CHAPTER 1

Where It All Comes From

Since the earliest times, humans have sought for better materials to use in fabricating the objects they needed. Early humans satisfied many requirements by gathering plants for food and fiber, and they used wood to make early tools and shelter. Stone and native metals, especially copper, were also used to make tools and weapons. The materials that represented the dominant technology employed to fabricate useful objects generally identify the ages of humans in history. The approximate time periods corresponding to these epochs are designated as follows:

<table>
<thead>
<tr>
<th>Early</th>
<th>Late</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stone Age</td>
<td>Copper Age</td>
</tr>
</tbody>
</table>

? → 4500 BC → 3000 BC → 1200 BC → 900 BC → 600 BC

The biblical Old Testament period overlaps with the Copper, Bronze, and Iron Ages, so it is natural that these metals are mentioned frequently in the Bible and in other ancient manuscripts. For example, iron is mentioned about 100 times in the Old Testament, copper 8 times, and bronze more than 150 times. Other metals that were easily obtained (tin and lead) are also described numerous times. In fact, production of metals has been a significant factor in technology and chemistry for many centuries. Processes that are crude by modern standards were used many centuries ago to produce the desired metals and other materials, but the source of raw materials was the same then as it is now. In this chapter, we will present an overview of inorganic chemistry to show its importance in history and to relate it to modern industry.

1.1 The Structure of the Earth

There are approximately 16 million known chemical compounds, the majority of which are not found in nature. Although many of the known compounds are of little use or importance, some of them would be difficult or almost impossible to live without. Try to visualize living in a world without concrete, synthetic fibers, fertilizer, steel, soap, glass, or plastics. None of these materials is found in nature in the form in which it is used, yet they are all produced from naturally occurring raw materials. All of the items listed and an enormous number of others are created by chemical processes. But created from what?
It has been stated that chemistry is the study of matter and its transformations. One of the major objectives of this book is to provide information on how the basic raw materials from the earth are transformed to produce inorganic compounds that are used on an enormous scale. It focuses attention on the transformations of a relatively few inorganic compounds available in nature into many others whether or not they are at present economically important. As you study this book, try to see the connection between obtaining a mineral by mining and the reactions that are used to convert it into end use products. Obviously, this book cannot provide the details for all such processes, but it does attempt to give an overview of inorganic chemistry and its methods and to show its relevance to the production of useful materials. Petroleum and coal are the major raw materials for organic compounds, but the transformation of these materials is not the subject of this book.

As it has been for all time, the earth is the source of all of the raw materials used in the production of chemical substances. The portion of the earth that is accessible for obtaining raw materials is that portion at the surface and slightly above and below the surface. This portion of the earth is referred to in geological terms as the earth’s crust. For thousands of years, humans have exploited this region to gather stone, wood, water, and plants. In more modern times, many other chemical raw materials have been taken from the earth and metals have been removed on a huge scale. Although the techniques have changed, we are still limited in access to the resources of the atmosphere, water, and, at most, a few miles of depth in the earth. It is the materials found in these regions of the earth that must serve as the starting materials for all of our chemical processes.

Because we are at present limited to the resources of the earth, it is important to understand the main features of its structure. Our knowledge of the structure of the earth has been developed by modern geoscience, and the gross features shown in Figure 1.1 are now generally accepted. The distances shown are approximate, and they vary somewhat from one geographical area to another.

The region known as the upper mantle extends from the surface of the earth to a depth of approximately 660 km (400 mi). The lower mantle extends from a depth of about 660 km to about 3000 km (1800 mi). These layers consist of many substances, including some compounds that contain metals, but rocks composed of silicates are the dominant materials. The upper mantle is sometimes subdivided into the lithosphere, extending to a depth of approximately 100 km (60 mi), and the asthenosphere, extending from approximately 100 km to about 220 km (140 mi). The solid portion of the earth’s crust is regarded as the lithosphere, and the hydrosphere and atmosphere are the liquid and gaseous regions, respectively. In the asthenosphere, the temperature and pressure are higher than in the lithosphere. As a result, it is generally believed that the asthenosphere is partially molten and softer than the lithosphere lying above it.

