

## CHAPTER 22

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# MARINE BIOCHEMISTRY: AN OVERVIEW

### INTRODUCTION

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Thus far, a simple model compound— $C_{106}(H_2O)_{106}(NH_3)_{16}PO_4$ —has been used to represent an average molecule of organic matter. In reality, marine organic matter is composed of a great variety of molecules, ranging from low molecular weight hydrocarbons, such as methane, to high molecular weight complexes, such as humic acids. The marine biogeochemistry of specific organic molecules is the subject of Part 4.

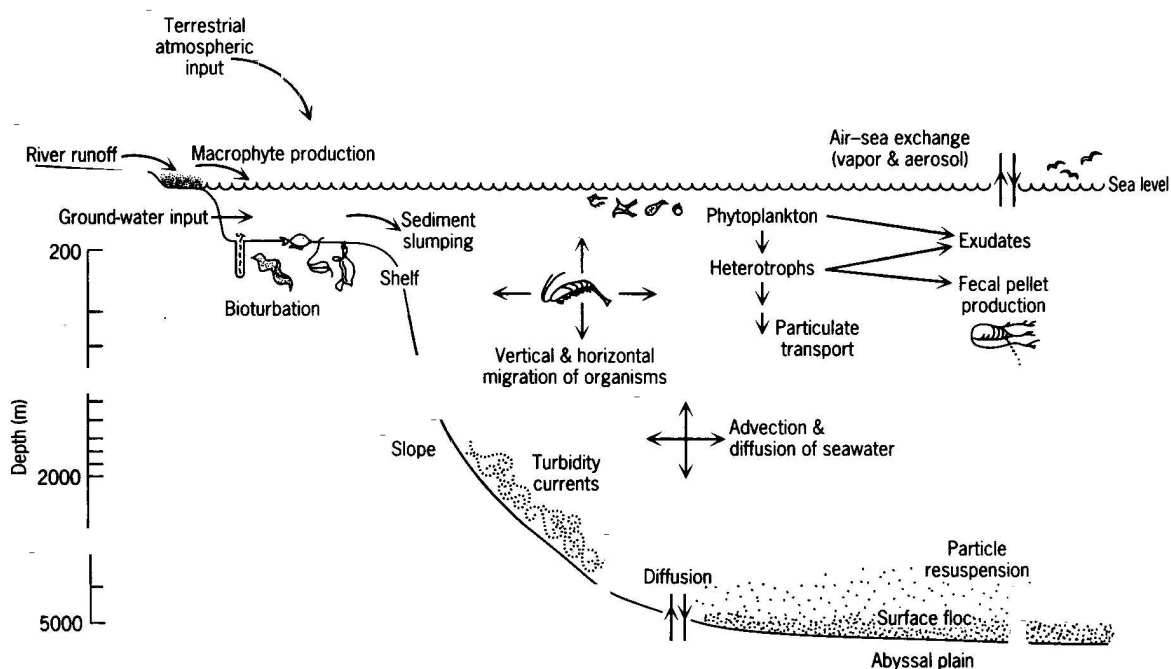
Organic compounds are molecules that contain carbon, with the exception of the simple oxides ( $CO$ ,  $CO_2$ ,  $HCO_3^-$ ,  $H_2CO_3$ ,  $CO_3^{2-}$ ), elemental forms (diamonds and graphite), and carbonate minerals. They vary greatly in molecular weight and structure. Most contain oxygen and hydrogen. Nitrogen, sulfur, and phosphorus can also be present, but usually in lesser amounts. Most organic compounds are produced during metabolic reactions. As a result, their marine distributions are largely controlled by the activities of marine organisms, such as those illustrated in Figure 22.1. Since equilibrium is rarely achieved in biologically mediated reactions, the distribution of organic compounds is the result of kinetic, rather than thermodynamic, controls.

Organic compounds constitute a relatively small elemental reservoir. Nevertheless, they have great influence on important parts of the crustal-ocean factory. Some of these impacts are discussed in this and the rest of the chapters of Part 4. This chapter also includes a discussion of the different conceptual approaches used in the study of organic biogeochemistry and a description of the molecular structures of the most abundant classes of marine organic compounds.

### THE IMPORTANCE OF ORGANIC COMPOUNDS IN THE MARINE ENVIRONMENT

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Organic compounds are of great importance in the crustal-ocean factory because of their influence on marine life. For example, they constitute most



**FIGURE 22.1** Factors that influence the distribution of organic matter in the marine environment.

of the tissues, as well as some of the structural parts of all organisms. Organic compounds are also the primary food source for heterotrophs. Besides consuming them, organisms use organic compounds as communicating agents. For example, many organisms excrete organic compounds, called pheromones, that attract mates. Toxic molecules are used for defense against competitors and predators. Still others are used to deactivate the toxic properties of some compounds. This is usually achieved by the formation of relatively inert complexes or by enhancing degradation rates. Due to their potent physiological activity, many of these compounds have proven useful to humans, primarily as drugs, lubricants, cosmetics, and food additives.

Organic matter also affects the mechanical properties of sediments. The largest such impact is an increase in cohesion between particles that limits resuspension. Sedimentary organic matter is the sole food source for the heterotrophic members of the benthos. These organisms also alter the physical, chemical, and geological characteristics of the sediment. For example, deposit feeders change the size distribution of particles by “gluing” detritus into fecal pellets. This type of bioturbation homogenizes chemical gradients and increases the supply of  $O_2$  to the sediments. Other organisms construct burrows and feeding tubes which cause chemical and geological heterogeneity in the sediments as illustrated in Figure 12.1.

Upon introduction to seawater, all particles are rapidly covered with a coating of organic matter. Due to its net negative charge, this coating adsorbs cations. Since the particles eventually sink to the seafloor, they remove a significant amount of cations, primarily trace metals, from seawater. These coatings also represent an energy-rich food source to microorganisms. As a result, bacteria, protozoa, and fungi, are commonly found growing on particles. If the particle has a large enough surface area, it will be successively colonized by higher trophic levels, such as tunicates and sponges. This process is termed **biofouling**. To prevent this overgrowth, ship hulls are painted with toxic compounds, such as tributyltin. Unfortunately, some of these chemicals dissolve in seawater and have lethal effects on nontarget organisms.

Sedimentary organic matter is of particular interest to humans for two reasons. First, most petroleum is marine in origin, having been produced by the diagenesis and catagenesis of detrital phytoplankton tissues. Secondly, the steady-state balance of nutrients,  $O_2$  and  $CO_2$  in the crustal-ocean factory appears to be stabilized by feedbacks that involve the burial of organic matter in the sediments. Thus down-core variations in the organic matter content of marine sediments provide a paleoceanographic record of changes in such phenomena as primary production, water circulation, and atmospheric chemistry.

## CONCEPTUAL AND ANALYTICAL APPROACHES USED TO STUDY THE MARINE BIOGEOCHEMISTRY OF ORGANIC COMPOUNDS

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Due to recent improvements in analytical technology, marine chemists are now able to detect and identify a bewildering number of organic compounds. Most are present at very low concentrations. Nevertheless, many substances remain uncharacterized. Several conceptual strategies have been developed to cope with these problems and are discussed below.

### Analyses of Operationally Defined Fractions

Due to analytical limitations, the concentrations of organic compounds are often determined as operationally defined fractions. For example, POM (particulate organic matter) is defined as that fraction of organic matter that does not pass through a glass-fiber filter. The nominal pore size of this filter is  $0.4 \mu\text{m}$ . Since the effective pore size decreases during the filtration, some of the organic matter retained on the filter is somewhat smaller than  $0.4 \mu\text{m}$ . In addition, dissolved organic matter adsorbs to particles and hence constitutes part of the operationally defined POM fraction.

Despite these drawbacks, the chemical characterization of operationally defined fractions has provided insight into the biogeochemistry of organic matter. This has typically involved the measurement of such bulk properties as the %C, %N, and the C/N of POM, as well as the concentrations of

particulate organic carbon (POC) and nitrogen (PON) in seawater. Similar analyses have been done on other operationally defined fractions whose acronyms are given in Table 22.1.

Spectral properties, such as the absorption of infrared light, are also used to categorize broad classes of organic matter. For example, the high molecular weight fraction of DOM (called humic substances) absorbs infrared light at many frequencies and with varying intensity, as shown in Figure 22.2. The shape of the absorbance spectrum reflects the type of bonds present in the organic compounds. Though specific structures cannot be identified, differences in peak shape and position can be used to distinguish terrestrial from marine humic substances, as shown in Figure 22.2.

Other information on complex mixtures of organic compounds can be obtained without explicitly identifying the structure of each component. For example, the source of an oil spill can be identified by using a gas chromatograph to “fingerprint” the petroleum. In this instrument, the complex mixture is first heated, causing the compounds to volatilize. A stream of inert gas pushes the compounds onto a long, narrow column that is packed or coated with special materials. In the former case, the column (2 to 3 m long) is packed with diatomaceous earth that has been impregnated with a high-boiling-point liquid. Alternatively, the liquid is applied as a thin film onto the inside wall of a very narrow (0.2–0.5 mm), very long (25–50 m) column. The liquid is termed the stationary phase.

The compounds dissolve in or are adsorbed by this stationary phase to a degree that is determined by their boiling points. Those compounds that are not strongly retained by the column are rapidly pushed to the other end by the stream of inert gas. The compounds that are strongly retained by the column migrate at slower rates. Since the boiling point is inversely related to molecular weight, the smallest compounds tend to elute from the column first.

The time required for elution is called the retention time. As a substance elutes from the column, its presence is signaled by a detector that transforms

**TABLE 22.1**  
Operationally Defined Fractions of  
Organic Matter<sup>a</sup>

<i>Operational Fraction</i>	<i>Abbreviation</i>
Particulate organic matter	
Dissolved organic matter	
Particulate organic carbon	
Dissolved organic carbon	
Dissolved inorganic carbon	
Particulate organic nitrogen	
Dissolved organic nitrogen	
Dissolved inorganic nitrogen	

<sup>a</sup>Also included are some inorganic fractions.



