic matter. This hypothesis, known as *selective preservation*, has gained wide acceptance. The difference between these views, however, is not as great as it might initially seem, as it is widely agreed that even highly resistant molecules experience some bacterial alteration (e.g., defunctionalization, hydrogenization) and that some degree of recondensation is involved in kerogen formation.

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 Killips and Killips (1993) and divide them into four groups. These groups differ in both composition (Figure 14.34) 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 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.

KEROGEN CLASSIFICATION

Kerogen is usually classified into one of three types, based on bulk H/C and O/C ratios (Figure 14.35). *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 is derived primarily 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

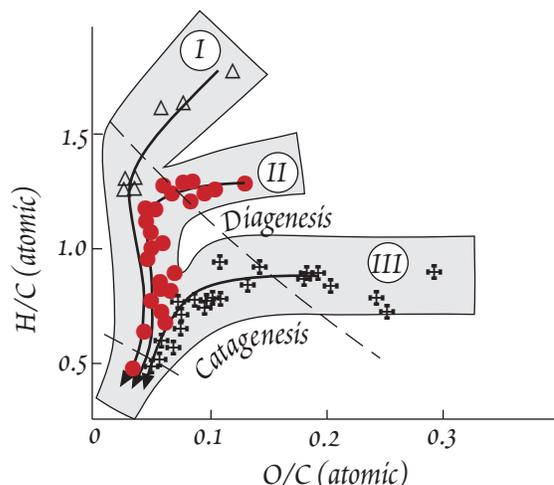


Figure 14.35. H/C and O/C ratios of the three types of Kerogen. Open triangles: Type I, closed red circles: Type II, crosses: Type III. Arrows show the direction of compositional evolution during diagenesis and subsequent thermal maturation (catagenesis and metagenesis). Dashed lines show boundaries between regions of diagenesis, catagenesis, and metagenesis. After Tissot and Welte (1984).

[†] 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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(<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 14.34 and 14.35 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 TypeII-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.

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 3 fractions: *asphaltenes*, *resins*, and *petroleum*. These fractionations are defined, like humic substances, by their solubility. *Maltenes* are soluble in light hydrocarbons such as hexane, whereas *asphaltenes* are not. *Maltenes* can further be separated into *petroleum*, which consists of a variety of hydrocarbons, and *resins*. *Resins* and *asphaltenes*, unlike hydrocarbons, are rich in heteroatoms such as N, S, and O. *Resins* tend to be somewhat richer in hydrogen (H/C atomic ~ 1.4) and poorer in N, S, and O (7-11 wt %) than *asphaltenes* (H/C atomic ~ 1.2, N, S, O ~ 8 - 12 %). Both have molecular weights greater than 500 and commonly several thousand. *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.

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.

THERMAL EVOLUTION OF ORGANIC MATTER AND PETROLEUM GENERATION

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 other bitumens, *asphaltenes* and *resins*. Collectively, this bitumen fraction is called *oil* or *crude oil* and is, of course, of great economic interest. At temperatures above 150-175° C, methane and graphite are the ultimate products, created in a process called *metagenesis*.

One of the principal effects of diagenesis is the condensation of 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. 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

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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 14.35.

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 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 14.36 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 thus those attached to the kerogen structure with heteroatoms or merely trapped within it. Thus the hydrocarbon fraction of bitumens in immature kerogen is dominated by "geochemical fossils" or biomarkers, i.e., molecules that have lost their functional groups but whose basic skeleton is preserved. A few examples include:

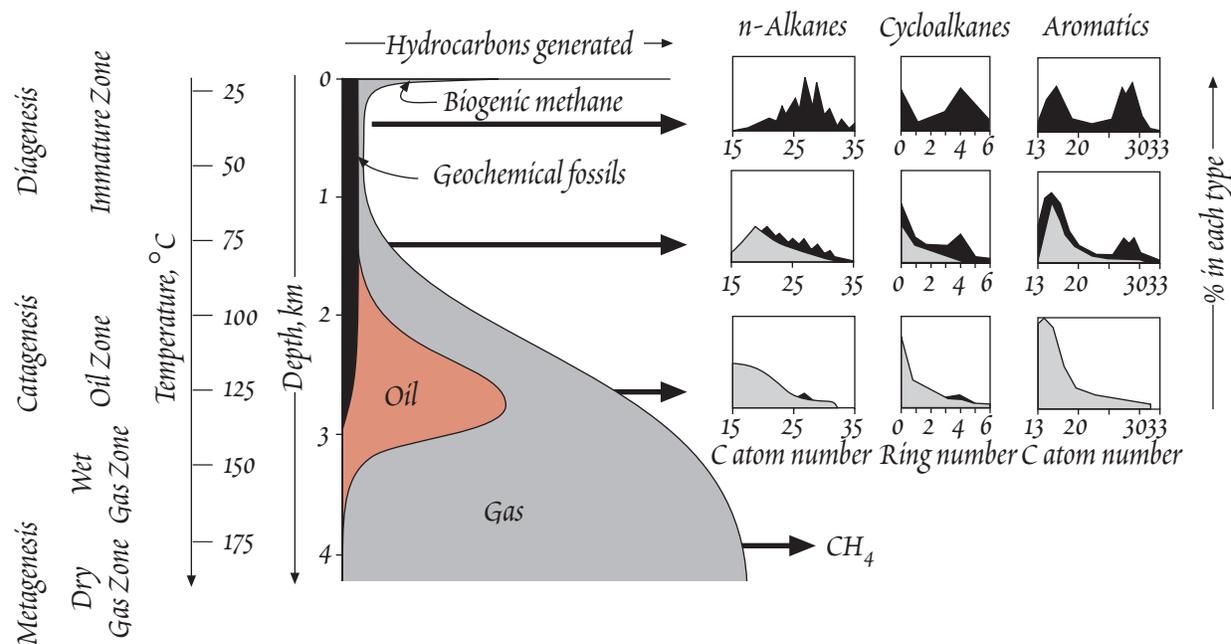


Figure 14.36. General scheme for hydrocarbon generation as a function of depth and temperature. Composition of the hydrocarbons generated is shown in the graphs to the right. Temperature and depth scales assume a geothermal gradient of 40° per km. After Tissot and Welte (1984).

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

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. Thus the hydrocarbons generated in the "oil window" of catagenesis show a maximum abundance at relatively low carbon number ($\sim C_{10}$) and steadily decreasing abundance with increasing carbon number.

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. 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. 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 14.36 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 such refractory kerogen is methane.

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. The mechanisms of migration of hydrocarbons are not fully understood, but probably involve both passage through microfractures and diffusion through the kerogen matrix. Migration will continue until the petroleum reaches either 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 a sandstone. Expulsion efficiencies vary

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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. 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, called *water washing*, will deplete the petroleum in these water-