The core lies farther below the mantle, and two regions constitute the earth’s core. The outer core extends from about 3000 km (1800 mi) to about 5000 km (3100 mi), and it
consists primarily of molten iron. The inner core extends from about 5000 km to the center of the earth about 6500 km (4000 mi) below the surface, and it consists primarily of solid iron. It is generally believed that both core regions contain iron mixed with other metals, but iron is the major component.

The velocity of seismic waves shows unusual behavior in the region between the lower mantle and the outer core. The region where this occurs is at a much higher temperature than is the lower mantle, but it is cooler than the core. Therefore, the region has a large temperature gradient, and its chemistry is believed to be different from that of either the core or mantle. Chemical substances that are likely to be present include metallic oxides such as magnesium oxide and iron oxide, as well as silicon dioxide, which is present as a form of quartz known as stishovite that is stable at high pressure. This is a region of very high pressure with estimates being as high as perhaps a million times that of the atmosphere. Under the conditions of high temperature and pressure, metal oxides react with...
SiO$_2$ to form compounds such as MgSiO$_3$ and FeSiO$_3$. Materials that are described by the formula (Mg,Fe)SiO$_3$ (where (Mg,Fe) indicates a material having a composition intermediate between the formulas noted earlier) are also produced.

1.2 Composition of the Earth’s Crust

Most of the elements shown in the periodic table are found in the earth’s crust. A few have been produced artificially, but the rocks, minerals, atmosphere, lakes, and oceans have been the source of the majority of known elements. The abundance by mass of several elements that are major constituents in the earth’s crust is shown in Table 1.1.

Elements such as chlorine, lead, copper, and sulfur occur in very small percentages, and although they are of great importance, they are relatively minor constituents. We must remember that there is a great difference between a material being present and it being recoverable in a way that is economically practical. For instance, throughout the millennia, gold has been washed out of the earth and transported as minute particles to the oceans. However, it is important to understand that although the oceans are believed to contain billions of tons of gold, there is at present no feasible way to recover it. Fortunately, compounds of some of the important elements are found in concentrated form in specific localities, and as a result they are readily accessible. It may be surprising to learn that even coal and petroleum that are used in enormous quantities are relatively minor constituents of the lithosphere. These complex mixtures of organic compounds are present to such a small extent that carbon is not among the most abundant elements. However, petroleum and coal are found concentrated in certain regions, so they can be obtained by economically acceptable means. It would be quite different if all the coal and petroleum were distributed uniformly throughout the earth’s crust.

1.3 Rocks and Minerals

The chemical resources of early humans were limited to the metals and compounds on the earth’s surface. A few metals (e.g., copper, silver, and gold) were found uncombined (native) in nature, so they have been available for many centuries. It is believed that the iron first used may have been found as uncombined iron that had reached the earth in the form of meteorites. In contrast, elements such as fluorine and sodium are produced by electrochemical reactions, and they have been available a much shorter time.

Table 1.1: Abundances of Elements by Mass

<table>
<thead>
<tr>
<th>Element</th>
<th>O</th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Ca</th>
<th>Na</th>
<th>K</th>
<th>Mg</th>
<th>H</th>
<th>All others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage</td>
<td>49.5</td>
<td>25.7</td>
<td>7.5</td>
<td>4.7</td>
<td>3.4</td>
<td>2.6</td>
<td>2.4</td>
<td>1.9</td>
<td>0.9</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Most metals are found in the form of naturally occurring chemical compounds called minerals. An ore is a material that contains a sufficiently high concentration of a mineral to constitute an economically feasible source from which the metal can be recovered. Rocks are composed of solid materials that are found in the earth’s crust, and they usually contain mixtures of minerals in varying proportions. Three categories are used to describe rocks based on their origin. Rocks that were formed by the solidification of a molten mass are called igneous rocks. Common examples of this type include granite, feldspar, and quartz. Sedimentary rocks are those that formed from compacting of small grains that have been deposited as a sediment in a river bed or sea, and they include such common materials as sandstone, limestone, and dolomite. Rocks that have had their composition and structure changed over time by the influences of temperature and pressure are called metamorphic rocks. Some common examples are marble, slate, and gneiss.

