B1) Atomic Chemistry and Bonding

All matter is made up of atoms, and all atoms are made up of three main particles known as **protons**, **neutrons** and **electrons**. As summarized in the following table, protons are positively charged, neutrons are uncharged and electrons are negatively charged. The negative charge of one electron balances the positive charge of one proton. Both protons and neutrons have a mass of 1, while electrons have almost no mass.

Elementary particle	Charge	Mass
Electron	-1	~0
Proton	+1	1
Neutron	0	1

The simplest atom is that of hydrogen, which has one proton and one electron. The proton forms the nucleus of hydrogen, while the electron orbits around it. All other elements have neutrons as well as protons in their nucleus. The positively-charged protons tend to repel each other, and the neutrons help to hold the nucleus together. For most of the 16 lightest elements (up to oxygen) the number of neutrons is equal to the number of protons. For most of the remaining elements there are more neutrons than protons, because with increasing numbers of protons concentrated in a very small space, more and more extra neutrons are needed to overcome the mutual repulsion of the protons in order to keep the nucleus together. The number of protons is the **atomic number**, the number of protons plus neutrons is the **atomic weight**. For example, silicon has 14 protons, 14 neutrons and 14 electrons. Its atomic number is 14 and its atomic weight is 28. The most common isotope of uranium has 92 protons and 146 neutrons. Its atomic number is 92 and its atomic weight is 238 (92+146).

Electron orbits around the nucleus of an atom are arranged in what we call **shells** [see the first few pages of Chapter 2]. The first shell can hold only two electrons, while the next shell will hold only eight electrons. Subsequent shells can hold more electrons, but the *outermost* shell of any atom will hold no more than eight electrons. These outermost shells are generally involved in bonding between atoms, and bonding takes place between atoms that do not have the full complement of eight electrons in their outer shells (or two in the first shell for the very light elements).

To be chemically stable, an atom seeks to have a full outer shell (i.e., 8 electrons for most elements, or 2 electrons for the very light elements). This is accomplished by lending, borrowing, or sharing electrons with other atoms. Elements that already have their outer orbits filled are considered to be inert; they do not readily take part in chemical reactions. These "noble" elements include the gases in the right-hand column of the periodic table: helium, neon, argon etc.

Sodium has 11 electrons, 2 in the first shell, 8 in the second, and 1 in the third. Sodium readily gives up this third shell electron, and because it loses a negative charge it becomes positively charged [pages 38 and 39]. Chlorine, on the other hand, has 17 electrons, 2 in the first shell, 8 in the second, and 7 in the third. Chlorine readily accepts an eighth electron for its third shell, and thus becomes negatively charged. In changing their number of electrons these atoms become

ions - the sodium a positive ion or **cation**, the chlorine a negative ion or **anion**. The electronic attraction between these ions is known as an **ionic bond**. Electrons can be thought of as being *transferred* from one atom to another in an ionic bond. Common table salt (NaCl) is a mineral composed of chlorine and sodium linked together by ionic bonds [see Figure 2.6]. The mineral name for NaCl is **halite**.

An element like chlorine can also form bonds without forming ions. For example two chlorine atoms, which each seek an eighth electron in their outer shell, can share an electron in what is known as a **covalent bond**, to form the gas Cl_2. Electrons are *shared* in a covalent bond.

