

which subducting lithosphere, including oceanic crust, overlying sediment and underlying mantle lithosphere, might contribute to island arc magmas. These questions have been most successfully addressed through isotope

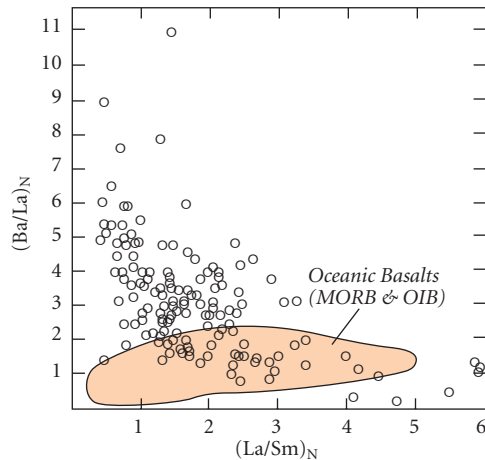


Figure 11.44 Relative alkali–alkaline earth enrichment of IAV illustrated by plotting the $(\text{Ba/La})_N$ ratio vs. the $(\text{La/Sm})_N$ ratio. The subscript N denotes normalization to chondritic values. Perfit *et al.* (1980). With permission from Elsevier.

geochemistry. Sr isotope ratios are generally higher, and Nd isotope ratios generally lower than in MORB, with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios around 0.7033–0.7037 and ϵ_{Nd} of +6 to +8 being fairly typical of intra-oceanic IAV. This range overlaps considerably with MORB and OIB; there is, however, a tendency for IAV to have slightly higher Sr isotope ratios for a given Nd isotope ratio and hence plot to the right of the oceanic basalt array on a Nd–Sr isotope ratio plot such as Figure 11.12. This shift to higher Sr isotope ratios is thought to reflect a contribution of subducted oceanic crust to IAV magma sources. Weathering and hydrothermal alteration of the oceanic crust shifts Sr isotope ratios of the oceanic crust toward seawater (higher) values, but does not affect Nd isotope ratios because of the extremely low concentration of Nd in seawater.

Clear evidence of sediment involvement comes from Pb isotope studies of island arc volcanics, beginning with the work of Armstrong and Cooper (1971). As Figure 11.45 shows, $^{206}\text{Pb}/^{204}\text{Pb}$ isotope ratios overlap MORB values, but $^{207}\text{Pb}/^{204}\text{Pb}$ ratios are typically higher in IAV than most oceanic basalts. They tend to form steeper arrays on $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ plots, and overlap the field of marine sediments. For most island arcs, Pb isotope ratios in the volcanic rocks

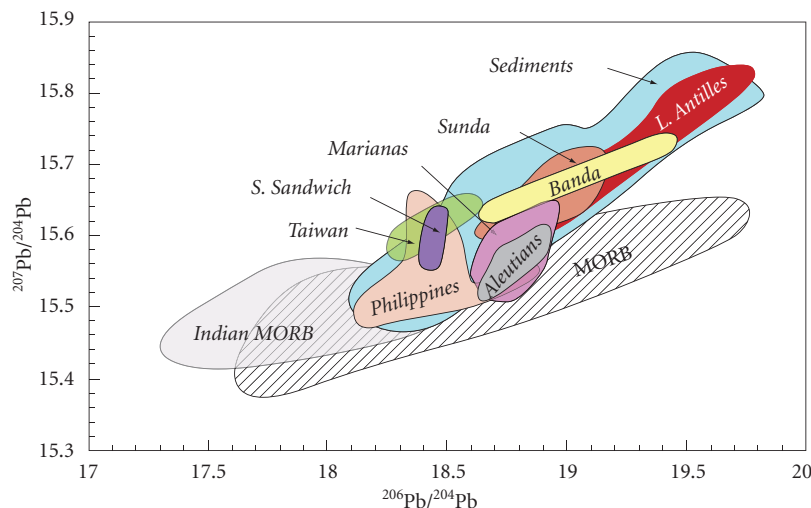


Figure 11.45 Pb isotope ratios in island arc volcanics. Fields for the South Sandwich, Lesser Antilles, Aleutians, Marianas, Philippines, Taiwan, Banda and Sunda arcs are compared with fields for Atlantic and Pacific MORB (field labeled MORB) and Indian Ocean MORB, and modern marine sediments.

lie between sediment local to the arc and the MORB field (Karig and Kay, 1981). On the whole then, Pb in island arc magmas appears to be a mixture of Pb from local sediment and local upper mantle.

Finally, ^{10}Be provides unequivocal evidence of sediment involvement in IAV magma sources. As we found in Chapter 8, ^{10}Be is a cosmogenic isotope produced in the atmosphere by cosmic ray spallation of ^{14}N . It has a half-life of only 1.5 million years, so we would not expect to find significant amounts of ^{10}Be in the Earth's interior; any present when the Earth formed has long since decayed away. ^{10}Be created in the atmosphere is purged by rainfall and is strongly absorbed by clays of sediment and soil. Tera *et al.* (1986) found measurable quantities ($>10^6$ atoms per gram) of ^{10}Be in some arc lavas, while ^{10}Be was completely absent in non-arc lavas. The interpretation is that the ^{10}Be originates from sediment subducted to the magma genesis zone.

Subducted sediment appears to influence the trace element compositions of arc lavas as well. Plank and Langmuir (1993) carried out a careful study of the composition of volcanic rocks from eight arcs and the sediments being subducted beneath them. By analyzing representative samples from the sediments and considering the proportions of sediment types being carried beneath the arc, they estimated the flux of elements being carried by sediment beneath the arc. They found they could relate the degree of enrichment of most incompatible elements to the sediment flux of that element. For example, the Ba/Na and Th/Na ratios (after correction for fractional crystallization to 6% MgO) correlate strongly with the Ba and Th sediment fluxes (Figure 11.46). Different arcs are enriched to different degrees in these elements: for example, the Lesser Antilles arc has moderate Th/Na ratios but low Ba/Na ratios. The difference appears to be due to the difference in the sediment flux.