**FIGURE 22.2.** Comparison of IR spectra of humic acids from terrestrial soils (A–C) and marine sediments (D–G). Identification of IR bands: (1) aliphatic C–H; (2) C=O; (3 and 5) amides; (4) aromatic C=C; and (6) C–O in polysaccharides. *Source:* From A. Y. Huc, B. Durand, and F. Jacquin, reprinted with permission from the *Bulletin de L'ENSAIA De Nancy*, vol. 16, p. 71, copyright © 1974 by L'Institut National Polytechnique de Lorraine (ENSAIA), Nancy, France.

some physical or chemical property of the substance into a measurable electrical signal. This detector records the information as a peak whose area is directly proportional to the compound's abundance.

Gas chromatographs are able to completely separate the components of simple mixtures, producing chromatograms with sharp, symmetric peaks, such as those shown in Figure 22.3a. The components of complex mixtures are not as well separated due to similarities in molecular structures that cause their solubilities and boiling points to be nearly identical. As a result, some of these compounds co-elute and appear as large humps on the gas chromatograms, as illustrated in Figure 22.3b. Though the specific compounds that contribute to this hump are not identifiable, its shape is unique to the mixture and can be

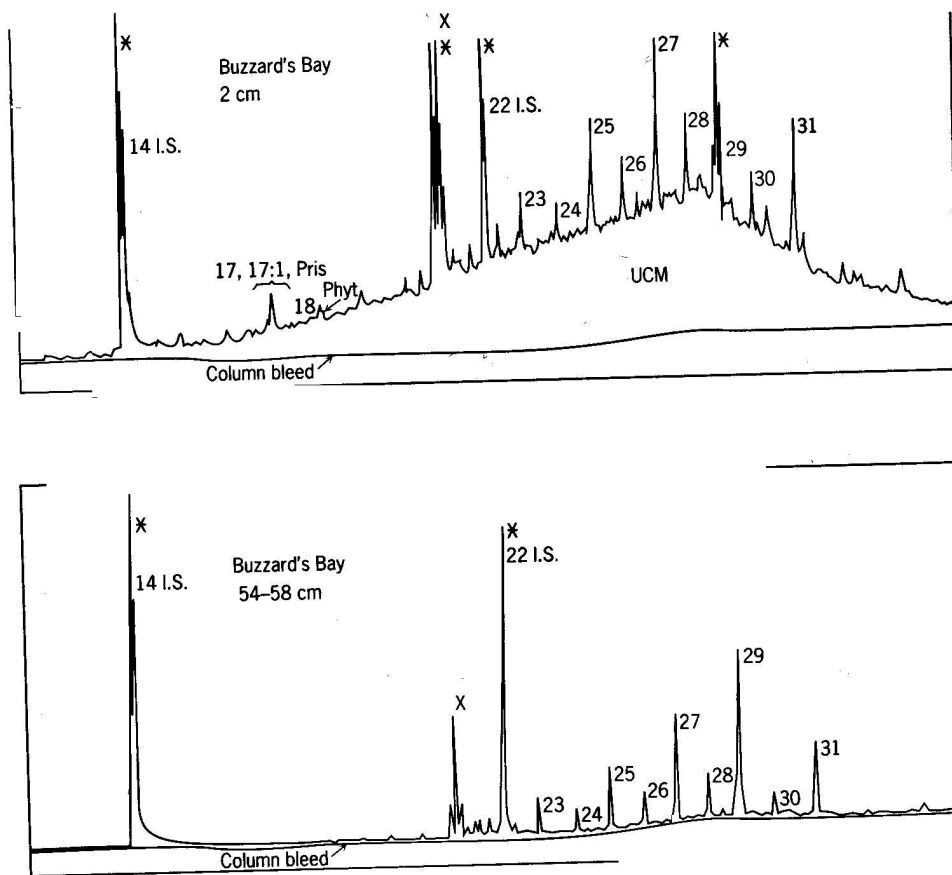


FIGURE 22.3. Gas chromatograms of anthropogenic petroleum hydrocarbons from two depths in a coastal marine sediment: (a) 54 to 58 cm below the sediment surface and (b) surface sediment. The degradation and migration of petroleum compounds is responsible for the decrease in mixture complexity with increasing depth. Some of the petroleum compounds in the surface sediments contribute to the hump which is identified only as an unresolved complex mixture (UCM). Peaks identified by an asterisk were brought on scale by use of an auto attenuator. Peaks identified as I.S. are internal standards. X is used to designate groups of unsaturated compounds of unknown structure. *Source:* From J. W. Farrington, N. M. Frew, P. M. Gschwend and B. W. Tripp, reprinted with permission from *Estuarine and Coastal Marine Science*, vol. 5, p. 797, copyright © 1977 by Kluwer Academic Publishers, Dordrecht, The Netherlands.

used as a fingerprint for matching purposes. This has been used to identify the source of petroleum present in a spill, as oil is naturally variable in chemical composition. Thus the identity of the polluter can be determined by comparing gas chromatograms of oil obtained from all likely sources, such as ships' fuel

tanks. The chemical composition of petroleum is discussed further in Chapter 26 and petroleum pollution in Chapter 30.

The molecular structures of each peak in a well-resolved gas chromatogram can be identified by **mass spectrometry**. This combination of technologies is called GC-MS and is illustrated schematically in Figure 22.4. As a compound elutes off the chromatographic column it is passed into the mass spectrometer. Bombardment with a high-energy beam of electrons creates molecular ions that can spontaneously break up into fragments. The masses and relative abundances of the fragments are detected electronically and reported as a mass spectrum. An onboard computer compares this spectrum to those of known molecules to establish a best match and hence the likely identity of the compound. Once the compound has been identified, its presence in other gas chromatograms, obtained under similar operating conditions, can be determined from its retention time.

### Biomarkers and Source Tracers

Certain organic molecules are synthesized by only one type of marine organism. For example, the sterol dinosterol is synthesized only by dinoflagellates. These compounds are termed **biomarkers** because their presence provides unequivocal evidence for their source (i.e., biological production by that specific organism).

In most cases, a particular compound or class of compounds is synthesized by several kinds of organisms. For example, lignins are structural polymers synthesized by all woody terrestrial plants. Since lignin is relatively inert, some is transported by rivers into the ocean and buried in nearshore sediments. Thus its relative abundance in marine sediments can be used to determine the contribution of terrestrial organic matter to the deposit.

Most organic compounds synthesized in the marine environment are very labile. They are released into seawater by either (1) exudation, (2) excretion, or (3) cell lysis following the death of the organism. Once in seawater, most are rapidly degraded by microbes. In some cases the degradation products can be used to identify the source compound. For example, phaeophytin and phytol are unique products of the decomposition of chlorophyll.

The distribution of specific compounds in the water column can also provide information on biogeochemical processes. As shown in Figure 22.5, adenosine triphosphate (ATP) concentrations are highest at the sea surface. ATP is introduced into seawater as a result of cell lysis that occurs shortly after death. Once in seawater, ATP is rapidly degraded. Thus high concentrations are the result of a rapid supply that must be supported by high rates of biological production. Since biological productivity is concentrated in the surface waters, this is the site of highest ATP concentrations.

The smaller concentration maximum located at 400 m suggests the occurrence of relatively high rates of microbially mediated decomposition of detrital POM. This maximum is probably supported by the in situ degradation of detrital POM derived from biological activity in the surface waters. This conclusion is supported by the wintertime increase in ATP concentrations at

