4. Minerals: rock's elementary building block

4.1. What is a mineral?

A **mineral** is a naturally occurring solid inorganic substance composed of a regular 3D arrangement of atoms repeating in all directions (**crystal lattice**). Each mineral can be identified with a chemical formula. For example:

Quartz: SiO_2
Olivine: $(Fe, Mg)_2SiO_4$
Halite: $NaCl$
Calcite: $CaCO_3$
Pyrite: FeS_2
Hematite: Fe_2O_3

A mineral growing freely form **crystals** whose external geometrical shape reflects the internal regular arrangement of atoms. The crystal structure of a mineral — or crystal lattice — depends on its chemical composition. It also depends on the temperature and pressure at which it formed. For example, graphite and diamond have the same chemical composition (carbon) but they formed in very different conditions of pressure and temperature, and therefore are characterized by very different crystal structures. Since diamond forms at very high pressure deep inside the Earth's crust, the atoms of carbon in diamond are more densely packed than in graphite. Minerals with the same chemical composition but with different crystal structures, like diamond and graphite, are called **polymorphs**.

4.2. Structure of matter and chemical bonds

Minerals are made of atoms. The simplest representation of an **atom** is a nucleus composed of protons and neutrons surrounded by electrons occupying different orbits, or shells. There are a specific number of electrons that can occupy each orbit. Since atoms are electrically neutral, the number of protons in the nucleus is equal to the number of electrons. Each element is characterized by a specific number of proton(s)/electron(s) called the **atomic number**, e.g. H (1), C (6), N (7), and O (8). Atoms of a given element characterized by different numbers of neutrons are different **isotopes** of that element. For example, the notation for an isotope of carbon that has 6 protons and 6 neutrons is carbon-12, or ^{12}C. Two other isotopes of carbon are ^{13}C (6 protons and 7 neutrons) and ^{14}C (6 protons and 8 neutrons). There are two types of isotopes: **stable isotopes** and **radioactive isotopes** (or radioisotopes). The latter decays into stable or radioactive isotopes over time while emitting radiations. For example, ^{14}C is radioactive and decays into the stable isotope ^{14}N.

Since a neutron has a certain mass, different isotopes of a same element have a different mass.

The mass of an atom can be approximated to the sum of masses of the protons and neutrons in the nucleus. By convention, the mass of the isotope of carbon ^{12}C (6 protons and 6 neutrons) is 12 atomic mass units. The **atomic mass** of an isotope is the sum of the number of protons and neutrons forming the nucleus. The atomic mass of an element depends on the relative abundances of its isotopes (e.g. the atomic mass of carbon is 12.011 because ^{12}C is by far the most abundant isotope of carbon, i.e. 98.9% of all carbon).

The electrons participating in chemical bonds are usually those of the outermost shell. Chemical bonds allow the atoms to achieve a more stable electronic configuration. There is an optimal number of electrons on the outermost shell which can be achieved through chemical bonds. For example, the optimal configuration for C, N and O is to have 8 electrons occupying the outermost shell. In minerals, three types of chemical bonds exist: the **covalent bond**, the **ionic bond** and the **metallic bond**.

In **Covalent bonds**, an atom shares one or more electrons with another atom. The electrons of one atom are attracted by the positively charged nucleus of the other atom and vice versa. This configuration results in very strong chemical bonds.

Example: diamond in which each atom of carbon is surrounded by 4 other atoms of carbon and each atom shares 4 electrons with its neighbors. Note that another mineral has the same chemical composition: graphite. However, graphite has a very different crystal structure. In graphite, the atoms of carbon are arranged in sheets. Within each sheet atoms are held together by covalent bonds but what holds these sheets together is a much weaker type of chemical bond (similar to the metallic bond described below). This makes graphite much less hard than diamond. The softness of graphite can be observed every time one uses a pencil to write or to draw. Pencil cores are made of graphite.

In **Ionic bonds**, an atom gains one or more electrons from another atom (transfer of electron(s)). An atom that has lost one or more electrons is called a **cation** (positively charged ion). An atom that has gained one or more electrons is called an **anion** (negatively charged ion). The ionic bond results from the attraction between ions of opposite charges.

Example: NaCl (halite or table salt) in which the atom of chlorine that has gained one electron is negatively charged (anion Cl^-) and attracted by the positively charged sodium (cation Na^+).

In **Metallic bonds**, atoms which have a strong tendency to lose electrons (and become cations) are surrounded by free-moving electrons (delocalized electrons). The cations are held together by their attraction to the surrounding electrons.

Example: copper which has one electron on the outermost shell that is only weakly attracted by the nucleus. In the metal copper, these outer electrons are not bounded to the nuclei and move freely. The cations Cu^+ are held together by their attraction to the free electrons surrounding them.

The most common mineral family on Earth is the family of *silicate minerals*. Silicate minerals are often characterized by a combination of covalent and ionic bonds. The basic structural unit of silicate minerals is **the silicon-oxygen tetrahedron or $[SiO4]^{4-}$** (silicate anion) in which one atom of silicon is surrounded by 4 atoms of oxygen and shares one electron with each oxygen. Each atom of oxygen can share one electron with another atom of silicon (covalent bond) or can bind with a positively charged ion (ionic bond).