11.6.4.4 Magma genesis in subduction zones

Now that we have an overview of the composition of arc magmas, let's consider in more detail the processes that lead to the unique geochemistry of island arc magmas. Most geochemists and petrologists believe that arc magmas are produced primarily within the

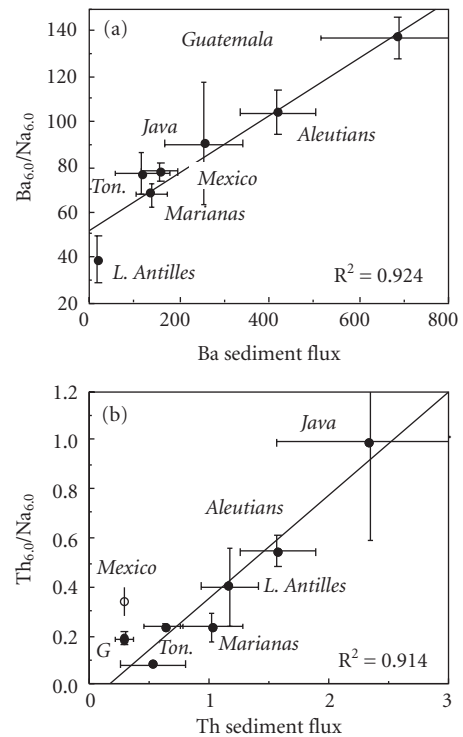


Figure 11.46 Relationship between $\text{Ba}/\text{Na}_{6,0}$ and $\text{Th}/\text{Na}_{6,0}$ in volcanic rocks from eight arcs, and Ba and Th sediment flux beneath those arcs. Horizontal bars represent uncertainty in the amount of sediment subducted; vertical bars reflect the variance of the ratio in the arc volcanics. G, Guatemala; M, Mexico; J, Java; T, Tonga; Mar, Marianas; Al, Aleutians; Ant, Lesser Antilles. Reprinted by permission from McMillan Publishers Ltd: From Plank and Langmuir (1993).

mantle wedge, the triangular region of mantle overlying the subducting slab. The evidence for this is as follows:

1. Primary arc magmas differ only slightly in their major element chemistry from oceanic basalts, which are definitely mantle-derived; the andesitic nature of many arc magmas probably results from fractional crystallization in a crustal or subcrustal magma chamber. It is therefore most likely IAV are partial melts of peridotite rather than subducted basalt or sediment.
2. Radiogenic isotopic and trace element systematics generally allow only a small fraction of sediment (generally a few

percent or less) to be present in arc magma sources. Relatively high $^3\text{He}/^4\text{He}$ ratios in arc lavas confirm a mantle source.

3. Rare earth patterns of island arc magmas are consistent with these magmas being generated by partial melting of peridotite, but not by partial melting of eclogite, which would be the stable form of subducted basalt at 100 km depth (the subducting lithosphere is typically located at about 100 to 120 km depth beneath island arc volcanoes). Because the heavy rare earths partition strongly into garnet (e.g., Figure 7.16), melts of eclogite should show steep rare earth patterns, with low concentrations of the heavy rare earths. This is not generally the case. Rare high-magnesium andesites, sometimes called “adakites” (after a well-documented occurrence on Adak Island in the Aleutians) with steep rare earth patterns may represent exceptions to this rule and may indeed be generated by small extents of melting of subducted oceanic crust (Kay, 1978; Defant and Drummond, 1990). It is possible that such “slab melts” were more common several billion years ago.

If IAV magmas are not melts of the slab, how do they acquire the geochemical signature or “flavor” of subducting oceanic crust and sediment? Dehydration and migration of the evolved hydrous fluid has long been suspected as the primary means by which the subducting slab influences the composition of IAV magmas. For example, White and Dupré (1986) modeled the observed enrichment of Lesser Antilles low-K basalts in incompatible elements, assuming the source was a mixture of depleted mantle and sediment, using Nd isotope ratios to calculate the fraction of sediment. This simple model predicted the concentrations of the rare earths and Th reasonably well, but the enrichment of Pb, Cs, Rb, U, K, Ba, and Sr was greater than predicted. These are the elements expected to partition into hydrous fluid, suggesting their enrichment was due to preferential partitioning into and transport by aqueous fluids. The elemental fractionation that must occur during transport from the subducting slab into the mantle wedge is further illustrated in Figure 11.47. Ba/La ratios in Marianas arc lavas plot systematically above a mixing line