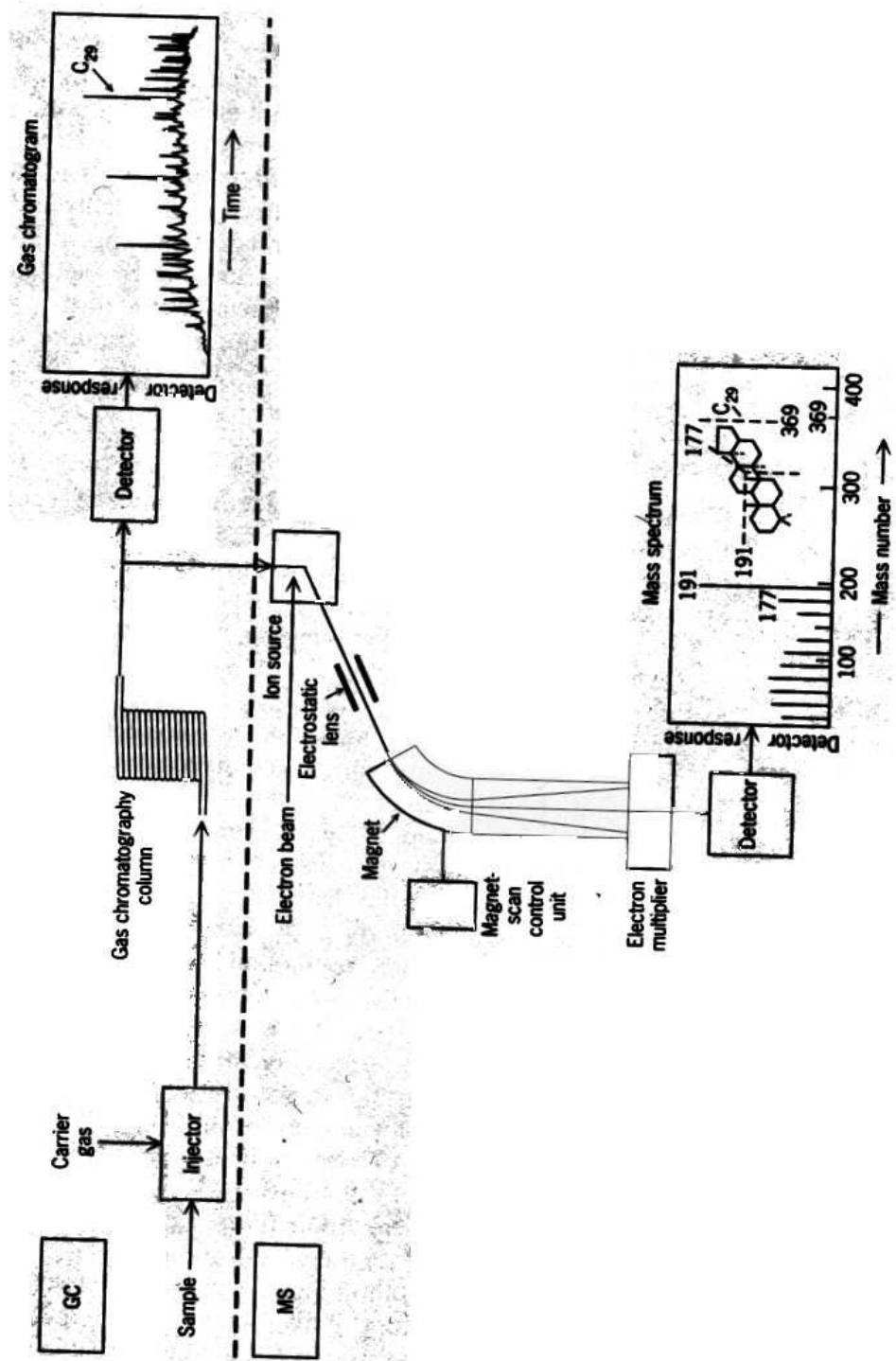


FIGURE 22.4. GC-MS analysis of organic compounds.



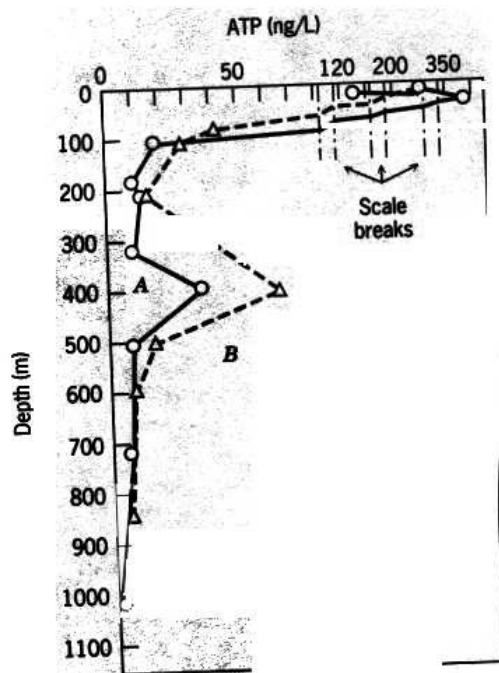


FIGURE 22.5. Depth profile of ATP concentrations at a site off the coast of California. Samples were collected in (A) May 1965 at 33°N 119°W and (B) October 1965 at 33°N 117°W. Source: From O. Holm-Hansen and C. H. Booth, reprinted with permission from *Limnology and Oceanography*, vol. 11, p. 515, copyright © 1966 by the American Society of Limnology and Oceanography, Seattle, WA.

mid depth. Since vertical segregation is greatest during the summer, the largest amount of POM will have sunk out of the surface waters by the beginning of winter. Apparently most of these particles are neutrally buoyant at approximately 400 m and so support increased rates of microbial activity, especially during early winter.

### Isotopes as Tracers of the Source and Fate of Marine Organic Compounds

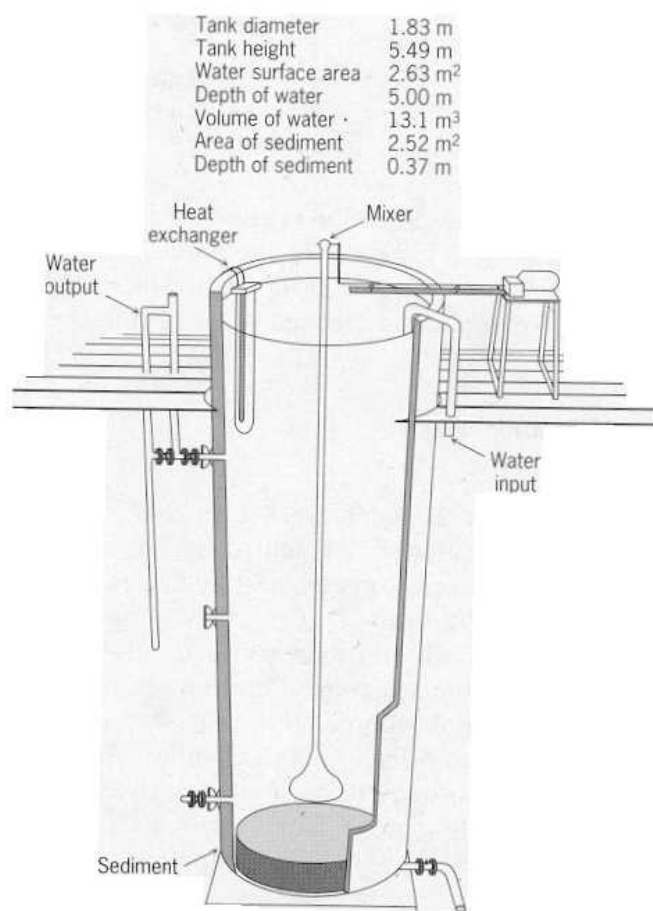
Isotopes of a particular element are atoms that have the same number of protons, but different numbers of neutrons. The naturally occurring stable isotopes of carbon, nitrogen, oxygen, and hydrogen have been used as source tracers. For example, the ratio of  $^{13}\text{C}$  to  $^{12}\text{C}$  is lower in terrestrial POM than in marine POM. Because these ratios are relatively constant, the contribution of terrestrial organic matter to coastal marine sediments can be inferred from its relative carbon isotope composition. These measurements are made by mass spectrometry and are discussed in Chapter 29.

Some radioactive isotopes have also been used to determine the mechanisms and rates at which some organic compounds decompose. To do this, a small amount of radioactively labelled compound is introduced into a sample of seawater or sediment. The fate of this compound is traced by periodically analyzing various fractions of the sample. The results of these studies are somewhat questionable as the seawater and sediment are not in their in situ states during the experiment. It is also assumed that the radioactively labeled compound is an appropriate analog for some fraction of "real" marine organic matter.

## Artificial Ecosystems

As noted on page 375, laboratory experiments on seawater and sediments are not likely to produce chemical changes similar to those that occur in situ. One approach used to better mimic real conditions has been to create very large artificial ecosystems. Though designed to function as much like the natural ocean as possible, they can also be controlled and sampled efficiently. Some of the largest artificial ecosystems are the MERL tanks (Marine Ecosystems Research Laboratory) operated by the University of Rhode Island on Narragansett Bay.

As illustrated in Figure 22.6, these tanks are approximately 16 ft high and 5 ft in diameter. They contain about 1 ft of sediment and 13,000 liters of water, which is slowly trickled in from the bay. The outflow rate is set so the water volume does not change over time. With a stirring device and the top of the



**FIGURE 22.6.** Cross-sectional view and dimensions of a MERL tank. *Source:* From J. B. Frithsen, A. A. Keller, and M. E. Q. Pilson, reprinted with permission from the *MERL Series, Report No. 3*, copyright © 1985 by the Marine Ecosystems Research Laboratory, University of Rhode Island, Narragansett, RI.

tank open, the tanks function much like the neighboring bay. Typical experiments involve monitoring the effects of some perturbation, like the introduction of nutrients or pesticides, on the water, sediment, and biota in the tank.

## GENERAL CLASSES OF ORGANIC COMPOUNDS

Organisms obtain chemical energy by degrading organic compounds. This general process is termed **catabolism**. Some of this energy is used to build large biomolecules that provide structural support and energy storage. The general process of organic matter synthesis is termed **anabolism** and is illustrated in Figure 22.7. The reaction pathways in both anabolism and catabolism tend to be species specific. Many produce unique compounds that thus can be used as biomarkers.

A great number of reactions occur during anabolism and catabolism. As a result, organisms produce a myriad of organic molecules. These compounds are classified into groups based on similarities in structure and the presence of certain functional groups. The most common of these functional groups are listed in Table 22.2. Most organic compounds that are naturally found in the marine environment can be classified as either hydrocarbons, carbohydrates, lipids, fatty acids, amino acids, or nucleic acids. Examples of each are given below, along with some of their polymers.

### Hydrocarbons

**Hydrocarbons** are organic compounds composed solely of carbon and hydrogen atoms. Marine organisms synthesize a great variety of these compounds. These chains of carbon atoms vary greatly in number and some are branched, as

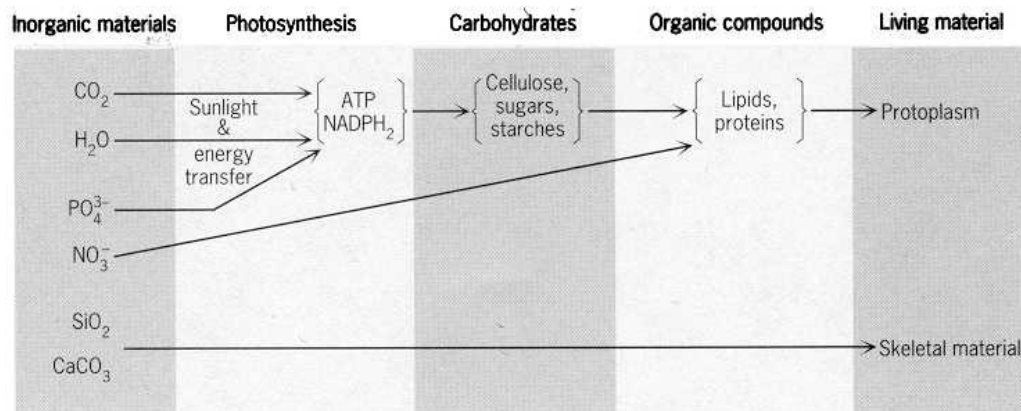

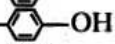


FIGURE 22.7. Various steps in the production of living material. Source: From *The World Ocean: An Introduction to Oceanography*, W. A. Anikouchine and R. W. Sternberg, copyright © 1981 by Prentice Hall, Inc., Englewood Cliffs, NJ, p. 379. Reprinted by permission.