Examples:

(1) Quartz (SiO_2) is one of the most common silicate minerals in the continental crust. Quartz is composed of a juxtaposition of silicon-oxygen tetrahedra. Each atom of oxygen is linked to 2 silicon atoms by electron sharing (covalent bonds). There is only one type of chemical bond in this mineral, i.e. covalent bond.

(2) Olivine is a silicate rich in Mg and/or Fe with the formula $(Fe, Mg)_2SiO_4$. It is very abundant in the upper mantle and also common in the oceanic crust. In olivine, the silicon-oxygen tetrahedra are linked to the metallic cations Fe^{2+} or Mg^{2+} by ionic bonds. The 4- charge of each silicate anion is balanced by two metallic cations of 2+ charges each. Therefore, there are two types of chemical bond in this mineral: covalent and ionic bonds.

There are many other combinations of silicate anions and other elements which produce a broad variety of crystal structures in the family of silicate minerals (e.g. single-chain silicates, double-chain silicates, sheet silicates…).

4.3. Formation of minerals

Crystallization is the process by which atoms in a gas or a liquid assemble in an orderly 3D pattern (crystal lattice) to form a solid substance (mineral crystal).

The formation of minerals can occur in the following five contexts:

(1) *Saturation*: When dissolved anions and cations in an aqueous solution reach a certain concentration, they become saturated, and if water is removed by evaporation or if more ions are added to the solution, the anions and cations combine to form crystals. One example is the precipitation of salt NaCl (halite = "table salt") when seawater evaporates in a pond, lake or embayment isolated from the open sea. The rock produced by accumulation of minerals precipitated from saturated brines is called *evaporite* (see chapter on sedimentary rocks).

(2) *Phase change* *(liquid-solid, gas-solid)*: Crystals can form when the temperature of a liquid drops and the liquid solidifies into a solid − **solidification**. This happens when water freezes to form ice. It also happens when *magma* (molten rock) cools and minerals crystallize to form a solid rock, i.e. igneous rock (see chapter on igneous rocks). The transformation of a gas into a solid without transiting by the liquid phase is called **deposition**.

(3) *Biomineralization*: Many organisms are capable of precipitating minerals to form a skeleton or shell. Our bones and teeth are mineralized structures. In the marine world, the most common biomineral is calcium carbonate (**CaCO$_3$**). It is produced by diverse organisms, such as reef corals, coralline algae, mollusks, urchins, sea stars, and foraminifera (one kind of large single-celled organism). Another common biomineral is silica (**SiO$_2$**) and is produced by siliceous sponges and several groups of marine microorganisms such as radiolarians and diatoms. Tooth enamel and bones are composed of hydroxyapatite ($Ca_5(PO_4)_3(OH)$).

(4) *Chemical weathering*: change in rock mineralogy at/near Earth's surface (e.g., reactions involving interactions between rocks and rainwater, such as the transformation of <u>orthoclase</u> (K-feldspar), common in granite, into <u>kaolinite</u>, a clay mineral: 2 $\underline{KAlSi_3O_8}$ + 2 H_2CO_3 + H_2O → <u>$Al_2Si_2O_5(OH)_4$</u> + 4 SiO_2 + 2 K^+ + 2 HCO_3^-).

(5) *Metamorphism*: recrystallization of a preexisting rock, when the rock in question is subjected to variations in temperature and pressure (for example, as the rock becomes buried deeper and deeper into the crust) or when the rock is in contact with hot hydrothermal fluid. <u>The transformation occurs at the solid state</u> (see chapter on metamorphic rocks).

4.4. Common families (or classes) of minerals

Silicate minerals: They are the most common minerals. They form most of the Earth's mantle and crust. Some details about their structure have already been provided above (see also the slides).

Carbonates: The most common carbonate mineral is $CaCO_3$, already mentioned above in relation with biological mineralization. The basic structural unit of carbonates is the carbonate anion $(CO_3)^{2-}$. In carbonate minerals, carbonate anions are arranged in sheets and are bound to cations located between the sheets. In the case of $CaCO_3$, the cations are Ca^{2+}. Calcium carbonate can also precipitate abiologically in seawater saturated in Ca^{2+} and $(CO_3)^{2-}$ or even (in relatively rare cases) crystallize out of a cooling magma (e.g., the igneous rock called carbonatite).

Halides and ***sulfates***: Minerals that often form in the context of saturated brines leading to the formation of evaporites. The most common halide mineral is halite (NaCl). Another common mineral that can form during evaporation of seawater is gypsum. The basic structural unit of sulfates is the sulfur-oxygen tetrahedron, i.e. an atom of sulfur surrounded by four atoms of oxygen (SO_4^{2-}). In the case of gypsum, water is also present in the crystal lattice and the chemical formula of gypsum is $CaSO_4.2H_2O$. When gypsum is buried under younger layers of sedimentary rocks, the increasing pressure and temperature "squeeze" water molecules out of the mineral, and gypsum becomes a mineral called anhydrite ($CaSO_4$).