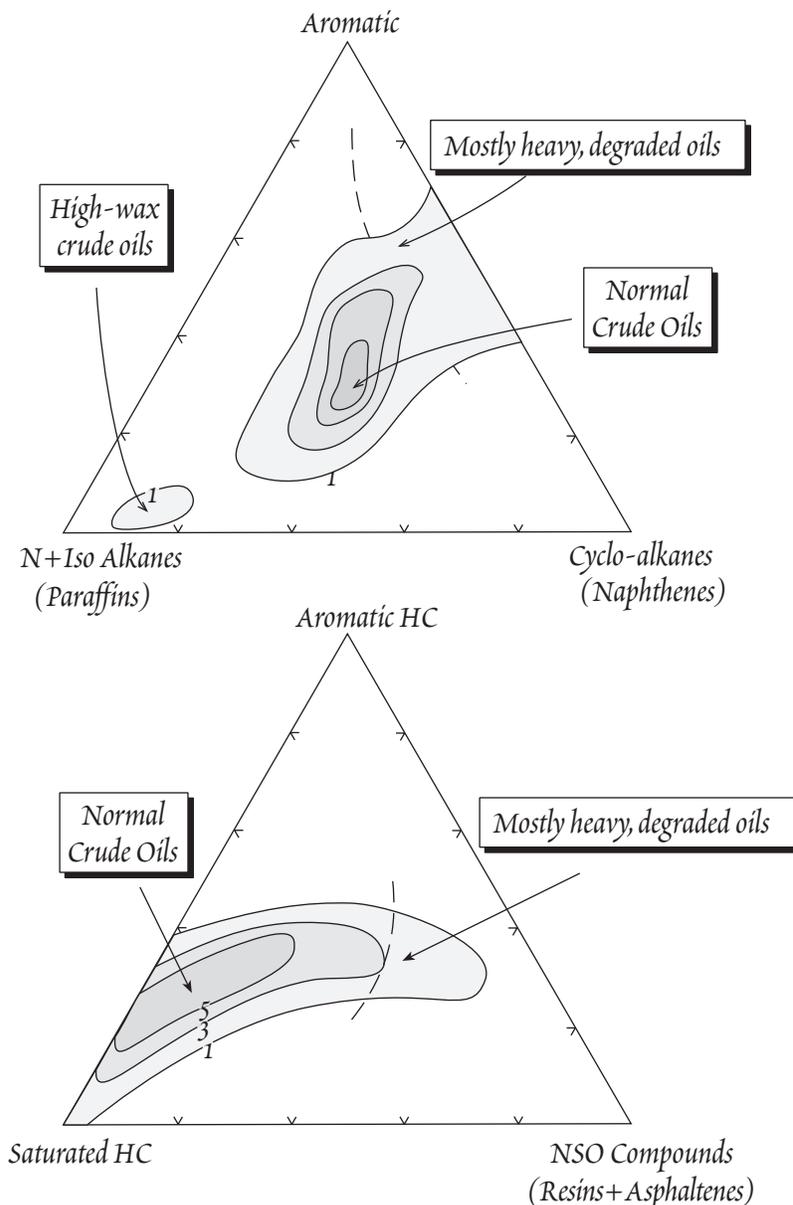


Figure 14.37. Ternary diagrams representing the composition of crude oils. (a) Isofrequency contours of hydrocarbons boiling above 210°C in 541 crude oils divided between aromatics, cyclic-, and n- and isoalkanes. (b) Isofrequency contours of saturated hydrocarbons, aromatic hydrocarbons, and NSO compounds (wt percent in the fraction boiling above 210°C) in 636 crude oils. From Tissot and Welte (1984).

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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.

COMPOSITION OF CRUDE OILS

Figure 14.37 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. The distribution of n-alkanes differs widely between various types of crudes as may be seen in Figure 14.38. Among cycloalkanes, those with 2 to 4 rings generally predominate. Alkylated compounds dominated 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% kerosine (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%.

COMPOSITIONAL EVOLUTION OF COAL

Coal, as we noted earlier, forms from organic-rich sediments typically deposited in swamps. Two types of coals are recognized: sapropelic and humic. Humic 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, that of sapropelic coals is exinite.

The evolution of coal, illustrated in Figure 14.39, 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 diagenesis, while the geochemical stage of coalification is comparable to catagenesis. During peatification, bacterial and fungal attack results in depolymerization and defunctionalization of the original biomolecules. 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 , CO_2 , H_2O) and condensation of the degradation products into humic substances. As in diagenesis, the concentrations