**TABLE 22.2**  
 The Most Common Functional Groups  
 Found in Naturally Occurring Organic  
 Compounds (R = any other organic  
 structure)

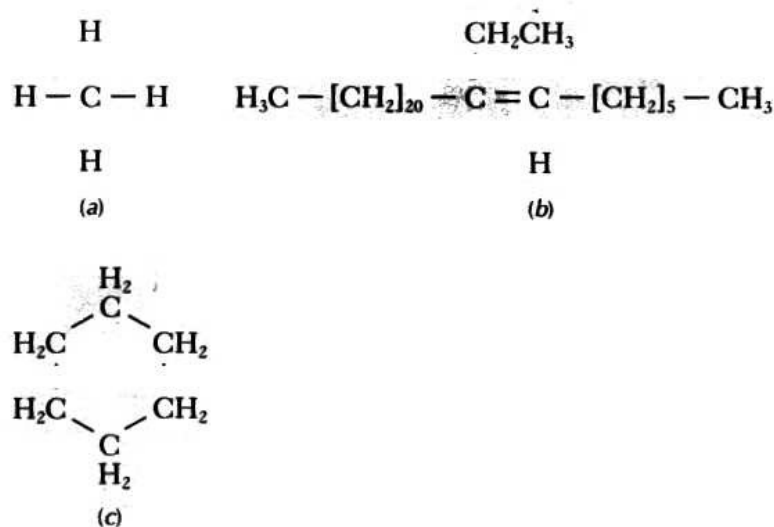
<i>Common Name</i>	<i>Molecular Formula or Structure</i>
	R—COOH
	R—OH
	R— 
	R—  —OH
	R—NH <sub>2</sub>
	R <sub>2</sub> —NH
	R <sub>3</sub> N

illustrated in Figure 22.8. Some have double bonds. To indicate their relative hydrogen deficiency, these compounds are said to be “unsaturated.”

In general, hydrocarbon production does not appear to be species specific and hence these compounds are not useful as biomarkers. Hydrocarbons are also produced by the fragmentation of large biomolecules during catagenesis and can form large deposits called petroleum.

## Carbohydrates

Carbohydrates and lipids are the most important cellular reservoirs of chemical energy. The simple carbohydrates are composed of single sugar molecules, of



**FIGURE 22.8.** Structures of some hydrocarbons: (a) methane, (b) branched and unsaturated C<sub>31</sub> hydrocarbon, and (c) cyclohexane.

which glucose is an example. Its structure, along with those of the other common simple sugars, is given in Figure 22.9.

Complex carbohydrates are formed by the linking of many simple sugars. The resulting polymers are also called polysaccharides. The most common are illustrated in Figure 22.10. Cellulose is a structural and rather chemically inert component of terrestrial plants. Alginic acid is synthesized by marine algae and has medicinal properties. The exoskeletons of crustacea are composed of chitin.

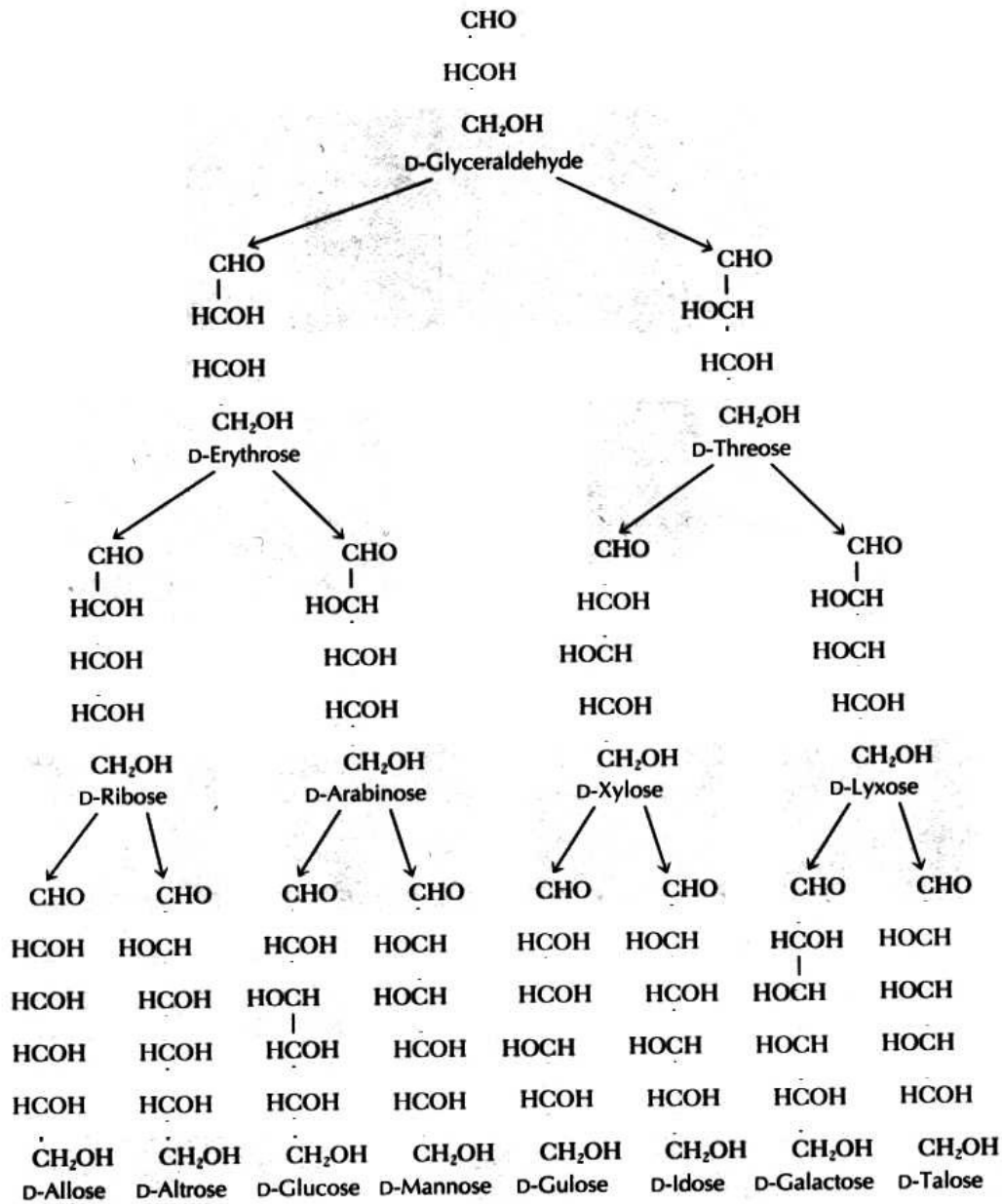


FIGURE 22.9. The simple sugars.

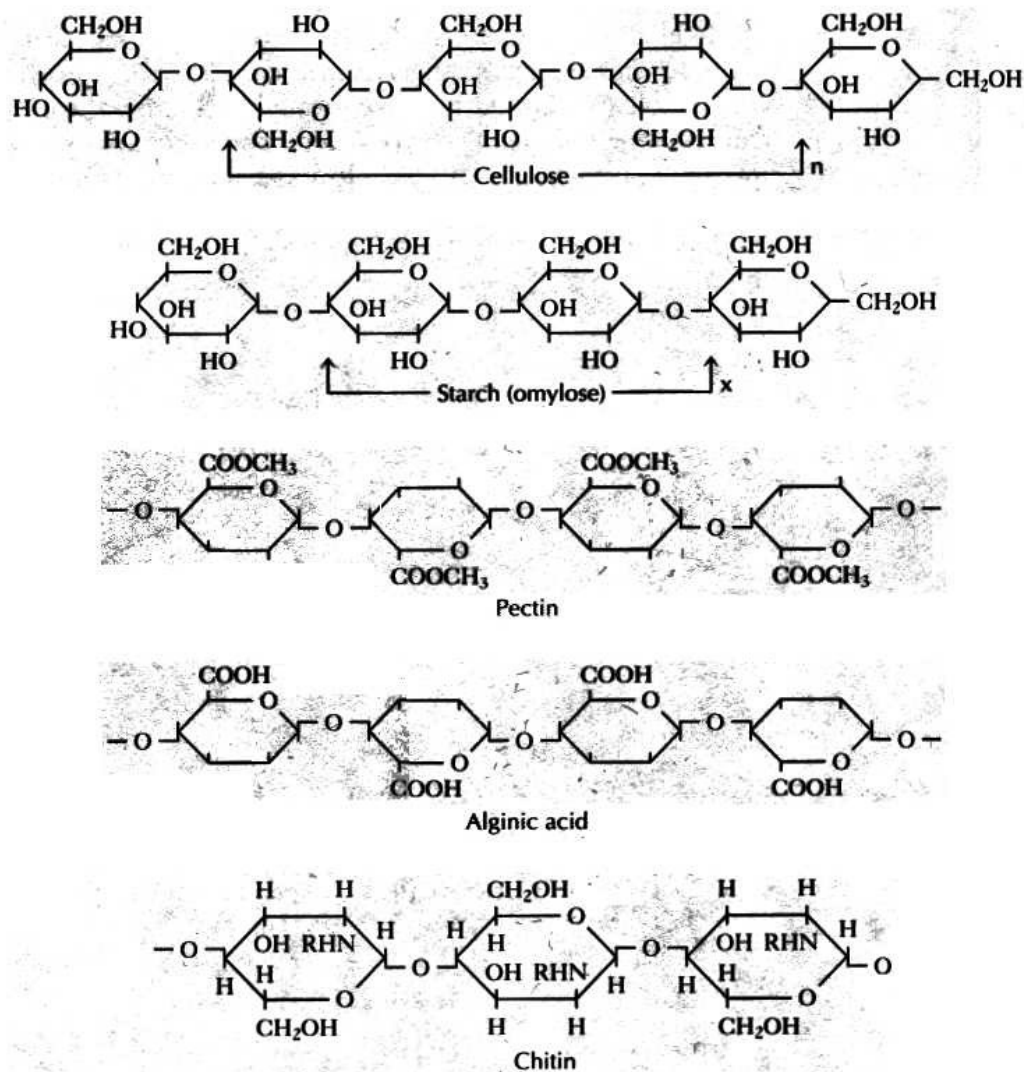


FIGURE 22.10. Some typical polysaccharides.