Carbon has 6 protons and 6 electrons, 2 in the inner shell and 4 in the outer shell. Carbon would need to gain or lose 4 electrons to have a filled outer shell, and this would create too great a charge imbalance for the ion to be stable. On the other hand, carbon can share electrons to create covalent bonds. Each carbon atom shares electrons with adjacent carbon atoms. In the mineral diamond the carbon atoms are linked together in a three-dimensional framework, where every bond is a strong covalent bond. In the mineral graphite the carbon atoms are linked together in a two-dimensional hexagonal framework of covalent bonds. Graphite is soft because the bonding between these sheets is relatively weak. [Fig. 2.10]
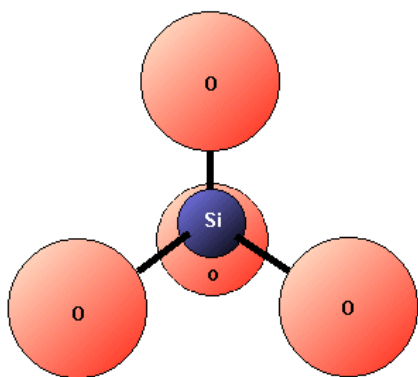
Silicon and oxygen bond together to create a silica tetrahedron (a pyramid shape with O at each corner and Si in the middle – see figure to the left and [Figure 2.21]), which is the building block of the many different silicate minerals. The bonds in a silica tetrahedron have some of the properties of covalent bonds and some of the properties of ionic bonds. As a result of the ionic character, silicon becomes a cation (with a charge of +4) and oxygen becomes an anion (with a charge of -2), hence the net charge of a silica tetrahedron SiO_4 is -4. As we will see later, silica tetrahedra are linked together in a variety of ways to form most of the common minerals of the crust.

Most minerals are characterized by ionic or covalent bonds, or a combination of the two, but one other type of bond which is geologically important is the metallic bond. Elements that behave as metals have outer electrons that are relatively loosely held. When bonds between such atoms are formed these electrons can move freely from one atom to another. A metal can thus be thought of as an array of positively charged nuclei immersed in a sea of mobile electrons. This characteristic accounts for two very important properties of metals: their electrical conductivity and their malleability.

B2) Non-silicate Minerals

A mineral is a naturally occurring, inorganic, solid with a definite composition and a regular internal crystal structure.

Regular structure	atoms are arranged in a consistent, regular and repeating three-dimensional pattern
Definite composition	must have a specific chemical composition, or a restricted range of compositions (e.g., the mineral olivine can have compositions ranging from Mg_2SiO_4 to Fe_2SiO_4)
Solid	excludes liquids (such as water, although frozen water is a mineral)
Inorganic	excludes substances produced solely by living organisms (e.g., wood or pearl, but not calcite, because although calcite is made by marine organisms, it also forms inorganically)
Naturally occurring	excludes substances which are only man-made (e.g., some solids that have all of the other properties of minerals, but do not exist in nature)

All minerals are characterized by a specific three-dimensional pattern which is known as a lattice or crystal structure. These structures range from the simple cubic pattern of halite (NaCl), [as shown on Figure 2.6], to the very complex patterns of some silicate minerals. As described earlier, two minerals, (graphite and diamond are an example), may have the same composition, but very different crystal structures and properties.

In order for a crystal to grow, the elements must be present in the appropriate proportions, the physical and chemical conditions must be favourable, and there must be sufficient time for the atoms to become arranged.

Physical and chemical conditions include factors such as temperature, pressure, the presence of water, the pH and the amount of oxygen available. Time is one of the most important factors because it takes time for atoms to become ordered. If time is limited the mineral grains will remain very small.

Most of the minerals that make up the rocks around us form through the cooling of **magma**—a body of molten rock. At the high temperatures that exist deep within the earth some geological materials are liquid. As these magmas rise up through the crust, either by volcanic eruption, or by more gradual processes, they cool enough so that the minerals within them will crystallize. If the cooling process is rapid (minutes, hours or days) the components of the minerals will not have time to become ordered and form large crystals before the rock becomes solid. The resulting rock will be very fine-grained (i.e., it will have very small crystals). In some cases the cooling will be so fast (seconds) that the texture will be glassy - which means that it has no crystals at all. If the cooling is slow (from years to millions of years) the degree of ordering will be higher and relatively large minerals will form.

Minerals can also form in several other ways, as follows:
- precipitation from aqueous solution (from water flowing underground, from evaporation of a lake or inland sea, and in some cases directly from sea water)
- metamorphosis - under conditions of elevated temperature and pressure new minerals can form directly from the elements within existing minerals
- organically - the minerals within shells (primarily calcite), and teeth and bones (primarily apatite) are formed by organisms (these organically formed minerals are still called minerals because they can also form inorganically)

Volcanic glass is not composed of minerals because the magma has cooled too rapidly for crystals to grow, although over time (millions of years) the volcanic glass may crystallize into various silicate minerals. Opal is known as a mineraloid, because although it has all of the other properties of a mineral, it does not have a specific structure. Pearl is not a mineral because it can only be produced by organic processes.