The lithosphere consists primarily of rocks and minerals. Some of the important classes of metal compounds found in the lithosphere are oxides, sulfides, silicates, phosphates, and carbonates. The atmosphere surrounding the earth contains oxygen, so several metals such as iron, aluminum, tin, magnesium, and chromium are found in nature as the oxides. Sulfur is found in many places in the earth’s crust (particularly in regions where there is volcanic activity), so some metals are found combined with sulfur as metal sulfides. Metals found as sulfides include copper, silver, nickel, mercury, zinc, and lead. A few metals, especially sodium, potassium, and magnesium, are found as the chlorides. Several carbonates and phosphates occur in the lithosphere, and calcium carbonate and calcium phosphate are particularly important minerals.

### 1.4 Weathering

Conditions on the inside of a rock may be considerably different from those at the surface. Carbon dioxide can be produced by the decay of organic matter, and an acid-base reaction between CO₂ and metal oxides produces metal carbonates. Typical reactions of this type are the following:

\[
\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \quad (1.1)
\]

\[
\text{CuO} + \text{CO}_2 \rightarrow \text{CuCO}_3 \quad (1.2)
\]

Moreover, because the carbonate ion can react as a base, it can remove H⁺ from water to produce hydroxide ions and bicarbonate ions by the reaction

\[
\text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{OH}^- \quad (1.3)
\]

Therefore, as an oxide mineral “weathers,” reactions of CO₂ and water at the surface lead to the formation of carbonates and bicarbonates. The presence of OH⁻ can eventually cause
part of the mineral to be converted to a metal hydroxide. Because of the basicity of the oxide ion, most metal oxides react with water to produce hydroxides. An important example of such a reaction is

$$\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$$  \hspace{1cm} (1.4)

As a result of reactions such as these, processes in nature may convert a metal oxide to a metal carbonate or a metal hydroxide. A type of compound closely related to carbonates and hydroxides is known as a basic metal carbonate, and these materials contain both carbonate ($\text{CO}_3^{2-}$) and hydroxide ($\text{OH}^-$) ions. A well-known material of this type is $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ or $\text{Cu}_2\text{CO}_3(\text{OH})_2$, which is the copper-containing mineral known as *malachite*. Another mineral containing copper is *azurite*, which has the formula $2 \text{CuCO}_3 \cdot \text{Cu(OH)}_2$ or $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, so it is quite similar to malachite. Azurite and malachite are frequently found together because both are secondary minerals produced by weathering processes. In both cases, the metal oxide, CuO, has been converted to a mixed carbonate/hydroxide compound. This example serves to illustrate how metals are sometimes found in compounds having unusual but closely related formulas. It also shows why ores of metals frequently contain two or more minerals containing the same metal.

Among the most common minerals are the feldspars and clays. These materials have been used for centuries in the manufacture of pottery, china, brick, cement, and other materials. Feldspars include the mineral *orthoclase*, $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, but this formula can also be written as $\text{K}_2\text{Al}_2\text{Si}_6\text{O}_{16}$. Under the influence of carbon dioxide and water, this mineral weathers by a reaction that can be shown as

$$\text{K}_2\text{Al}_2\text{Si}_6\text{O}_{16} + 3\text{H}_2\text{O} + 2\text{CO}_2 \rightarrow \text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O} + 2\text{KHCO}_3 + 4\text{SiO}_2$$  \hspace{1cm} (1.5)

The product, $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, is known as *kaolinite*, and it is one of the aluminosilicates that constitutes clays used in making pottery and china. This example also shows how one mineral can be converted into another by the natural process of weathering.

### 1.5 Obtaining Metals

Because of their superior properties, metals have received a great deal of attention since the earliest times. Their immense importance now as well as throughout history indicates that we should describe briefly the processes involved in the production and use of metals. The first metal to be used extensively was copper because of its being found uncombined, but most metals are found combined with other elements in minerals. Minerals are naturally occurring compounds or mixtures of compounds that contain chemical elements. As we have mentioned, a mineral may contain some desired metal, but it may not be available in sufficient quantity and purity to serve as a useful source of the metal. A commercially usable source of a desired metal is known as an ore.
Most ores are obtained by mining. In some cases, ores are found on or near the surface, making it possible for them to be obtained easily. To exploit an ore as a useful source of a metal, a large quantity of the ore is usually required. Two of the procedures still used today to obtain ores have been used for centuries. One of these methods is known as *open pit mining*, and in this technique the ore is recovered by digging in the earth’s surface. A second type of mining is *shaft mining*, in which a shaft is dug into the earth to gain access to the ore below the surface. Coal and the ores of many metals are obtained by both of these methods. In some parts of the United States, huge pits can be seen where the ores of copper and iron have been removed in enormous amounts. In other areas, the evidence of strip mining coal is clearly visible. Of course, the massive effects of shaft mining are much less visible.