## Lipids

**Lipids** are a diverse group of compounds that are soluble in nonpolar solvents and insoluble in water. As shown in Table 22.3, lipids are classified as complex or simple. The complex lipids contain various fatty acids that are attached to a “backbone” molecule, such as shown in Figure 22.11.

These compounds are commonly used in cells as a means of energy storage. A complex lipid that is a solid at room temperature is called a fat or wax. Those which are liquids are termed oils. The fats tend to have higher molecular weights and are synthesized primarily by animals. Waxes and oils are more common to plants. The type of complex lipids biosynthesized by an organism is an adaptation to the temperature of its environment. For example, deep-dwelling fish are more apt to have low-molecular-weight lipids than surface-

**TABLE 22.3**  
Classification of Lipids

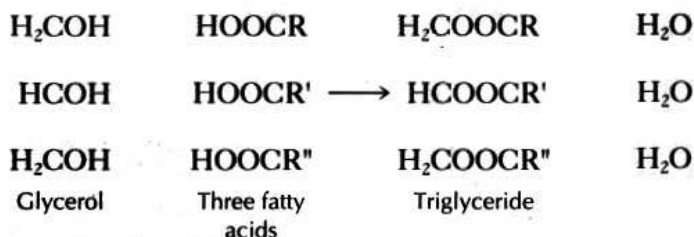
<i>Backbone</i>	
Complex	
Acylglycerols	Glycerol
Phosphoglycerides	Glycerol 3-phosphate
Sphingolipids	Sphingosine
Waxes	Nonpolar alcohols of high molecular weight
Simple	
Terpenes	
Steroids	
Prostaglandins	

dwelling fish. The relatively low freezing points of the smaller lipids keeps them from solidifying at the low temperatures encountered in the deep sea.

Fatty acids are hydrocarbons that have a terminal carboxylic acid group (R—COOH). As shown in Table 22.4, members of this group vary in chain length, degree of unsaturation, and branching. Some of these features are unique to certain organisms. For example, branched chains are produced during the microbial degradation of organic detritus.

Some phospholipids are a major component of cell walls. In these compounds, one of the alcohol groups in the backbone molecule (glycerol) is attached to an organophosphate. This group is relatively polar and hence water soluble. In comparison, the fatty acid groups are relatively insoluble. Thus the lipid molecules tend to form bilayers, as illustrated in Figure 22.12.

Simple lipids do not contain fatty acids. Pigments are examples of simple lipids. These colored organic compounds are synthesized in small amounts by most marine organisms. The most abundant are the chlorophylls, which are used by marine plants and some bacteria to convert solar energy into chemical energy. The structures of chlorophyll *a* and some other common photosynthetic pigments are illustrated in Figure 22.13. Carotene is orange and fucoxanthin is red. These compounds are characterized by a high degree of unsaturation. Note the central magnesium atom and numerous nitrogen atoms in the chlorophyll *a* molecule.



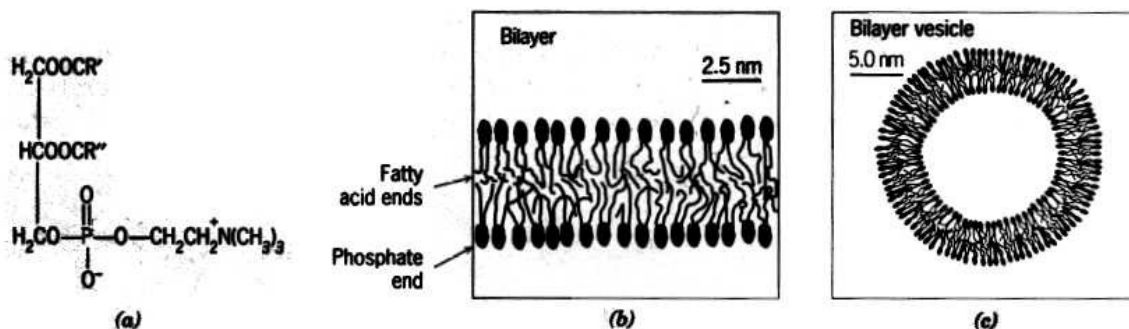
**FIGURE 22.11.** An example of a complex lipid.

**TABLE 22.4**  
Some Examples of Fatty Acids

Structure	Systematic Name	Common Name
<b>Saturated fatty acids</b>		
$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	<i>n</i> -Dodecanoic	Lauric
$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	<i>n</i> -Tetradecanoic	Myristic
$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	<i>n</i> -Hexadecanoic	Palmitic
$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	<i>n</i> -Octadecanoic	Stearic
$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$	<i>n</i> -Eicosanoic	Arachidic
$\text{CH}_3(\text{CH}_2)_{22}\text{COOH}$	<i>n</i> -Tetracosanoic	Lignoceric
<b>Unsaturated fatty acids</b>		
$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$		Palmitoleic
$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$		Oleic
$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$		Linoleic
$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$		Linolenic
$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_3\text{COOH}$		Arachidonic

Carotene, fucoxanthin, and xanthophyll are examples of terpenoids. This class of compounds is constructed of multiples of the five-carbon hydrocarbon isoprene. Terpenes (Figure 22.14) may be either linear or cyclic. Some molecules contain both types of structures as exemplified by vitamin A.

Sterols are simple lipids that have a base unit composed of three six-carbon and one five-carbon ring, as shown in Figure 22.15. They are ubiquitous in marine organisms, both as components of cell membranes and as metabolic regulators. As mentioned above, some sterols reflect specific sources. Cholesterol is the dominant sterol in zooplankton, while diatoms primarily synthesize the 24-methylsterols.  $\beta$ -sitosterol is synthesized primarily by higher-order land plants.



**FIGURE 22.12.** (a) A phosphoglyceride structure (e.g., phosphatidyl choline). (b) The orientation of these molecules in a model bilayer membrane. (c) The formation of a "cell" from a bilayer membrane. *Source:* From J. N. Israelachvili and N. W. Ninham, reprinted with permission from the *Journal of Colloid Interface Science*, vol. 58, p. 18, copyright © 1977 by Academic Press, Orlando, FL.



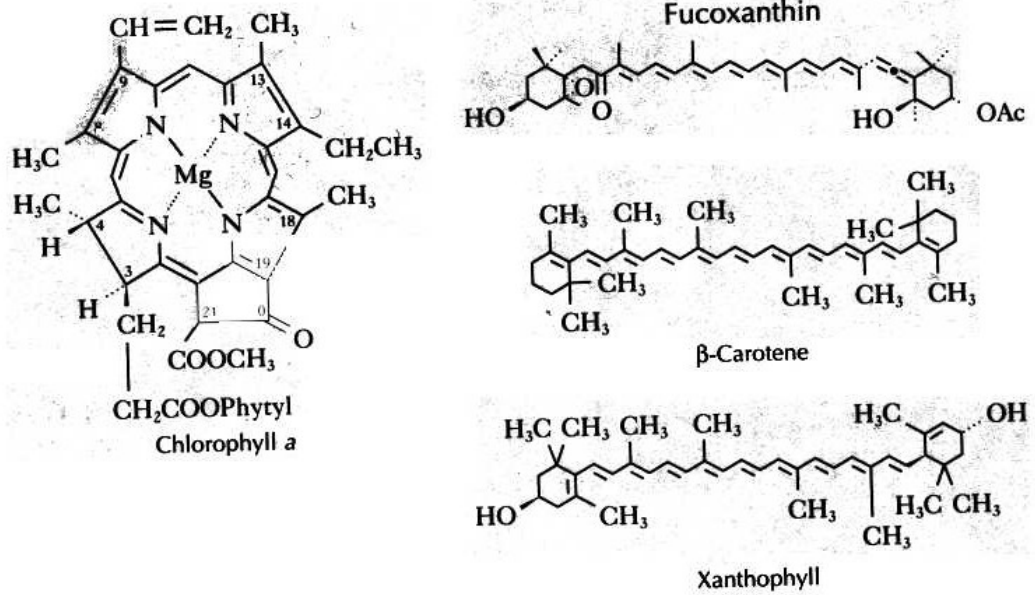


FIGURE 22.13. Structure of various plant pigments.