Most minerals are made up of a cation (a positively charged ion) or several cations, and an anion (a negatively charged ion) or an anion group. For example, in the mineral hematite (Fe_2O_3) the cation is Fe (iron) and the anion is O (oxygen). We group minerals into classes on the basis of their predominant anion or anion group. These include oxides, sulphides, carbonates and silicates, and others. Silicates are by far the predominant group in terms of their abundance within the crust and mantle, and they will be discussed later. Some examples of minerals from the different mineral groups are given below.

GROUP	EXAMPLES
Oxides	hematite (iron-oxide – Fe_2O_3), corundum (aluminum-oxide Al_2O_3), water-ice (H_2O)
Sulphides	galena (lead-sulphide - PbS), pyrite (iron-sulphide – FeS_2), chalcopyrite (copper-iron-sulphide – $CuFeS_2$)
Carbonates	calcite (calcium-carbonate – $CaCO_3$), dolomite (calcium-magnesium-carbonate – $(Ca,Mg)CO_3$
Silicates	quartz (SiO_2)*, feldspar (sodium-aluminum-silicate – $NaAlSi_3O_8$), olivine (iron or magnesium-silicate - $FeSiO_4$)
Halides	fluorite (calcium-flouride – CaF_2), halite (sodium-chloride - NaCl)
Sulphates	gypsum (calcium-sulphate – $CaSO_4 \cdot H_2O$), barite (barium-sulphate - $BaSO_4$)
Native elements	gold (Au), diamond (C), graphite (C), sulphur (S), copper (Cu)

*in quartz the anion is oxygen, and while it could be argued, therefore, that quartz is an oxide, it is always classed with the silicates

Oxide minerals have oxygen as their anion, but they exclude those with oxygen complexes such as carbonate (CO_3), sulphate (SO_4), silicate (SiO_2) etc. The most important oxides are the iron oxides hematite and magnetite. Both of these are important ores of iron. Corundum (Al_2O_3) is an abrasive, but can also be a gemstone in its ruby and sapphire varieties.

If the oxygen is also combined with hydrogen to form the hydroxyl anion (OH^-) the minerals is known as a **hydroxide**. Some important hydroxides are limonite and bauxite, which are ores of iron and aluminium.

Sulphides are minerals with the S^{-2} anion, and they include galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$) and molybdenite (MoS_2), which are the main ores of lead, zinc, copper and molybdenum respectively. Some other sulphide minerals are pyrite (FeS_2), pyrrhotite, bornite, stibnite, and arsenopyrite.

Sulphates are minerals with the SO_4^{-2} anion, and these include gypsum ($CaSO_4 \cdot 2H_2O$) and the sulphates of barium and strontium: barite ($BaSO_4$) and celestite ($SrSO_4$). In all of these cases the cation has a +2 charge which balances the -2 charge on the sulphate ion.

The **halides** are so named because the anions include the halogen elements chlorine, fluorine, bromine etc. Examples are halite (NaCl), sylvite (KCl) and fluorite (CaF_2).

The **carbonates** include minerals in which the anion is the CO_3^{-2} complex. The carbonate combines with +2 cations to form minerals such as calcite ($CaCO_3$), magnesite ($MgCO_3$), dolomite (($Ca,Mg)CO_3$) and siderite ($FeCO_3$). The copper minerals malachite and azurite are also carbonates.

In **phosphate** minerals the anion is PO_4^{-4}. The most important phosphate mineral is apatite ($Ca_5(PO_4)_3(OH)$).

Native minerals include only one element, such as gold, copper, sulphur or carbon[1].