Although mechanization makes mining possible on an enormous scale today, mining has been important for millennia. We know from ancient writings such as the Bible that mining and refining of metals have been carried out for thousands of years (for example, see Job, Chapter 28). Different types of ores are found at different depths, so both open pit and shaft mining are still in common use. Coal is mined by both open pit (strip mining) and shaft methods. Copper is mined by the open pit method in Arizona, Utah, and Nevada, and iron is obtained in this way in Minnesota.

After the metal-bearing ore is obtained, the problem is how to obtain the metal from the ore. Frequently, an ore may not have a high enough content of the mineral containing the metal to use it directly. The ore usually contains varying amounts of other materials (rocks, dirt, etc.), which is known as *gangue* (pronounced “gang”). Before the mineral can be reduced to produce the free metal, the ore must be concentrated. Today, copper ores containing less than 1% copper are processed to obtain the metal. In early times, concentration consisted of simply picking out the pieces of the mineral by hand. For example, copper-containing minerals are green in color, so they were easily identified. In many cases, the metal may be produced in a smelter located far from the mine. Therefore, concentrating the ore at the mine site saves on transportation costs and helps prevent the problems associated with disposing of the gangue at the smelting site.

The remaining gangue must be removed, and the metal must be reduced and purified. These steps constitute the procedures referred to as *extractive metallurgy*. After the metal is obtained, a number of processes may be used to alter its characteristics of hardness, workability, and other factors. The processes used to bring about changes in properties of a metal are known as *physical metallurgy*.

The process of obtaining metals from their ores by heating them with reducing agents is known as *smelting*. Smelting includes the processes of concentrating the ore, reducing the metal compound to obtain the metal, and purifying the metal. Most minerals are found mixed with a large amount of rocky material that usually is composed of silicates.
In fact, the desired metal compound may be a relatively minor constituent in the ore. Therefore, before further steps to obtain the metal can be undertaken, the ore must be concentrated. Several different procedures are useful to concentrate ores depending on the metal.

The flotation process consists of grinding the ore to a powder and mixing it with water, oil, and detergents (wetting agents). The mixture is then beaten into a froth. The metal ore is concentrated in the froth so it can be skimmed off. For many metals, the ores are more dense than the silicate rocks, dirt, and other material that contaminate them. In these cases, passing the crushed ore down an inclined trough with water causes the heavier particles of ore to separate from the gangue.

Magnetic separation is possible in the case of the iron ore taconite. The major oxide in taconite is \( \text{Fe}_3\text{O}_4 \) (this formula also represents \( \text{FeO}\cdot\text{Fe}_2\text{O}_3 \)), which is attracted to a magnet. The \( \text{Fe}_3\text{O}_4 \) can be separated from most of the gangue by passing the crushed ore on a conveyor under a magnet. During the reduction process, removal of silicate impurities can also be accomplished by the addition of a material that forms a compound with them. When heated at high temperatures, limestone, \( \text{CaCO}_3 \), reacts with silicates to form a molten slag that has a lower density than the molten metal. The molten metal can be drained from the bottom of the furnace or the floating slag can be skimmed off the top.

After the ore is concentrated, the metal must be reduced from the compound containing it. Production of several metals will be discussed in later chapters of this book. However, a reduction process that has been used for thousands of years will be discussed briefly here. Several reduction techniques are now available, but the original procedure involved reduction of metals using carbon in the form of charcoal. When ores containing metal sulfides are heated in air (known as roasting the ore), they are converted to the metal oxides. In the case of copper sulfide, the reaction is

\[
2 \text{CuS} + 3 \text{O}_2 \rightarrow 2 \text{CuO} + 2 \text{SO}_2
\]  

(1.6)

In recent years, the \( \text{SO}_2 \) from this process has been trapped and converted into sulfuric acid. Copper oxide can be reduced using carbon as the reducing agent in a reaction that can be represented by the following equation:

\[
\text{CuO} + \text{C} \rightarrow \text{Cu} + \text{CO}
\]  

(1.7)

For the reduction of \( \text{Fe}_2\text{O}_3 \), the equation can be written as

\[
\text{Fe}_2\text{O}_3 + 3 \text{C} \rightarrow 2 \text{Fe} + 3 \text{CO}
\]  

(1.8)

Because some metals are produced in enormous quantities, it is necessary that the reducing agent be readily available in large quantities and be inexpensive. Consequently, carbon is used as the reducing agent. When coal is heated strongly, volatile organic compounds are
driven off and carbon is left in the form of coke. This is the reducing agent used in the production of several metals.