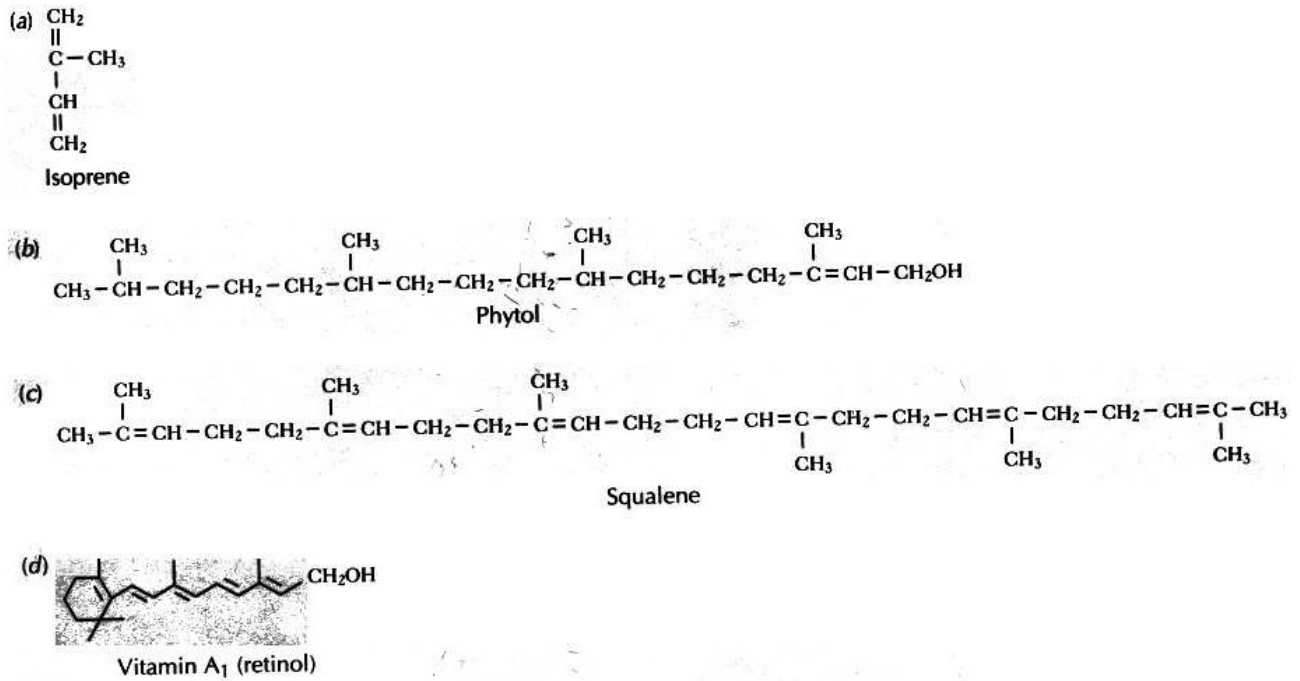


FIGURE 22.14. Examples of terpenes: (a) isoprene; (b) phytol, which is a side chain of chlorophyll a; (c) squalene; and (d) vitamin A.

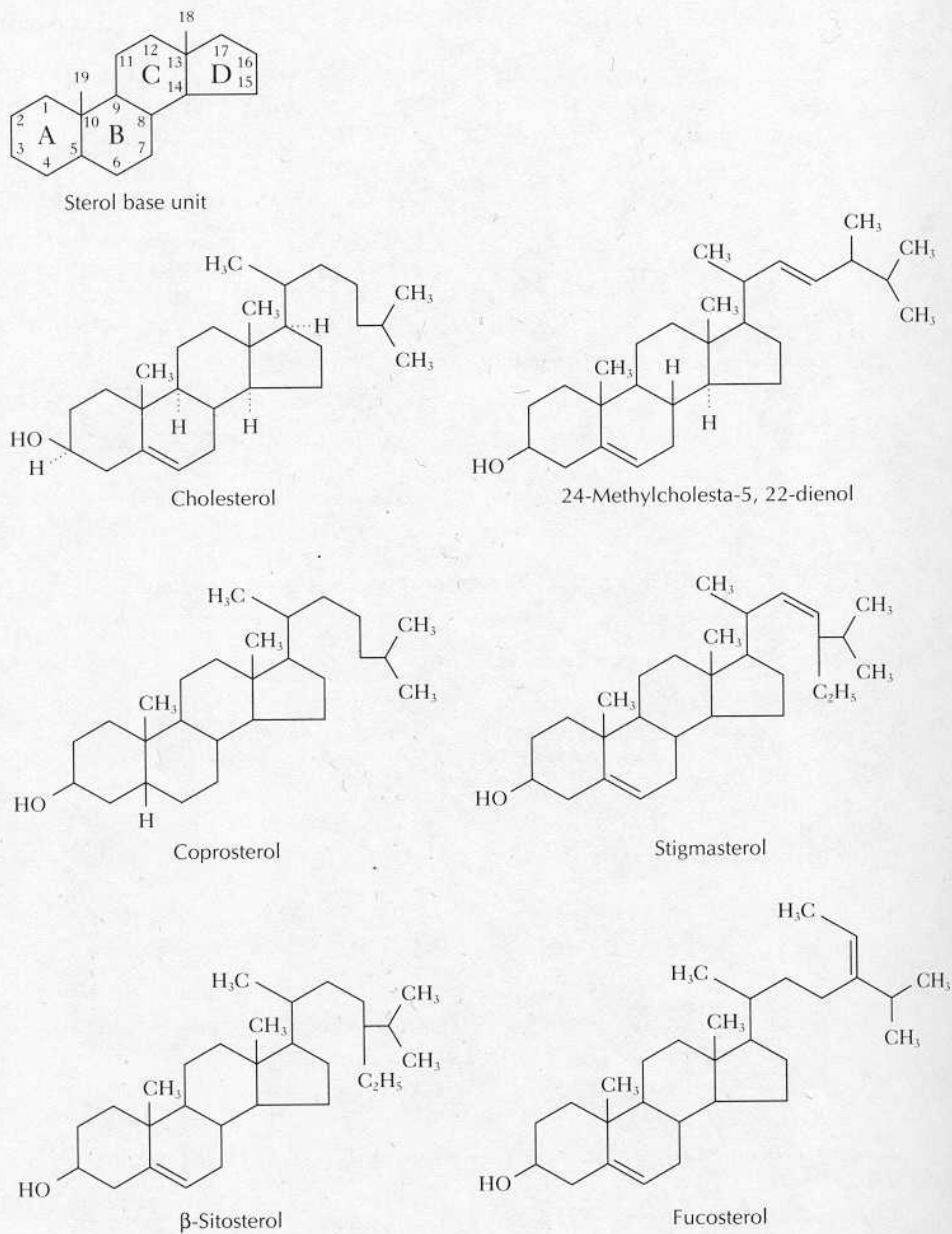


FIGURE 22.15. Sterol base unit and examples.

## Nucleic Acids

Nucleic acids are composed of an aromatic base, a five-carbon sugar, and a phosphate group. The five aromatic bases that can be present are illustrated in Figure 22.16 and cause the nucleic acids to be relatively nitrogen rich.

An example of a nucleic acid, or mononucleotide, is given in Figure 22.17a. When linked together, they form polymers called polynucleotides. RNA and DNA, which store and transmit genetic information within cells, are examples of polynucleotides. Nucleic acids are also part of energy-carrying molecules such as ATP and NADP (nicotinamide adenine dinucleotide phosphate).

## Amino Acids

Amino acids are the building blocks of proteins. These compounds all bear at least one amine group ( $R-NH_2$ ) and a carboxylic acid group ( $R-COOH$ ). The naturally occurring amino acids are listed in Table 22.5.

Amino acids become linked by reactions that occur between the amine group of one amino acid and the carboxylic acid of another. As shown in Figure 22.18, this polymerization also produces a molecule of water and hence is termed a condensation. Naturally occurring polypeptides with molecular weights in excess of 10,000 daltons are termed proteins. These biomolecules are ubiquitous in marine organisms and are not specific to particular species.

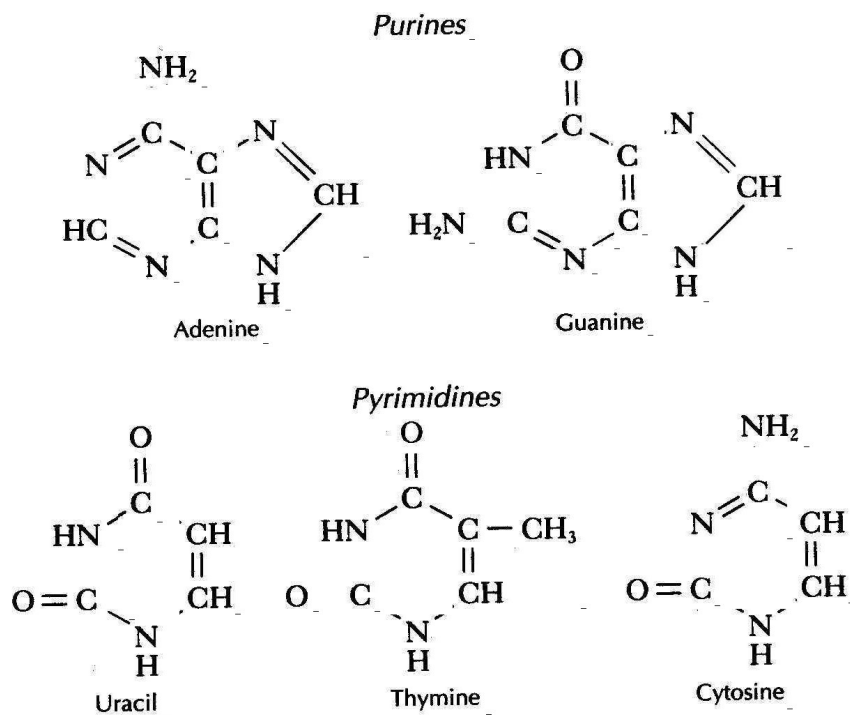


FIGURE 22.16. Aromatic bases present in nucleic acids.