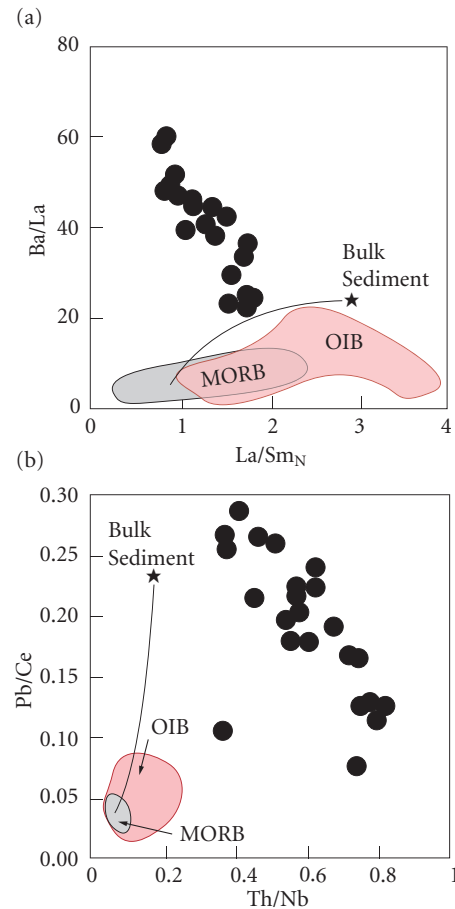


Figure 11.47 (a) Ba/La versus La/Sm_N (subscript N denotes the chondrite-normalized ratio) in Marianas arc lavas compared with those in MORB, OIB, and bulk sediment from ODP Hole 801b, located on the Pacific plate outboard of the Marianas arc. The line connecting MORB and sediment is a mixing curve. Ba enrichment in the arc cannot be explained simply by mixing of MORB and sediment. (b) Pb/Ce versus Th/Nb in Marianas arc lavas. Th is enriched more than can be explained by sediment–MORB mixing alone. Elliott *et al.* (1997) suggested sediment melting is responsible. Modified from Elliott *et al.* (1997). Reproduced with permission of the American Geophysical Union.

between MORB and sediment subducting beneath the arc (sampled in ODP Hole 801) on a plot of Ba/La vs. La/Sm. The same is true of Th/Nb ratios (Figure 11.47b), which are systematically higher than predicted from simple MORB–sediment mixing. Elliott *et al.* (1997) concluded from these relationships and $^{230}\text{Th}/^{232}\text{Th}$ isotope ratios (recall that

^{230}Th is the intermediate daughter of ^{238}U) that both a hydrous fluid and a silicate melt were involved in transport of sediment. They proposed that the melt was a result of hydrous partial melting of the subducted sediments. Melting is necessary to account for the fractionation between Th and Nb, neither of which is particularly soluble in aqueous fluids. Furthermore, lavas with the highest Th/Nb also show the greatest light rare earth enrichment. Subsequent dehydration and melting experiments by Johnson and Plank (1999) confirmed the need for melting to transport elements such as Th into the magma genesis zone of the subarc wedge.

This brings us to what is perhaps the most fundamental question: why does melting occur at all in an area where cold lithosphere is descending? The answer is water. Water lowers the solidus of rock and leads to enhanced melting at any given temperature compared

with dry conditions; water released by the subducting slab migrates into the overlying hotter mantle wedge where it induces melting. The extent of this effect had been somewhat uncertain, in large part due to experimental difficulties. This has now been largely resolved and it is clear that the effect is a large one. Figure 11.48 is a P-T phase diagram (chapters 3 and 4) based on the work of Grove *et al.* (2006) and shows that under water-saturated conditions, the peridotite solidus is depressed by hundreds of degrees compared with the “dry solidus”. At 1.5 GPa (corresponding roughly to 50 km depth in the Earth), peridotite begins to melt at over 400°C cooler temperatures than under “dry” conditions. The effect is even larger at higher pressure.

Figure 11.48 also shows that at pressures above about 2 GPa, ilmenite along with chlorite would be stable at and above the solidus. The stability of ilmenite is particularly significant because Nb and Ta strongly partition into it. Thus the characteristic Nb-Ta depletion of island arc lavas, and indeed the entire continental crust (Figure 11.40), may be due to residual ilmenite being present during the initial states of melting deep within the arc.

Figure 11.49 summarizes magma generation at subduction zones. Sediment and hydrothermally altered oceanic crust carry water and incompatible elements into the mantle as

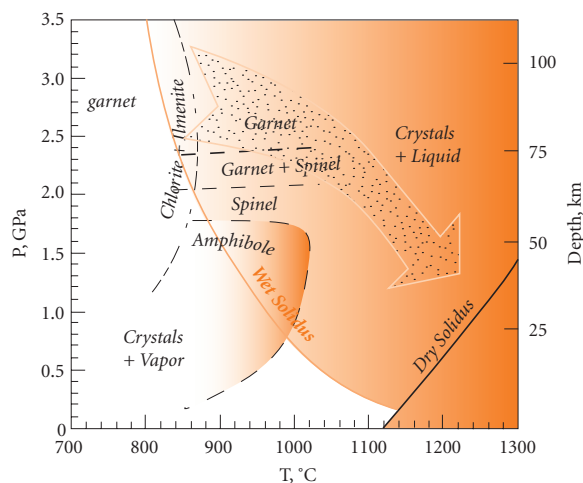


Figure 11.48 Experimentally based phase diagram for the system peridotite + water. The peridotite dry solidus is from Hirschmann (2000). Under “wet” conditions, meaning vapor present, peridotite begins to melt along the curve labeled “wet solidus” at temperatures hundreds of degrees lower. Curved dashed lines are the chlorite + ilmenite- and amphibole-out curves. Straight dashed lines illustrate the progressive replacement of spinel with garnet. The broad stippled arrow shows the path the melts take in T-P space as they rise through the mantle wedge (Figure 11.49). Modified from Grove *et al.* (2006). With permission from Elsevier.