Extractive metallurgy today involves three types of processes. Pyrometallurgy refers to the use of high temperatures to bring about smelting and refining of metals. Hydrometallurgy refers to the separation of metal compounds from ores by the use of aqueous solutions. Electrometallurgy refers to the use of electricity to reduce the metal from its compounds.

In ancient times, pyrometallurgy was used exclusively. Metal oxides were reduced by heating them with charcoal. The ore was broken into small pieces and heated in a stone furnace on a bed of charcoal. Remains of these ancient furnaces can still be observed in areas of the Middle East. Such smelting procedures are not very efficient, and the rocky material remaining after removal of the metal (known as slag) contained some unrecovered metal. Slag heaps from ancient smelting furnaces show clearly that copper and iron smelting took place in the region of the Middle East known as the Arabah many centuries ago. Incomplete combustion of charcoal produces some carbon monoxide,

\[2 \text{C} + \text{O}_2 \rightarrow 2 \text{CO}\] (1.9)

and carbon monoxide may also cause the reduction of some of the metal oxide as shown in these reactions:

\[\text{Cu}_2\text{O} + \text{CO} \rightarrow 2 \text{Cu} + \text{CO}_2\] (1.10)

\[\text{Fe}_2\text{O}_3 + 3 \text{CO} \rightarrow 2 \text{Fe} + 3 \text{CO}_2\] (1.11)

Carbon monoxide is also an effective reducing agent in the production of metals today.

Because of its ease of reduction, copper was the earliest metal smelted. It is believed that the smelting of copper took place in the Middle East as early as about 2500 to 3500 BC. Before the reduction was carried out in furnaces, copper ores were probably heated in wood fires at a much earlier time. The metal produced in a fire or a crude furnace was impure so it had to be purified. Heating some metals to melting causes the remaining slag (called dross) to float on the molten metal where it can be skimmed off or the metal can be drained from the bottom of the melting pot. The melting process, known as cupellation, is carried out in a crucible or “fining” pot. Some iron refineries at Tel Jemmeh have been dated from about 1200 BC, the early Iron Age. The reduction of iron requires a higher temperature than that for the reduction of copper, so smelting of iron occurred at a later time.

Although copper may have been used for perhaps 8000 to 10,000 years, the reduction of copper ores to produce the metal has been carried out since perhaps 4000 BC. The reduction of iron was practiced by about 1500 to 2000 BC (the Iron Age). Tin is easily reduced, and somewhere in time between the use of charcoal to reduce copper and iron, the
reduction of tin came to be known. Approximately 80 elements are metals and approximately 50 of them have some commercial importance. However, there are hundreds of alloys that have properties that make them extremely useful for certain applications. The development of alloys such as stainless steel, magnesium alloys, and Duriron (an alloy of iron and silicon) has occurred in modern times. Around approximately 2500 BC, it was discovered that adding about 3% to 4% of tin to copper made an alloy that has greatly differing properties from those of copper alone. That alloy, bronze, became one of the most important materials, and its widespread use resulted in the Bronze Age. Brass is an alloy of copper and zinc. Although brass was known several centuries BC, zinc was not known as an element until 1746. It is probable that minerals containing zinc were found along with those containing copper, and reduction of the copper also resulted in the reduction of zinc producing a mixture of the two metals. It is also possible that some unknown mineral was reduced to obtain an impure metal without knowing that the metal was zinc. Deliberately adding metallic zinc reduced from other sources to copper to make brass would have been unlikely because zinc was not a metal known in ancient times and it is more difficult to reduce than copper.

After a metal is obtained, there remains the problem of making useful objects from the metal, and there are several techniques that can be used to shape the object. In modern times, rolling, forging, spinning, and other techniques are used to fabricate objects from metals. In ancient times, one of the techniques used to shape metals was by hammering the cold metal. Hammered metal objects have been found in excavations throughout the world.