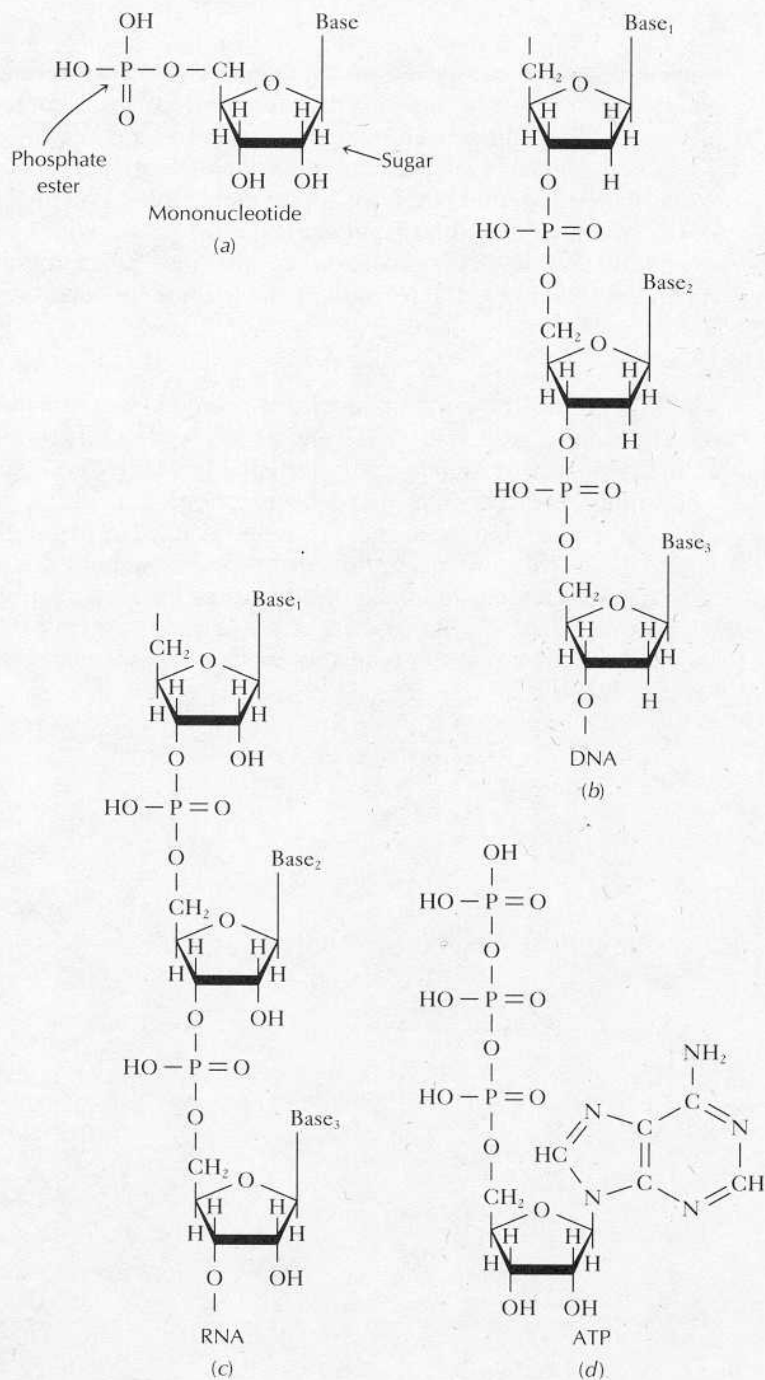


FIGURE 22.17. Structures of (a) a mononucleotide, (b) DNA, (c) RNA, and (d) ATP.

**TABLE 22.5**  
Principal Amino Acids Derived from Proteins

<i>I. Aliphatic amino acids</i>	
<b>A. Monoaminiomonocarboxylic acids</b>	
Glycine	$  \begin{array}{c}  \text{H} \quad \text{H} \quad \text{O} \\  \diagdown \quad   \quad    \\  \text{N} \quad \text{C} \quad \text{C} \quad \text{OH} \\  \diagup \quad   \\  \text{H} \quad \text{H} \\  \text{H} \quad \text{H} \quad \text{O} \\  \quad \quad    \\  \text{H} \quad \text{C} - \text{C} \quad \text{C} \quad \text{OH}  \end{array}  $
Alanine	$  \begin{array}{c}  \text{H} \quad \text{N} \\  \diagdown \quad / \\  \text{H} \quad \text{H}  \end{array}  $
Valine	$(\text{CH}_3)_2\text{CHCH}(\text{NH}_2)\text{COOH}$
Leucine	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{COOH}$
Isoleucine	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_2)\text{COOH}$
Serine	$\text{HOCH}_2\text{CH}(\text{NH}_2)\text{COOH}$
Threonine	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{NH}_2)\text{COOH}$
<b>B. Sulfur-containing amino acids</b>	
Cysteine	$\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH}$
Methionine	$\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
<b>C. Monoaminodicarboxylic acids and their amides</b>	
Aspartic acid	$\text{HOOCCH}_2\text{CH}(\text{NH}_2)\text{COOH}$
Asparagine	$\text{NH}_2\text{COCH}_2\text{CH}(\text{NH}_2)\text{COOH}$
Glutamic acid	$\text{HOOCCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
Glutamine	$\text{NH}_2\text{COCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
<b>D. Basic amino acids</b>	
Lysine	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
Hydroxylysine	$\text{NH}_2\text{CHCH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OH}_2)\text{COOH}$
Arginine	$\text{NH}_2\text{C}(\text{NH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$
Histidine	$  \begin{array}{c}  \text{H} \\    \\  \text{N} - \text{C} - \text{CH}_2\text{CH}(\text{NH}_2)\text{COOH} \\  / \quad   \\  \text{H} \quad \text{C} \quad    \\  \quad \quad \backslash \quad / \\  \quad \quad \text{N} \quad \text{CH}  \end{array}  $

(Continued on next page.)

**TABLE 22.5 (Continued)**  
Principal Amino Acids Derived from Proteins

<i>II. Aromatic amino acids</i>	
Phenylalanine	
Tyrosine	
<i>III. Heterocyclic amino acids</i>	
Tryptophan	
Proline	
Hydroxyproline	
Histidine (see above)	

Source: From *Marine Chemistry*, R. A. Horne, copyright © 1969 by John Wiley & Sons, Inc., New York, p. 246. Reprinted by permission.

Proteins are important components of enzymes as well as of structural parts and connective tissues. For example, chitin is a polymer composed of amino acids and sugars. Amino sugars are also found in bacterial cell walls, as shown in Figure 22.19.

### Humic Substances

Forty to 80 percent of marine DOM is composed of macromolecules (300–300,000 daltons) that are extremely variable in structure and elemental composition. These humic substances appear to form abiotically from fragments of biomolecules generated during the microbial degradation of organic matter.

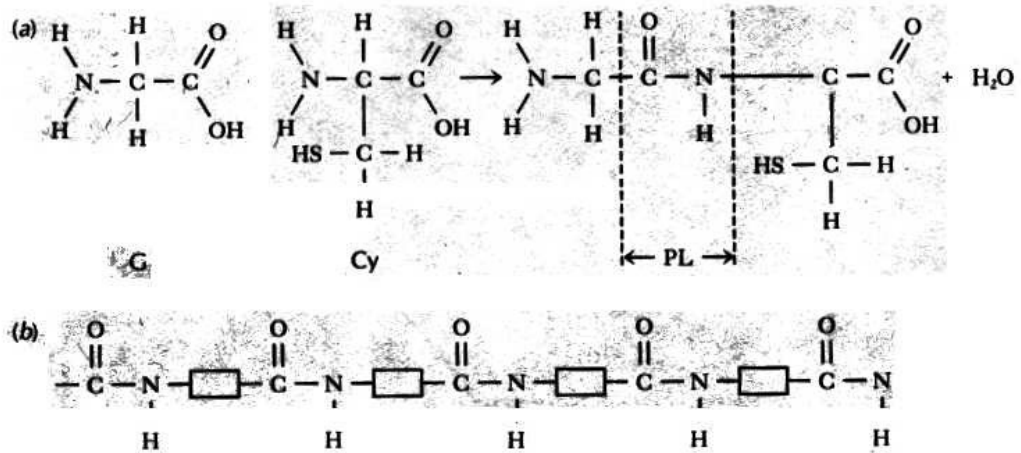


FIGURE 22.18. (a) The condensation of two amino acids and (b) diagrammatic representation of a protein, showing the peptide linkage (PL) between the amino acids.

They are also components of solids, such as sediment, soil, and peat. In addition to their compositional complexity and variability, humic substances are relatively inert. As a result, they are difficult to study, so little is known of their structure or biogeochemistry. Their marine chemistry is discussed in the next chapter.