The **silicate** minerals include the elements silicon and oxygen in varying proportions ranging from SiO_2 to SiO_4. These are discussed at length below.
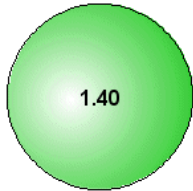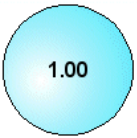
---
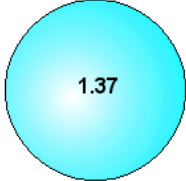
[1] As noted above, the element carbon can exist in two "native" forms, one being diamond, the other graphite. Both of these minerals are made up only of carbon, but they have <u>very</u> different properties because of differences in the way the atoms are bonded together. In diamond all of the bonds between the carbon atoms are very strong covalent bonds. Graphite is made up of sheets of carbon atoms bonded covalently, but the sheets are only loosely held together [Fig. 2-10].

B3) Silicate Minerals

The vast majority of the minerals that make up the rocks of the earth's crust are silicate minerals. These include minerals such as quartz, feldspar, mica, amphibole, pyroxene, olivine, and a great variety of clay minerals. The building block of all of these minerals is the **silica tetrahedron**, a combination of four oxygen atoms and one silicon atom. These are arranged such that planes drawn through the oxygen atoms describe a tetrahedron (a four-faced object)—which is a pyramid with a triangular base [Figure 2.21]. Since the silicon ion has a charge of +4 and each of the four oxygen ions has a charge of -2, the silica tetrahedron has a net charge of -4.

In silicate minerals these tetrahedra are arranged and linked together in a variety of ways, from single units to complex frameworks [Fig. 2.23]. The simplest silicate structure, that of the mineral **olivine**, is composed of isolated tetrahedra[2] bonded to iron and/or magnesium ions. In olivine the -4 charge of each silica tetrahedron is balanced by the addition of two **divalent** (i.e., +2) iron or magnesium cations. Olivine can be either Mg_2SiO_4 or Fe_2SiO_4, or some combination of the two. This type of substitution is known as *solid solution*. As shown below, the divalent cations of magnesium and iron are quite close in radius, (0.73 angstroms versus 0.62)[3]. Because of this size similarity, and because they are both divalent cations, iron and magnesium can readily substitute for each other in this, and in many other crystal lattices.

Table of the ionic radii of ions commonly found in rock-forming minerals

---

[2] In olivine, unlike most other silicate minerals, the silica tetrahedra are not bonded to each other. They are, however, bonded to the iron or magnesium within the olivine.

[3] An *angstrom* is the unit commonly used for the expression of atomic-scale dimensions. One angstrom is 10^{-10} m or 0.0000000001 m. The symbol for an angstrom is: Å . (ie an A with a little circle over it)

In the mineral **pyroxene** silica tetrahedra are linked together in a single chain, where one oxygen from each tetrahedron is shared with the adjacent tetrahedron. The result is that the oxygen to silicon ratio is lower than in olivine, (3:1 instead of 4:1), the net charge per silicon atom is atom is less (-2 instead of -4) and fewer cations are necessary to balance that charge. Pyroxene compositions are of the type $MgSiO_3$ or $FeSiO_3$, or some combination of these, which is written as $(Mg,Fe)SiO_3$, where the elements in the brackets can be present in any proportion.

In **amphibole** structures the silica tetrahedra are linked in a double chain that has an oxygen to silicon ratio lower than that of pyroxene, and hence still fewer cations are necessary to balance the charge. Amphibole compositions can be very complex. Hornblende, for example, can include sodium, potassium, calcium, magnesium, iron, aluminum, silicon, oxygen, fluorine and the hydroxyl ion (OH^{-1}).

In **mica** structures the silica tetrahedra are arranged in continuous sheets. **Biotite** mica is a **ferromagnesian** silicate mineral (like olivine, pyroxene and amphibole) in that it includes iron and/or magnesium. **Chlorite** is another similar mineral which commonly includes magnesium. In **muscovite** the only cations present are aluminum and potassium, and hence it is not a ferromagnesian silicate mineral. All of these minerals also have water in their structure. Bonding between sheets is relatively weak, and this accounts for the well developed one-directional cleavage.

Apart from muscovite, biotite and chlorite, there is a great variety of other **sheet silicates** (or **phyllosilicates**) which usually exist as clay-sized fragments (i.e., less than 0.004 mm). These include **kaolinite**, **illite** and **smectite**, and although they are difficult to study because of their very small size, they are actually extremely important components of rocks and especially of soils.