Cold working certain metals causes them to become harder and stronger. For example, if a wire made of iron is bent to make a kink in it, the wire will break at that point after flexing it a few times. When a wire made of copper is treated in this way, flexing it a few times causes the wire to bend in a new location beside the kink. The copper wire does not break, and this occurs because flexing the copper makes it harder and stronger. In other words, the metal has had its properties altered by cold working it.

When a hot metal is shaped or “worked” by forging, the metal retains its softer, more ductile original condition when it cools. In the hot metal, atoms have enough mobility to return to their original bonding arrangements. The metal can undergo great changes in shape without work hardening occurring, which might make it unsuitable for the purpose intended. Cold working by hammering and hot-working (forging) of metal objects have been used for many centuries in the fabrication of metal objects.

1.6 Some Metals Today

Today, as in ancient times, our source of raw materials is the earth’s crust. However, because of our advanced chemical technology, exotic materials have become necessary for processes that are vital yet unfamiliar to most people. This is true even for students in
chemistry courses at the university level. For example, a chemistry student may know little about niobium or bauxite, but these materials are vital to our economy.

An additional feature that makes obtaining many inorganic materials so difficult is that they are not distributed uniformly in the earth’s crust. It is a fact of life that the major producers of niobium are Canada and Brazil, and the United States imports 100% of the niobium needed. The situation is similar for bauxite, major deposits of which are found in Brazil, Jamaica, Australia, and French Guyana. In fact, of the various ores and minerals that are sources of important inorganic materials, the United States must rely on other countries for many of them. Table 1.2 shows some of the major inorganic raw materials, their uses, and their sources.

<table>
<thead>
<tr>
<th>Material</th>
<th>Major Uses of Products</th>
<th>Sources</th>
<th>Percentage Imported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bauxite</td>
<td>Aluminum, abrasives, refractories, $\text{Al}_2\text{O}_3$</td>
<td>Brazil, Australia, Jamaica,</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Guyana</td>
<td></td>
</tr>
<tr>
<td>Niobium</td>
<td>Special steels, titanium alloys</td>
<td>Canada, Brazil</td>
<td>100</td>
</tr>
<tr>
<td>Graphite</td>
<td>Lubricants, crucibles, electrical components, pencils, nuclear moderator</td>
<td>Mexico, Canada, Sri Lanka,</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Madagascar</td>
<td></td>
</tr>
<tr>
<td>Manganese</td>
<td>Special steels, paints, batteries</td>
<td>South Africa, Brazil, France,</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Australia</td>
<td></td>
</tr>
<tr>
<td>Mica</td>
<td>Electrical equipment, paints</td>
<td>India, Brazil, China, Belgium</td>
<td>100</td>
</tr>
<tr>
<td>Strontium</td>
<td>Glasses, ceramics, paints, TV tubes</td>
<td>Mexico</td>
<td>100</td>
</tr>
<tr>
<td>Rare earth metals</td>
<td>Batteries for hybrid vehicles and electronics</td>
<td>China</td>
<td>~100</td>
</tr>
<tr>
<td>Diamonds</td>
<td>Cutting tools, abrasives</td>
<td>South Africa, Zaire</td>
<td>98</td>
</tr>
<tr>
<td>Fluorite</td>
<td>HF, steel making</td>
<td>Mexico, Morocco, South Africa,</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Canada</td>
<td></td>
</tr>
<tr>
<td>Platinum</td>
<td>Catalysts, alloys, metals (Pt, dental uses, Pd, Rh, Ir, surgical appliances Ru, Os)</td>
<td>South Africa, Russia</td>
<td>88</td>
</tr>
<tr>
<td>Tantalum</td>
<td>Electronic capacitors, chemical equipment</td>
<td>Germany, Canada, Brazil,</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Australia</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>Stainless steel, leather tanning, plating, alloys</td>
<td>South Africa, Turkey,</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zimbabwe</td>
<td></td>
</tr>
<tr>
<td>Tin</td>
<td>Alloys, plating, making flat glass</td>
<td>Bolivia, Brazil, Malaysia</td>
<td>81</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Alloys, catalysts, magnets</td>
<td>Zambia, Zaire, Canada, Norway</td>
<td>75</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Alloys, batteries, plating, reactors</td>
<td>Canada, Australia, Mexico</td>
<td>66</td>
</tr>
<tr>
<td>Nickel</td>
<td>Batteries, plating, coins, catalysts</td>
<td>Canada, Norway, Australia</td>
<td>64</td>
</tr>
</tbody>
</table>
The information shown in Table 1.2 reveals that no industrialized country is entirely self-sufficient in terms of all necessary natural resources. Changing political regimes may result in shortages of critical materials. In the 1990s, inexpensive imports of rare earth metals from China forced the closure of mines in the United States. Increased demand for use in high-performance batteries and rising costs of rare earth metals are now causing some of those mines to reopen. Although the data shown in Table 1.2 paint a rather bleak picture of our metal resources, the United States is much better supplied with many nonmetallic raw materials.