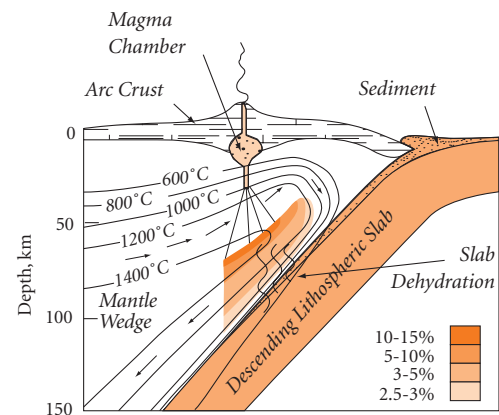


Figure 11.49 Cross-section of a subduction zone illustrating island-arc magma genesis. Arrows show the direction of mantle flow. Color shading indicates the predicted extent of partial melting in the mantle wedge resulting from the addition of water. Modified from Grove *et al.* (2006). With permission from Elsevier.

oceanic lithosphere is subducted. Where the sediment pile is thick, such as in the Lesser Antilles and Sunda arcs, some or most of the sediment is scraped off creating *accretionary prisms*, but both seismic and geochemical evidence indicate that some 100 m thickness or more is subducted. Compression during the early phases of subduction drives off much of the unbound water occupying pores and veins in the subduction lithosphere. This water sometimes emerges as “seeps” in accretionary prisms and supports chemosynthetic communities. In other cases, it hydrates and serpentinizes the overlying shallow mantle. So much water is liberated that the serpentine is mobilized and can emerge as serpentine mud volcanoes, such as those found in the Marianas forearc.

As the subducting lithosphere encounters increasing temperature and pressure it is metamorphosed, with water-rich minerals progressively replaced by water-poor ones and ultimately by anhydrous minerals. The water released in these reactions rises into the overlying mantle wedge. The wedge immediately above the subducting slab has an inverted thermal gradient: temperature decreases with depth because the cold subducting slab acts as a heat sink. Immediately above the slab, the mantle is too cold to melt, even though it is water saturated. However, 10 km above the slab, temperatures approach 1000°C, below the dry solidus, but well above the wet solidus. Consequently, melting begins. These initial melts may contain as much as 28% water (Grove *et al.*, 2006), but as they rise, continued melting progressively dilutes the water content.

Work over the past couple of decades has produced evidence directly relating water content to melting in subduction zones. Stolper and Newman (1994) showed that water concentrations correlated inversely with the concentrations of moderately incompatible elements, such as Ti, Zr, and Na, in lavas from the Marianas back-arc spreading center. Since water, or H, effectively behaves as an incompatible element itself, this requires explanation. Stolper and Newman (1994) proposed that extent of melting varied inversely with the amount of H₂O-rich component in the source mixture. The smallest extents of melting (about 5%) occur in H₂O-poor sources and give rise to incompatible

element-rich basalts, while the highest extents (over 20%) give rise to H₂O-rich and incompatible element-poor basalts. Stolper and Newman (1994) focused on back-arc basalts because they erupt at under several km of water, where pressure prevents degassing of the lavas. Degassing typically results in the loss of all volatiles in subaerially erupted lavas, so measuring their water contents is generally meaningless. Kelley *et al.* (2010) got around this problem by measuring the water content of melt inclusions, microscopic pockets of melt trapped in olivine crystals, in the lavas of Marianas arc volcanoes by using Fourier Transform Infrared Spectrometry (FTIR), which measures water content by measuring the absorption of infrared radiation by the O-H bond, and by ion probe. That study confirmed the results of Stolper and Newman (1994), again revealing an anticorrelation between water content and concentrations of moderately incompatible elements.

In summary, much of the continental crust has been produced through subduction zone magmatism. (This is certainly a bit ironic, since subduction zones are where oceanic crust and lithosphere are destroyed along with smaller amounts of continental crust. The graveyard of continental crust is also its nursery.) Magmatism in subduction zones results from *flux melting* – the lowering of the solidus by the addition of water. Virtually everywhere else on Earth melting results from decompression (see discussion in Chapter 7). Water also transfers the incompatible element and isotopic “flavor” of subducting oceanic crust and sediment to the mantle wedge melt generation zone, and from there into the crust formed by this magmatism. Partial melts of the oceanic crust and sediment can also carry this flavor into the magma genesis zone. These processes ultimately account for enrichment of continental crust in incompatible elements and its anomalous enrichment in fluid-mobile elements such as Pb. The distinctive negative Nb-Ta anomalies of continental crust and island arc lavas result from retention of these elements in residual ilmenite stabilized by hydrous melting conditions.

Although subduction-related volcanism seems to have been the dominant mode of crustal growth at least through the Proterozoic and Phanerozoic, other mechanisms have

played a role. The Wrangalia Terrane in NW British Columbia and Alaska is widely considered to consist in part of oceanic plateaus. The plateaus were produced over a mantle plume in Paleozoic times and later accreted to the North American continent by plate tectonic processes. The Coast Ranges of Oregon represent another example of accreted oceanic crust. Mantle plumes surfacing beneath continents also produce magmas that add mass to the continents. The most voluminous eruptions occur in the initial stages of the plume, when the large buoyant plume head approaches the surface. Under these circumstances, enormous volumes of basalt erupt. Examples of such flood basalts include the Siberian Traps, the Karoo of South Africa, the Deccan of India, the Parana of Brazil, and the Columbia River of the northwest US. Gravity anomalies suggest even greater volumes of basaltic magma were trapped at deep crustal levels. This process, whereby dense basaltic magma crystallizes near the base of the crust, is sometimes called underplating. This may be an important mechanism of crustal growth, but with few samples from this region, the overall importance of this process is difficult to evaluate.

Continental rifts can also be sites of voluminous eruption of basaltic magma. A well-documented example is the Proterozoic Keweenaw or Mid-Continent Rift of the US, which formed some 1 to 1.2 Ga ago. Though now mostly covered by Phanerozoic sediments, where it is exposed the rift consists of a trough 150 km wide and 1500 km long filled with up to 15 km of volcanics, primarily basalt, and clastic sediments derived from them. Modern examples of continental rifts include the Rio Grande Rift of New Mexico and the East African Rift. Rift volcanism could also produce significant underplating.