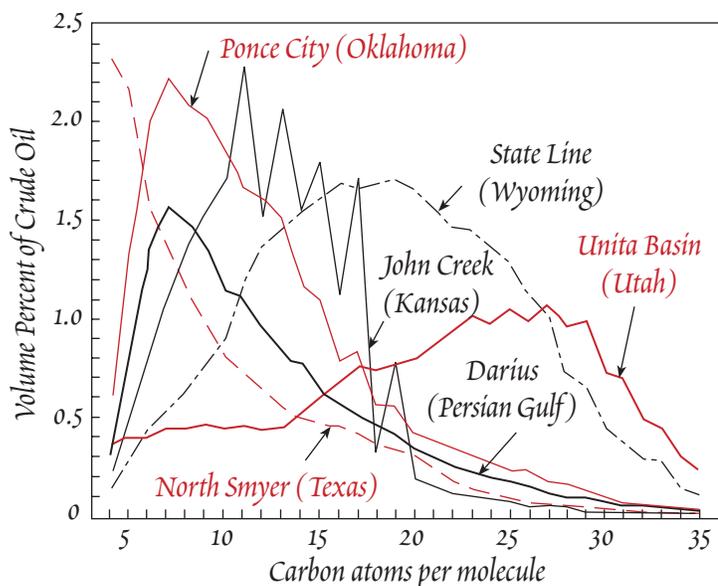


Figure 14.38. Distribution of n-alkanes in different crude oils. From Tissot and Welte (1984).

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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. 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 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 has decreased to 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.

ISOTOPE COMPOSITION OF HYDROCARBONS

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 frac-

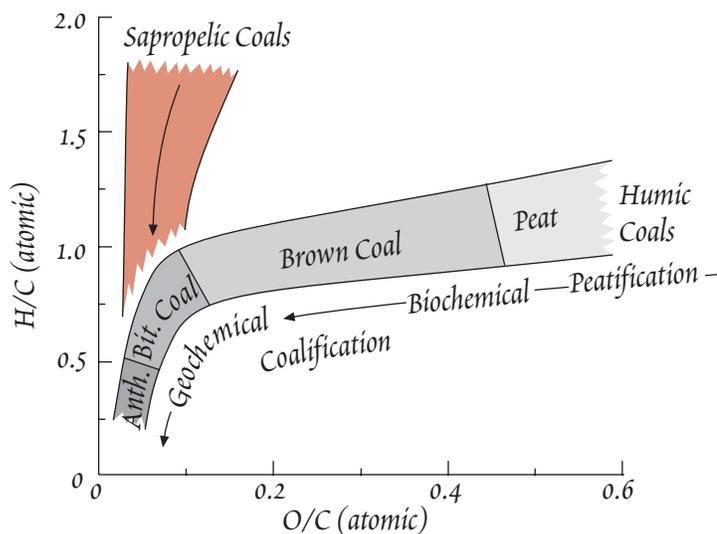


Figure 14.39. Chemical evolution of coals. After Killips and Killips (1993).

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tionation 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 δD_{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 $\delta^{15}N_{ATM}$ than marine plankton (Fogel and Cifuentes, 1993). $\delta^{15}N$ generally decreases somewhat during diagenesis due to bacterial utilization of short chain peptides following peptide bond hydrolysis (Macko, et al., 1993).

For the most part, isotopic fractionation of carbon during diagenesis of organic matter is small. As a result, the $\delta^{13}C$ of sedimentary organic matter is typically within a few permil of the $\delta^{13}C$ of the biomass 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 $\delta^{13}C$. 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 small. In immature kerogen, bitumens are depleted in $\delta^{13}C$ compared to kerogen, but this difference decreases with increasing maturity (Schoell, 1984). Sofer (1984) found that $\delta^{13}C$ of the oils are within 2‰ of the isotopic composition its source kerogen. Conkright and Sackett (1992) found that $\delta^{13}C$ 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.

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, however, cannot be used to discriminate between depositional environments as the isotopic differences between