1.7 Nonmetallic Inorganic Minerals

Many of the materials that are so familiar to us are derived from petroleum or other organic sources. This is also true for the important polymers and an enormous number of organic compounds that are derived from organic raw materials. Because of the content of this book, we will not deal with this vast area of chemistry but rather will discuss inorganic materials and their sources.

In ancient times, the chemical operations of reducing metals ores, making soap, dying fabric, and other activities were carried out in close proximity to where people lived. These processes were familiar to most people of that day. Today, mines and factories may be located in remote areas or they may be separated from residential areas so that people have no knowledge of where the items come from or how they are produced. As chemical technology has become more sophisticated, a smaller percentage of people understand its operation and scope.

A large number of inorganic materials are found in nature. The chemical compound used in the largest quantity is sulfuric acid, H₂SO₄. It is arguably the most important single compound, and although approximately 81 billion pounds are used annually, it is not found in nature. However, sulfur is found in nature, and it is burned to produce sulfur dioxide that is oxidized in the presence of platinum as a catalyst to give SO₃. When added to water, SO₃ reacts to give H₂SO₄. Also found in nature are metal sulfides. When these compounds are heated in air, they are converted to metal oxides and SO₂. The SO₂ is utilized to make sulfuric acid, but the process described requires platinum (from Russia or South Africa) for use as a catalyst.

Another chemical used in large quantities (about 38 billion pounds annually) is lime, CaO. Like sulfuric acid, it is not found in nature, but it is produced from calcium carbonate, which is found in several forms in many parts of the world. The reaction by which lime has been produced for thousands of years is

\[
\text{CaCO}_3 \xrightarrow{\text{heat}} \text{CaO} + \text{CO}_2
\]

Lime is used in making glass, cement, and many other materials. Cement is used in making concrete, the material used in the largest quantity of all. Glass is not only an important material for making food containers, but it is also an extremely important construction material.
Salt is a naturally occurring inorganic compound. Although salt is of considerable importance in its own right, it is also used to make other inorganic compounds. For example, the electrolysis of an aqueous solution of sodium chloride produces sodium hydroxide, chlorine, and hydrogen:

\[
2 \text{NaCl} + 2 \text{H}_2\text{O} \xrightarrow{\text{electricity}} 2 \text{NaOH} + \text{Cl}_2 + \text{H}_2
\]  \hspace{1cm} (1.13)

Both sodium hydroxide and chlorine are used in the preparation of an enormous number of materials, both inorganic and organic.

Calcium phosphate is found in many places in the earth’s crust. It is difficult to overemphasize its importance because it is used on an enormous scale in the manufacture of fertilizers by the reaction

\[
\text{Ca}_3(\text{PO}_4)_2 + 2 \text{H}_2\text{SO}_4 \rightarrow \text{Ca}(\text{H}_2\text{PO}_4)_2 + 2 \text{CaSO}_4
\]  \hspace{1cm} (1.14)

The Ca(H$_2$PO$_4$)$_2$ is preferable to Ca$_3$(PO$_4$)$_2$ for use as a fertilizer because it is more soluble in water. The CaSO$_4$ is known as gypsum and, although natural gypsum is mined in some places, that produced by the preceding reaction is an important constituent in wall board. The reaction is carried out on a scale that is almost unbelievable. About 65% of the more than 80 billion pounds of H$_2$SO$_4$ used annually goes into the production of fertilizers. With a world population that has reached 6 billion, the requirement for foodstuffs would be impossible to meet without effective fertilizers.