11.6.5 Refining the continental crust

Regardless of tectonic environment, nearly all mantle-derived magmas are mafic in composition: typically they are basaltic, but perhaps under circumstances of low pressure and high water content, mantle melting can yield basaltic or high-magnesian andesites. Even these rare mantle-derived andesites are notably poorer in SiO_2 and generally richer in MgO and FeO than the continental crust compositions listed in Table 11.11. While andesites do

predominate among subduction zone magmas, they are products of fractional crystallization of basaltic parents. If the continental crust has been produced by partial melting of the mantle, why then is it not basaltic in composition, as is the oceanic crust? Rudnick and Gao (2003) considered four possibilities:

1. Magmas have already evolved to andesitic composition by the time they cross the crust–mantle boundary (the Moho). The complementary mafic cumulates are left behind in the upper mantle. However, peridotite xenoliths from the upper mantle are predominantly restitic peridotite, not cumulates; hence this idea is not supported by observation.
2. Lower crustal floundering, or delamination, may occur when continental crust is thickened in compressional environments, such as convergent plate boundaries. The mafic lower crust is transformed into eclogite, which is denser than the underlying mantle. This process would preferentially remove the mafic part of the crust, leaving a residual crust that consequently becomes more silicic. A related process, not considered by Rudnick and Gao (2003) is subduction erosion. Lower crust is also somewhat more likely to be removed by subduction erosion than upper crust, but not to the extent of crustal floundering.
3. Preferential loss of Mg and Ca from continents by weathering and erosion. Mg is then taken up by the oceanic crust during hydrothermal alteration; Ca is precipitated as carbonate sediment. Both are returned to the mantle by subduction.
4. Under hotter conditions of the Archean, melting of subducting oceanic crust may have been much more common, giving rise to silicic melting, particularly the trondhjemite, tonalite, and granodiorite suites common to the Archean. However, Taylor and McLennan's (1985) estimate of Archean crustal composition is slightly more mafic than their estimate of present composition, which is inconsistent with this idea.

At present, the question of how the continental crust has evolved to obtain its present composition is still unresolved. This is thus clearly a fruitful area for future research.

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PROBLEMS

1. Assuming the Earth has a CI chondritic composition (Table 10.2), and using the values for the mass of the core and the mass of the mantle + crust in Table 11.1, calculate what the concentrations of Re, Ir, Mo, and Ag should be in the bulk silicate Earth if the core formed by an equilibrium process, when the silicate/metal partition coefficients are 5×10^{-4} , 5×10^{-5} , 8×10^{-4} , and 0.01, respectively. Compare your results with the primitive mantle and core values in Tables 11.3 and 11.4.

2. Calculate new bulk silicate Earth concentrations of Re, Ir, Mo, and Ag by adding 1% CI chondritic material to your results from Problem 1. Again compare these results with primitive mantle values of Table 11.3.
3. Assume that the bulk silicate Earth has a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7035, an initial ratio equal to BABI (0.69897) and an age of 4.45 Ga.
 - (a) Calculate the bulk silicate Earth $^{87}\text{Rb}/^{86}\text{Sr}$ ratio.
 - (b) Using your result in (a) and assuming that ^{86}Sr is 9.86% of Sr and ^{87}Rb is 27.83% of Rb (by mass), what is the bulk Earth Rb/Sr ratio?
4. Suppose a rising mantle plume is 220°C hotter than surrounding mantle and that the γ -olivine–Mg-perovskite transition occurs at 660 km depth in the surrounding mantle. Assume a homogenous mantle density of 3.5 g/cc at 660 km and above and the Clapeyron slope mentioned in section 11.2.4.2. At what depth does the γ -olivine–Mg-perovskite transition occur within the mantle plume?
5. Whether the γ -olivine–Mg-perovskite transition is endothermic or exothermic will affect mantle convection (i.e., sinking of lithospheric slabs, rise of mantle plumes). Discuss why this is so, explaining the effects of both endothermic and exothermic phase transitions on rising mantle plumes and sinking lithospheric slabs.
6. Use a mass balance approach and equations 11.22 through 11.28 to calculate the Nd concentration of the mantle depleted by continent formation (DMM). Take the initial and present chondritic $^{143}\text{Nd}/^{144}\text{Nd}$ ratios to be 0.506677 and 0.512638, the ϵ_{Nd} of the Earth to be +3.1, ϵ_{Nd} of the depleted mantle to be +9, the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the continental crust to be 0.123, and the average age of the continents (T) to be 2.0 Ga. Use the Nd concentrations of the silicate Earth and the continental crust given in Tables 11.4 and 11.11.

Chapter 12

Organic geochemistry, the carbon cycle, and climate

12.1 INTRODUCTION

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

In this chapter, we begin with a brief review of some basic biology and organic chemistry.

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

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

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

12.2 A BRIEF BIOLOGICAL BACKGROUND

Living organisms are the ultimate source of most, but not all, organic compounds in the environment. While life forms are extremely varied, the basic principles of cell operation are the same in all organisms. For example, all derive the energy they require through oxidation of organic compounds, all contain DNA (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 still find any one of several in biological textbooks. Figure 12.1 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*. The first two of these kingdoms consist only of simple unicellular organisms; all other organisms, including all multicellular organisms, are eukaryotes. Eubacteria and archeobacteria are collectively

called *prokaryotes*. They are distinguished from eukaryotes in that their DNA is not contained within a membrane-bound nucleus as is the case with eukaryotes; rather, the DNA of prokaryotes is simply concentrated within one or more regions, called nucleoids, of intracellular fluid, or cytoplasm (a protein solution). In contrast, the DNA of eukaryotes is contained within the cell nucleus, usually organized into chromosomes. In both eukaryotes and prokaryotes, messenger RNA (mRNA) 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 10 μm , and are therefore much larger than prokaryotes, which generally have largest dimensions of 1 μm 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 het-