### Nitrogenous Excretion Products

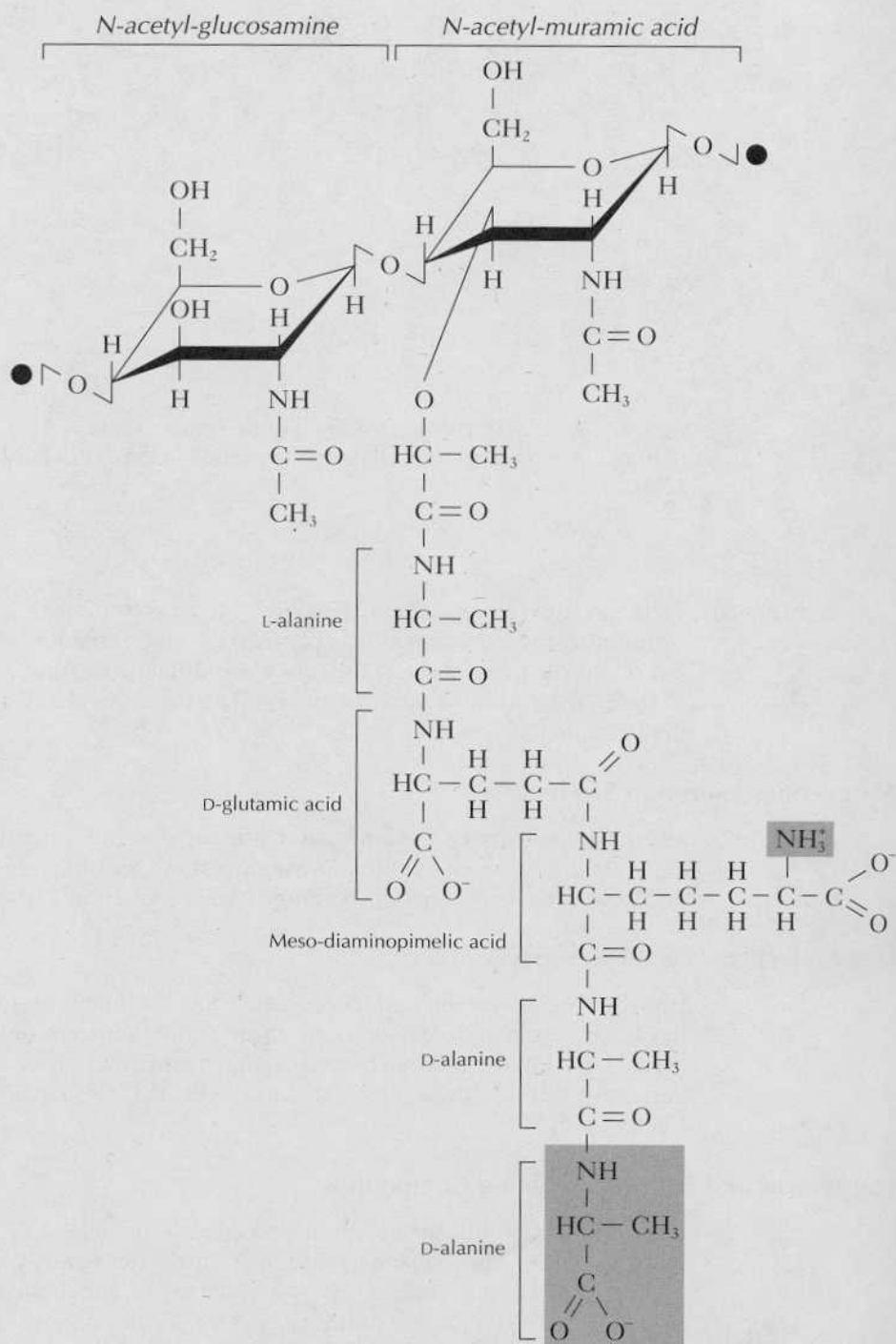
Marine organisms excrete nitrogen primarily as the ammonium ion. Lesser amounts are released as the following organic species: amino acids, urea, and uric acid. The structures of the latter two are given in Figure 22.20.

### Low-Molecular-Weight Carboxylic Acids

Low-molecular-weight carboxylic acids are produced and consumed during the Krebs cycle and glycolysis, so these compounds are ubiquitous in marine organisms. Phytoplankton release a significant fraction of their fixed carbon into seawater as low molecular carboxylic acids, such as those shown in Figure 22.21.

### Phosphorus and Sulfur-Containing Compounds

Organic compounds that contain phosphorus include ATP, NADP, and the phospholipids. The phosphate group is often temporarily attached to other organic compounds, such as pyruvate, as part of metabolic reactions, such as glycolysis. Most organic sulfur is present as the amino acids cysteine and methionine. Microbial degradation produces low molecular weight compounds, such as dimethyl sulfide and dimethyl disulfide, which have high vapor pressures





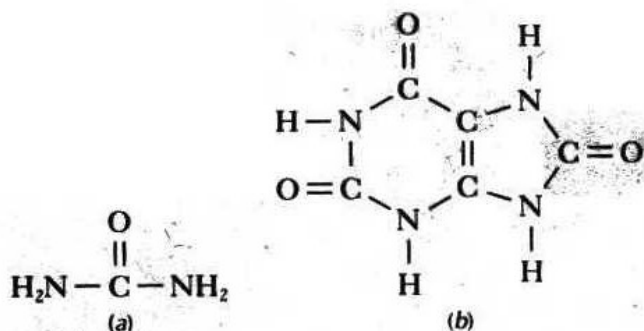


FIGURE 22.20. Structure of (a) urea and (b) uric acid.

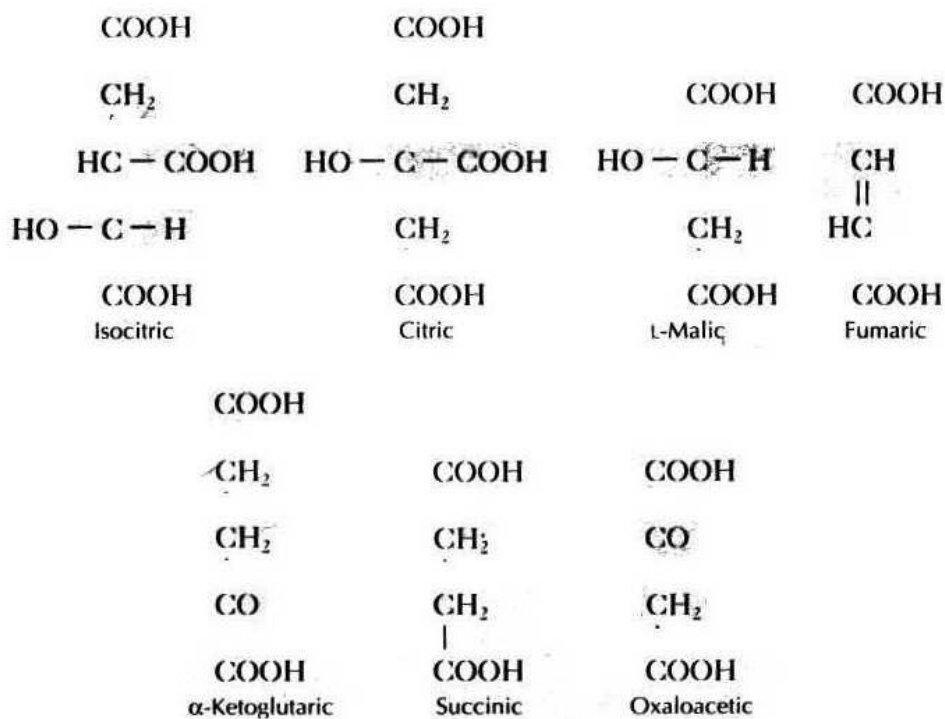


FIGURE 22.21. Structures of some di- and tricarboxylic acids.

FIGURE 22.19. The molecular structure of an amino sugar found in bacterial cell walls. The colored areas represent points of attachment of this macromolecule to the rest of the cell wall. The sugar units are joined end to end to form long, straight chains. The peptides form cross-links when the amino group of a meso-diaminopimelic acid in one chain replaces the terminal alanine in another chain.

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and are apt to diffuse across the air-sea interface. Small amounts of sulfur are also present in some polysaccharides, lipids, vitamins, and enzymes, most notably as ferredoxin.

## SUMMARY

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Organic compounds constitute a relatively small elemental reservoir. Nevertheless, they have great impact on important parts of the crustal-ocean factory, largely by influencing biological activity. For example, organic compounds compose most of the tissues, as well as some of the structural parts, of marine organisms. They are also the primary food for heterotrophs, while others function as toxins that inhibit or kill competitors and predators. Still others have positive influences, such as "neutralizing" the toxic effects of heavy metals by forming organometallic complexes, or attracting mates. Because of their ability to provoke physiological responses, many of these compounds have proven useful to humans, primarily as drugs, lubricants, cosmetics, and food additives.

The presence of organic matter affects the mechanical properties of marine sediments and also provides food for the benthos. In turn, these organisms alter the physical, chemical, and geological characteristics of the sediment. For example, bioturbating organisms homogenize chemical gradients and increase the supply of  $O_2$  to the sediments.

Sinking particles, like all surfaces, are covered by a film of organic matter. Due to its negative charge, this coating adsorbs metal ions and attracts heterotrophic bacteria. The former represents a significant sink for metals from the ocean and the latter promotes **biofouling**. Little of the organic matter synthesized in the euphotic zone reaches the seafloor due to efficient recycling in the water column by marine organisms. Some of the small fraction that does survive to become buried in the sediment is converted into petroleum as a result of diagenesis and catagenesis. Due to feedbacks in the crustal-ocean factory, the steady-state balance of nutrients,  $O_2$ , and  $CO_2$  in the ocean and atmosphere is stabilized by the processes that involve the burial of organic matter. Thus down-core variations in the organic matter content of marine sediments provide a paleoceanographic record of changes in such phenomena as primary production, water circulation, and atmospheric chemistry.

Organisms obtain chemical energy by degrading organic compounds. This general process is termed **catabolism**. Some of the resulting energy is used to build large biomolecules that provide structural support and store energy. The general process of organic matter synthesis is termed **anabolism**. The reaction pathways in these processes tend to be species specific and often produce compounds that can be used as **biomarkers**. As a result of the great number of anabolic and catabolic reactions, organisms produce a myriad of organic compounds. These molecules are classified into groups based on structural similarities. In the marine environment, most organic compounds fall into one

of the following general classes of biomolecules: **hydrocarbons, carbohydrates, lipids, fatty acids, amino acids, or nucleic acids.**

Due to analytical limitations, the concentrations of organic compounds are often determined as operationally defined fractions, such as **POM** and **DOM**. These fractions are typically characterized by bulk properties, such as their **%C, C/N**, and total concentrations in seawater, as well as by their unique absorbance spectra. Specific compounds and classes of compounds are identified and quantified by **mass spectrometry** following **gas chromatographic** separation. The biogeochemistry of organic matter has also been studied by tracing the fate of isotopically labelled compounds, particularly in artificial ecosystems.