Calcium phosphate is an important raw material in another connection. It serves as the source of elemental phosphorus that is produced by the reaction

\[
2 \text{Ca}_3(\text{PO}_4)_2 + 10 \text{C} + 6 \text{SiO}_2 \rightarrow \text{P}_4 + 6 \text{CaSiO}_3 + 10 \text{CO}
\]  \hspace{1cm} (1.15)

Phosphorus reacts with chlorine to yield PCl$_3$ and PCl$_5$. These are reactive substances that serve as the starting materials for making many other materials that contain phosphorus. Moreover, P$_4$ burns in air to yield P$_4$O$_{10}$, which reacts with water to produce phosphoric acid, another important chemical of commerce, as shown in the following equations:

\[
\text{P}_4 + 5 \text{O}_2 \rightarrow \text{P}_4\text{O}_{10}
\]  \hspace{1cm} (1.16)

\[
\text{P}_4\text{O}_{10} + 6 \text{H}_2\text{O} \rightarrow 4 \text{H}_3\text{PO}_4
\]  \hspace{1cm} (1.17)

Only a few inorganic raw materials have been mentioned and their importance described briefly. The point of this discussion is to show that although a large number of inorganic chemicals are useful, they are not found in nature in the forms needed. It is the transformation of raw materials into the many other useful compounds that is the subject of this book. As you study this book, keep in mind that the processes shown are relevant to the production of inorganic compounds that are vital to our way of life.
In addition to the inorganic raw materials shown in Table 1.2, a brief mention has been made of a few of the most important inorganic chemicals. Although many other inorganic compounds are needed, Table 1.3 shows some of the inorganic compounds that are produced in the largest quantities. Of these, only N₂, O₂, sulfur, and Na₂CO₃ occur naturally. Many of these materials will be discussed in later chapters, and in some ways they form the core of industrial inorganic chemistry. As you study this book, note how frequently the chemicals listed in Table 1.3 are mentioned and how processes involving them are of such great economic importance.

As you read this book, also keep in mind that it is not possible to remove natural resources without producing some environmental changes. Certainly, every effort should be made to lessen the impact of all types of mining operations on the environment and landscape. Steps must also be taken to minimize the impact of chemical industries on the environment. However, as we drive past a huge hole where open pit mining of iron ore has been carried out, we must never forget that without the ore being removed there would be nothing to drive. These thoughts are expressed in the following poem:

*The Iron Mine*

Men with their machines so great and powerful,
Scraping away at our only earth,
For the benefit of all who needed the goods,
Removing the iron of such a great worth.

Iron for the cars, trains, and ships,
To build bridges, buildings, and more,
The earth was so hastily removed,
In order to reach the precious ore.

Holes that cover much of the north,
Changing the scene while nature was taunted,
No matter how unsightly the remains,
Iron was taken for what we all wanted.

J. E. H.

References for Further Reading


Problems

1. What are the names of the solid, liquid, and gaseous regions of the earth’s crust?

2. What metal is the primary component of the earth’s core?

3. Elements such as copper and silver are present in the earth’s crust in very small percentages. What is it about these elements that makes their recovery economically feasible?

4. Explain the difference between rocks, minerals, and ores.

5. How were igneous rocks such as granite and quartz formed?

6. How were sedimentary rocks such as limestone and dolomite formed?

7. How were metamorphic rocks such as marble and slate formed?
8. What are some of the important classes of metal compounds found in the lithosphere?

9. Write the chemical equations that show how the process of weathering leads to formation of carbonates and hydroxides.

10. Why was copper the first metal to be used extensively?

11. Describe the two types of mining used to obtain ores.

12. Describe the procedures used to concentrate ores.

13. Metals are produced in enormous quantities. What two properties must a reducing agent have in order to be used in the commercial refining of metals?

14. Describe the three types of processes used in extractive metallurgy.

15. What was the earliest metal smelted? Why was iron not smelted until a later time?

16. Name three modern techniques used to shape metals.

17. Name two ancient techniques used to shape metals.

18. Briefly describe what the effect on manufacturing might be if the United States imposed a total trade embargo on a country such as South Africa.

19. Approximately 81 billion pounds of sulfuric acid are used annually. What inorganic material is the starting material in the manufacture of sulfuric acid?

20. What are some of the primary uses for lime, CaO?

21. What is the raw material calcium phosphate, Ca₃(PO₄)₂, used primarily for?