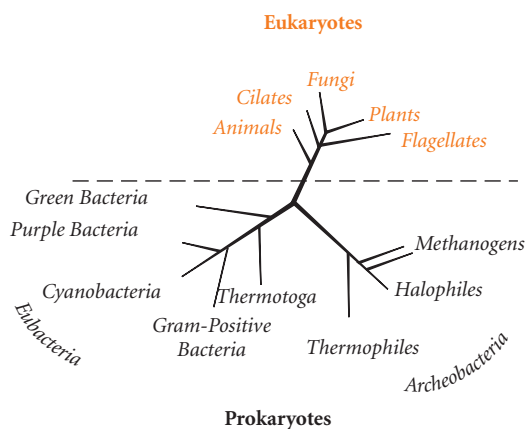


Figure 12.1 Phylogenetic relationships among organisms. The eubacteria and the archeobacteria constitute the prokaryotes; all other organisms are eukaryotes.

erotrophs. 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 is pathogenic. All chemosynthetic organisms are prokaryotes, as are most organisms capable of living without free oxygen (anaerobes). Archeobacteria may be found in extremely hostile environments such as saline lakes and fumaroles. Prokaryotes play the most important roles in converting the chemical products of life to organic substances found in sediments (“geopolymers”) and soils; thus they are of particular interest in geochemistry. Some prokaryotes reduce sulfate, others oxidize sulfide, some produce methane, while others consume it. Some bacteria reduce nitrogen to ammonia, a process called nitrogen fixation, others oxidize ammonia to nitrate (nitrification), and 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, synthesizes a number of essential nutrients that are then assimilated through intestinal walls. On the whole, bacteria, and more generally the unicellular organisms, or *microbes*, play a much more important role in biogeochemical cycling and geochemical processes than do the metazoans.

12.3 ORGANIC COMPOUNDS AND THEIR NOMENCLATURE

Organic chemistry can be an intimidating subject involving a bewildering array of compounds, and names for each, whose properties depend as much on the details of their structures as on their composition. A complex nomenclature of organic chemistry has evolved because simply referring to an organic compound by its chemical formula is not sufficient to identify the compound. Compositionally identical compounds can have different structures and different properties. This is, of course, true of inorganic compounds as well, for example, quartz and tri-

dymite or graphite and diamond, but isomers (i.e., compositionally identical but structurally distinct compounds) are particularly common among organic compounds. Organic nomenclature is in some sense a language unto itself. Like any language, organic nomenclature has a “grammar”. Once this grammar is mastered, the exact composition and structure of a compound can be communicated through its name alone. We will need to concern ourselves with only a part of that language.

We will make one simplification in the brief review of organic chemistry that follows: we will ignore the phenomenon known as *stereoisomerism*. Organic compounds that are otherwise structurally identical but are mirror images of one another are said to be *stereoisomers*. The difference in physical properties of stereoisomers can be quite small, no more than rotation of the plane of polarized light in an opposite sense, but the difference is often biochemically important. Stereoisomerism is usually less important from a geochemical perspective (but see Example 5.3), so in the interests of clarity, we will not discuss it further.

12.3.1 Hydrocarbons

Hydrocarbons are the simplest group of organic compounds in that they consist only of 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* hydrocarbons or *aliphatic* hydrocarbons, also called *paraffins*, or *alkanes*, which consist of a straight or branched chain of carbon and hydrogen atoms. If they are unbranched, they 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 3, and butane 4. 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

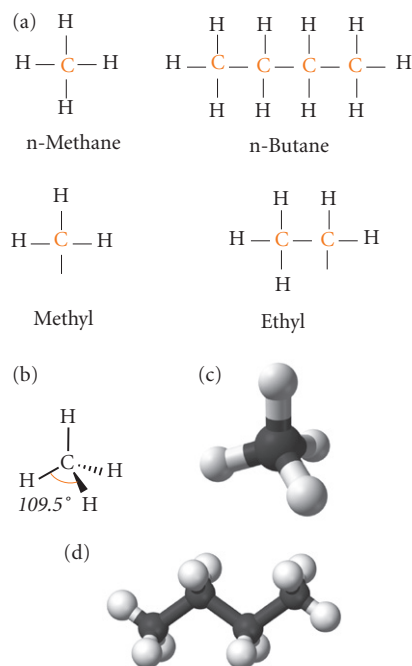


Figure 12.2 (a) Simple *n*-alkanes or chain hydrocarbons. The suffix “-ane” is used to refer to molecules and the suffix “-yl” is used to refer to equivalent radicals formed by removing a hydrogen. (b) A stereochemistry illustration of the methane molecule, showing the 109.5° angle between H-C-H bonds. The solid wedge indicates a bond coming out of the paper toward the viewer, a hashed wedge is one pointing away from the viewer, and a straight line is a bond in the plane of the paper. (c) Stick-drawing illustration of methane. (d) Stick illustration of *n*-butane.

removing a hydrogen from a terminal carbon are named by replacing the “-ane” suffix with “-yl”, e.g., methyl, butyl. As a group, the radicals formed from alkanes in this way are called *alkyls* (and thus the group name also conforms to the naming convention).