Sulfides: In sulfides the sulfide anion (S^{2-}) is bound to metallic cations (e.g. Fe^{2+}, Mg^{2+}, Cu^{2+}). An example of sulfide is pyrite (FeS_2). Sulfides are important because they represent a major source of metals for the industry (metal **ores**). A geological setting in which sulfides commonly form is the ocean floor near mid-ocean ridges. Seawater percolates through cracks in the ocean crust where it is heated near spreading centers (mid-ocean ridges). The hot seawater reacts with the rock of the ocean crust (basalt) and dissolves iron, zinc, copper and sulfur. When this hot water returns to the ocean and meets the cold seawater, the sudden drop of temperature triggers the precipitation of sulfides which accumulate around the hot spring and builds a chimney called a **hydrothermal vent** (also known as "black smoker"). Hydrothermal vents are of particular interest, not only because they are formed of metal sulfides, but also because they shelter a diverse ecosystem whose primary source of energy is not sunlight (photosynthesis) but chemical reactions (chemosynthesis, e.g., $CO_2 + 4H_2S + O_2 \rightarrow CH_2O + 4S + 3H_2O$). Chemosynthesis can be performed by specialized bacteria and can sustain a diverse ecosystem in the deep ocean without any sunlight! One theory about the origin of life on Earth suggests that the first unicellular organisms may have emerged near hydrothermal vents billions of years ago.

Oxides: In oxides the oxygen is bound to other atoms, usually metallic cations, via ionic bonds. One very common oxide and major source of iron for the industry (iron ore) is the iron oxide called hematite (Fe_2O_3). If the anion is not O^{2-} but OH^-, the mineral is called a hydroxide. Another iron ore is the iron hydroxide called goethite ($FeO(OH)$). Famous rock formations rich in iron oxide are the **banded iron formations**. These rocks are composed of thin layers of sediments rich in iron oxide. These rocks are usually Precambrian in age (older than 500×10^6 years). One hypothesis suggests that they formed when the oxygen produced by photosynthetic activity of cyanobacteria reacted with the dissolved iron in the ocean. Their study is important to understand the history of the atmospheric oxygen of our planet (see chapter on the evolution of life).

Native elements: Minerals composed of a single element. Sometimes they can be combined in alloys like the iron-nickel alloy of metallic meteorites. Other examples of native element minerals are native gold, native copper, sulfur, graphite and diamond.

4.5. Physical properties of minerals

Minerals can be characterized by their physical properties. Some of the properties that can be used to characterize and identify minerals are listed below.

Hardness: Harder minerals are able to scratch softer minerals. The hardest mineral is diamond which is able to scratch all the others. On the **Mohs scale** of hardness, diamond has a hardness of 10. The softest mineral is talc and has a hardness of 1. The hardness of a mineral depends on its structure and chemical bonds.

Cleavage: Many minerals tend to split along specific planes which depend on their crystal structure. Chemical bonds along these cleavage planes tend to be weaker and thus break more easily.

Fracture: a mineral may be broken along surfaces that are not cleavage planes. These surfaces are called fractures. The quality (shape and texture) of the broken surface is another criterion used to identify minerals (e.g. the conchoidal fracture of quartz, the splintery fracture of fibrous minerals like asbestos).

Luster: This property of minerals refers to the way the surface of a mineral reflects light. Different terms are used to qualify mineral luster (e.g. metallic, vitreous…).

Color: The color of a mineral is also a property that can be used in mineral identification. However, the color of a mineral may depend on the presence of tiny amounts of specific elements. For instance, quartz is colorless, but amethyst, a variety of quartz with trace amounts of Fe^{3+}, is violet. Citrine, another variety of quartz also containing Fe^{3+}, is yellow and can be obtain by heating amethyst. ***Streak*** refers to the color of the mark left by a mineral when it is scratched on an abrasive surface such as a plate of unglazed porcelain (e.g. the reddish-brown streak of hematite).

Density: The density of a mineral (g/cm^3) depends on how closely the atoms are packed and on the mass of individual atoms. Diamond and graphite are both composed of carbon but diamond is denser because the atoms of carbon in diamond are packed more closely. Fe-olivine (Fe_2SiO_4) and Mg-olivine (Mg_2SiO_4) have a similar structure but Fe-olivine is denser than Mg-olivine because the atomic mass of iron is much greater than that of magnesium. The density of minerals is commonly expressed in terms of ***specific gravity*** which is the ratio of the weight of a volume of a mineral to the weight of an equal volume of water at a temperature and pressure of reference. The specific gravity of water is 1. The specific gravity of halite is 2.16 and that of pyrite is 5.

Crystal habit: It is the shape of an individual crystal or an aggregate of crystals of a given mineral. The crystal habit of a mineral reflects the internal arrangement of atoms as well as the speed and direction of crystal growth.