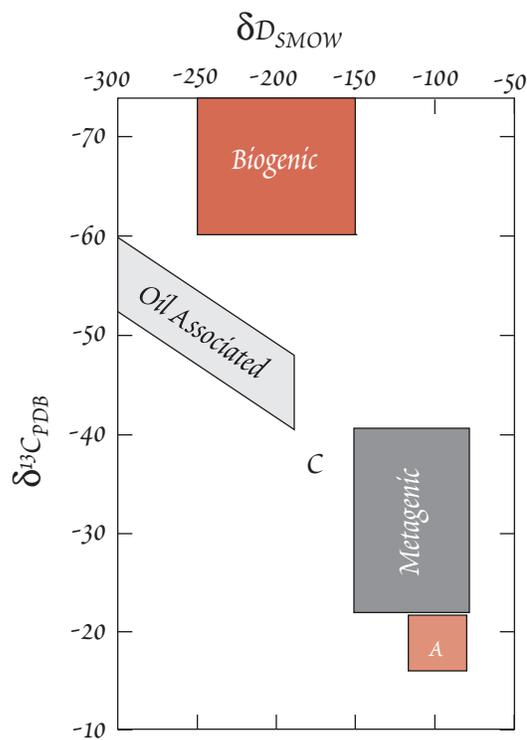


Figure 14.40. Isotopic composition of methane from various sources. "Biogenic" methane is methane produced by methanogens during diagenesis, "Oil Associated" is methane associated with oil, "C" indicates typical composition of methane in gas condensates, "Metagenic" is methane produced during metagenesis, "A" is the composition of abiogenic methane from mid-ocean ridge hydrothermal systems. Modified from Schoell (1984).

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marine and terrestrial organic matter are neither sufficiently large nor sufficiently systematic. Interestingly, δD in oil derived from shale source rocks are generally lower than those derived from carbonate source rocks (Schoell, 1984). The cause of this difference is unclear.

There can be significant fractionation of carbon and hydrogen isotopes in the generation of methane. As Figure 14.40 shows, methane produced by methanogenic bacteria, called "biogenic methane" during diagenesis is highly depleted in ^{13}C . Methane produced during catagenic 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 $\delta^{13}C$ (-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).

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PROBLEMS

1. Sketch the structure of the following:
 - a.) Citric acid: $\text{HO}(\text{CH}_2\text{CO}_2\text{H})_2\text{CO}_2\text{H}$
 - b.) Tartaric acid: $\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{H}$ (2,3,-dihydroxybutanedioic acid).
2. Write the chemical formula and sketch the structure of 2-hydroxy-propanoic acid (lactic acid).

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3. 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?

4. The first and second acidity constants of oxalic acid ($(\text{COOH})_2$) are $\text{pK}_{a1} = 1.23$ and $\text{pK}_{a2} = 4.19$. 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.

5. 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 $5 \times 10^{-4}\text{mol/g}$ 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_2L | $\text{pK}_{a1} = 1.9$ |
| | HL^- | $\text{pK}_{a2} = 1.9$ |
| | CuL | $\text{pK}_{\text{Cu}} = 7.7$ |
| "Catechol": | H_2L | $\text{pK}_{a1} = 6.8$ |
| | HL^- | $\text{pK}_{a2} = 10.0$ |
| | CuL | $\text{pK}_{\text{Cu}} = 17.3$ |

6. Repeat the calculation in Problem 5 above, but for pH 5.5. At this pH, the apparent stability constants are:

| | | |
|-------------|----------------------|--------------------------------|
| "Malonate": | H_2L | $\text{pK}_{a1} = 2.9$ |
| | HL^- | $\text{pK}_{a2} = 2.9$ |
| | CuL | $\text{pK}_{\text{Cu}} = 6.7$ |
| "Catechol": | H_2L | $\text{pK}_{a1} = 7.8$ |
| | HL^- | $\text{pK}_{a2} = 11.0$ |
| | CuL | $\text{pK}_{\text{Cu}} = 16.3$ |

7. 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 14.15? What values do you determine for constants a and b ? (HINT: Use linear regression.)

| | K_{OW} | K_{OM} |
|---------------------|-----------------|-----------------|
| acetophenone | 38.90 | 42.66 |
| benzene | 128.82 | 83.18 |
| tetrachloroethylene | 398.11 | 208.93 |
| naphthalene | 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 |

8. Sediment from a highly eutropic lake was found to have an organic carbon fraction of 5.8%. Using the adsorption partition coefficient for DDT listed in problem 7, predict the concentration of DDT in the sediment if the lake water has a DDT concentration of $3 \mu\text{g/l}$ and the sediment contains 5.8% organic matter.

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9. 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.

10. 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.