Alkanes are not, however, actually straight chains, although they are often represented that way, as they are Figure 12.2a, which shows methane and butane with bonds drawn as right angles. Figure 12.2b provides a “stereochemistry” illustration of methane, showing that the bond angles between hydrogens are actually 109.5°, not 90°. Figures 12.2c and d

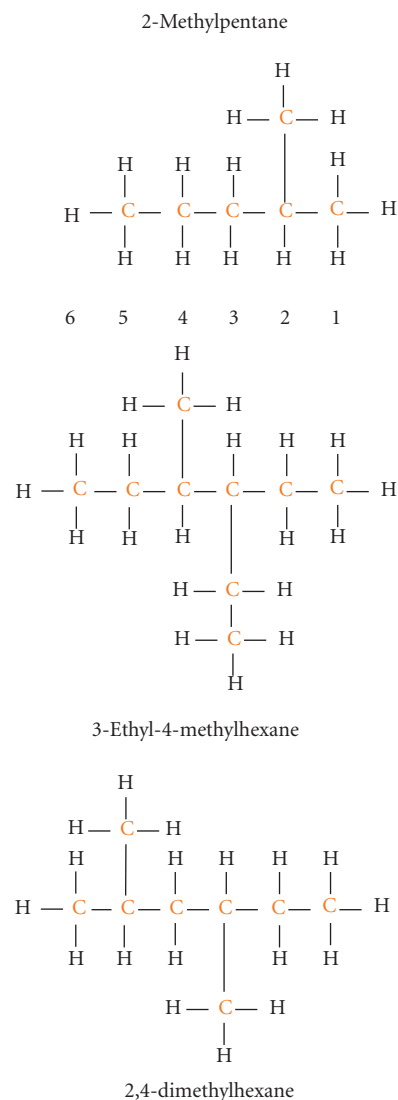


Figure 12.3 Some simple and branched hydrocarbon chains.

shows stick model illustrations of the methane and *n*-butane molecules.

Replacing one of the hydrogens with a carbon atom, to which additional hydrogens are attached, forms branched chains. 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 2-methylpentane (Figure 12.3). If more than one secondary group is attached, the groups are listed in alphabetical order, for

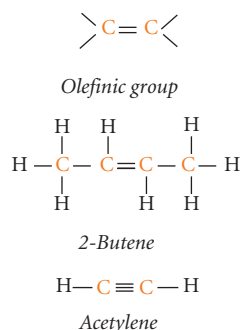


Figure 12.4 Some simple doubly and triply-bonded hydrocarbons.

example, 3-ethyl-4-methylhexane shown in Figure 12.3. 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 12.3.

Compounds where all carbon atoms have single bonds to 4 other atoms are said to be *saturated* hydrocarbons (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* hydrocarbons. Unsaturated, unbranched acyclic hydrocarbons having one double bond are named by replacing the suffix “-ane” by “-ene”, for example, 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 12.4. If there are more than two double bonds the ending becomes “-adiene”, “-atriene”, and so on. Generic names are *alkene*, *alkadiene*, for example. Triple carbon bonds are also possible, in which case the suffix becomes “-yne” for a single triple bond. Acetylene* (Figure 12.4) is an example of a compound containing triply bonded carbon. Particularly stable compounds result when carbon bonds are *conjugated*, that is, alter-

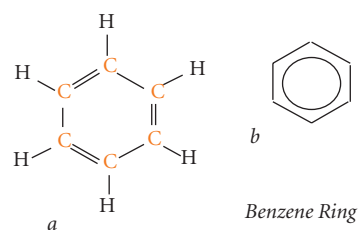


Figure 12.5 Two representations of the benzene ring, the foundation of aromatic hydrocarbons. In (b) the C and H atoms have been removed for clarity. Since all carbon-carbon bonds in the benzene ring are equivalent, (b) is actually a better representation than (a).

nately singly and doubly bonded, for example, $-\text{C}=\text{C}-\text{C}=\text{C}-$.

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 six conjugately bonded (i.e., alternating single and double bonds) carbon atoms lying in a single plane (Figure 12.5). Compounds based on this structure are particularly stable and are referred to as *aromatic*.† Representation of this structure as alternating single and double bonds is not entirely accurate. The carbon-carbon bond in a saturated alkane such as ethane is 1.54 Å in length; the double bond in ethylene is 1.33 Å in length. All carbon-carbon bonds in the benzene ring are found to be intermediate in length (1.40 Å). Thus bonding is delocalized, that is, all carbon-carbon bonds in the ring are of approximately equal strength and the double bonds appear to be shared among all carbon atoms in the ring. This delocalization is responsible for the particular stability of this structure. Several rings may be joined to form *polyaromatic units*.

* 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 naming conventions were developed, is an example of such an irregular term.

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

12.3.2 Functional groups

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

The most important functional groups are summarized in Figure 12.6. 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 $(\text{CH}_2\text{O})_n$. They are either aliphatic hydrocarbons or cyclic hydrocarbons in which some hydrogens have been replaced by OH. The carbonyl group ($\text{C}=\text{O}$) forms aldehydes when the “R” in Figure 12.6 is H, ketones when “R” is either an aliphatic or aromatic group,

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

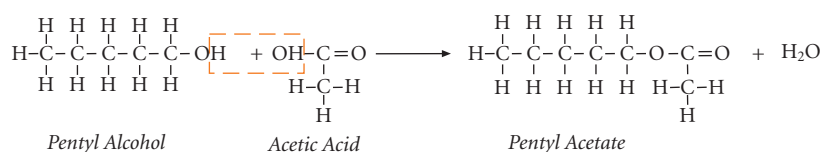
Figure 12.6 Important functional groups found in organic compounds.

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, methanoic acid is a carboxyl group with an attached H, ethanoic acid is a carboxyl group with an attached CH_3 , and 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*, while 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* (e.g., salicylic acid illustrated in Figure 12.7). 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.

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 is 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:



* Such a reaction, in which two molecules combine to form a larger molecule with the elimination of a small molecule (H_2O in this case), is called a condensation reaction or simply *condensation*. The reverse of this reaction is termed *hydrolysis*.

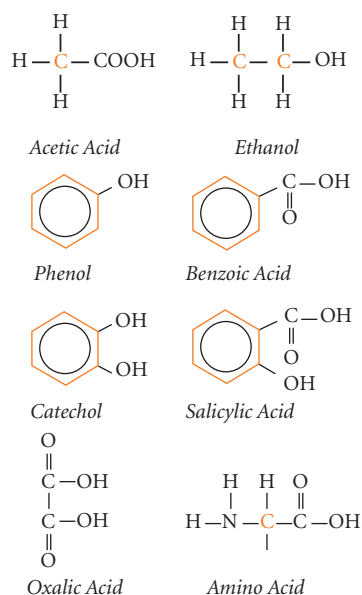


Figure 12.7 Some examples of compounds formed by substituting functional groups for hydrogen in basic hydrocarbon structures.

Another geologically and biologically important functional group is the *amino group*, NH_2 (the name being derived from ammonia, NH_3). *Amino acids*, the building blocks of proteins, consist of molecules containing both amino and carboxylic groups. Other important functional groups include the carbonyl group, consisting of a carbon that is double-bonded to oxygen, and thiol groups, where S replaces O in the OH group (i.e., SH). Figure 12.7 illustrates a few of the important compounds formed by replacement of hydrogen in basic hydrocarbons by one or more of these functional groups.

Organic compounds can contribute significantly to the pH balance of natural waters. The acid-base properties of organic compounds depend upon 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.

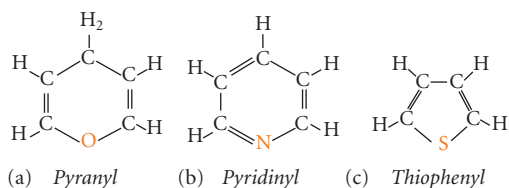


Figure 12.8 Examples of functional groups formed by replacing one carbon atom in the cyclic skeleton with atoms of O, N, and S. The names of the resulting compounds are (a) pyranyl, (b) pyridinyl, and (c) thiophenyl.

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

It is also possible to substitute other elements for carbon in the basic hydrocarbon structure; such atoms are known as *heteroatoms*. Examples are illustrated in Figure 12.8. 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.

12.3.3 Short-hand notations of organic molecules

For both aliphatic and cyclic molecules, the number of carbons in the ring or chain is commonly denoted with C followed by a subscript corresponding to the number of carbons, such as C_6 for hexane. It is often convenient to use this notation in condensed structural formulae of long-chained aliphatic compounds. The basic repeating unit of such chains is CH_2 . The number of repetitions can be expressed by enclosing the CH_2 in parentheses followed by a subscript indicating the number or repetitions, for example $(\text{CH}_2)_6$. Groups placed on the ends then precede and follow. Thus, for example, stearic acid, a fatty acid consisting of a 17-carbon chain with a

hydrogen on one end and a carboxyl group on the other, can be denoted as $\text{CH}_3(\text{CH}_2)_{16}\text{C}(\text{O})\text{OH}$. If a double carbon bond occurs, this is designated by $\text{CH}=\text{CH}$ inserted at the appropriate place. Thus palmitoleic acid, a common unsaturated fatty acid with the formula $\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{C}(\text{O})\text{OH}$ is a 15-carbon aliphatic compound with an olefinic unit between the 7th and 8th carbons, a H on one end, and a carboxyl acid group on the other. If an attached group occurs in the middle part of the chain, then the formula for the group is inserted in parentheses after the appropriate number of repetitions of the CH_2 unit, and a second $(\text{CH}_2)_n$ follows, n indicating the number of subsequent repetitions. Thus the formula for 3-methylhexane would be $\text{CH}_3(\text{CH}_2)_2(\text{CH}_3)(\text{CH}_2)_2\text{CH}_3$.

There are also several conventions for illustrating the structure of organic molecules. We have already seen one: the hexagon with an enclosed circle to denote the benzene ring (Figure 12.5). As in this illustration, carbons and hydrogens bonded to them are often omitted from representations of organic molecules. We infer a carbon at each bend of the line as well as hydrogens bonded to it. A similar shorthand may be used for aliphatic molecules as well, as illustrated in Figure 12.9. 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 of hydrogens is easily deduced as 4 minus the number of other bonds shown.

12.3.4 Biologically important organic compounds

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

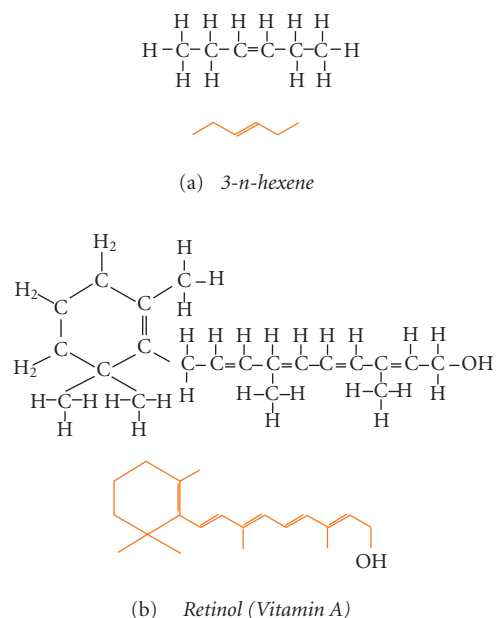


Figure 12.9 Short-hand structural representation of 3-*n*-hexene and retinol. Carbon and hydrogen atoms are not shown in the short-hand representations. Carbons occur at each joint in the lines as well as at ends of lines. Number of hydrogens bonded to each carbon is equal to 4 minus the number of other bonds shown.

review the chemistry of these biologically important compounds.

12.3.4.1 Carbohydrates

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

Carbohydrates, as we mentioned earlier, are related to hydrocarbons by substitution of