Silica tetrahedra are bonded in three-dimensional frameworks in both the feldspars and quartz.
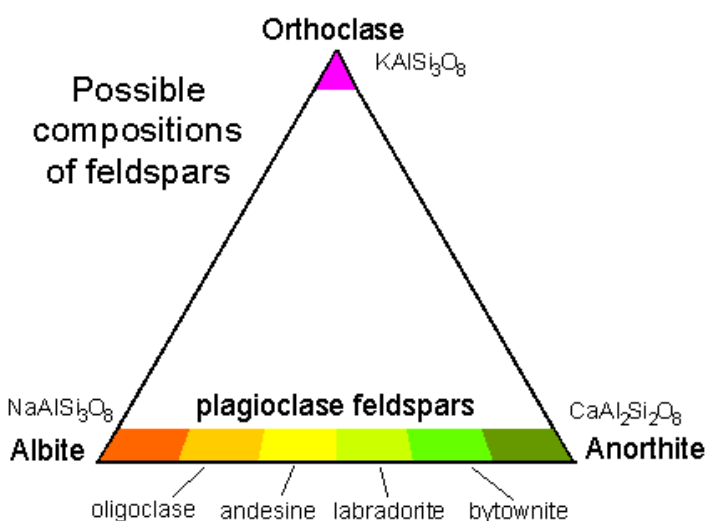
These minerals are non-ferromagnesian - that is they don't contain any iron or magnesium. They include aluminum, as well as potassium, sodium and calcium in various combinations.

The three **feldspar** "end-members" are orthoclase (potassium only), and two types of plagioclase: **albite** (sodium only) and **anorthite** (calcium only). As is the case for iron and magnesium in olivine, there is a continuous range of

compositions between albite and anorthite in plagioclase, because the calcium and sodium ions are almost identical in size (1.00 versus 0.99 angstroms). Any intermediate compositions between $CaAl_2Si_3O_8$ and $NaAlSi_3O_8$ can exist[4]. These intermediate plagioclases are: oligoclase (10-30% Ca), andesine (30-50% Ca), labradorite (50-70% Ca) and bytownite (70-90% Ca)[5]. **Orthoclase** ($KAlSi_3O_8$) has a slightly different structure, owing to the larger size of the potassium ion (1.37 angstroms). The ranges of the possible compositions of the feldspar minerals are shown on the figure above.

In **quartz** the silica tetrahedra are bonded in a "perfect" three-dimensional framework. Each tetrahedron is bonded to four other tetrahedra, the ratio of oxygen to silicon is 2:1 and the charge is balanced. There is no aluminum and there are no other cations such as sodium or potassium. The hardness, and lack of cleavage in quartz, are related to the fact that all of the bonds are the strong covalent/ionic bonds characteristic of the silica tetrahedron.

For an overview of the structures of the silicate minerals please have a look at this document: http://web.viu.ca/earle/geol111/silicate-structures.htm

---

[4] In olivine or pyroxene Fe^{2+} for Mg^{2+} can substitute for each other because they have the same charge and similar ionic radii. In plagioclase Ca^{2+} and Na^{1+} can substitute for each other because they have similar radii, but they do not have the same charge.   This problem is accounted for by corresponding substitution of Al^{3+} for Si^{4+}. Therefore, albite is $NaAlSi_3O_8$ while anorthite is $CaAl_2Si_2O_8$.

[5] There is no need to remember the names of the intermediate plagioclase minerals. You should know that they exist, and that the sodium end-member is albite ($NaAlSi_3O_8$) while the calcium end-member is anorthite ($CaAl_2Si_2O_8$). You should also know that the potassium end-member is orthoclase ($KAlSi_3O_8$) - which is sometimes referred to as *K-feldspar* or even *K-spar*.

Review questions

1. What is the electrical charge on a proton? A neutron? An electron? What are their relative masses?

2. Explain how the need for an atom's outer orbit to be filled with electrons contributes to bonding.

3. Why are helium and neon described as inert?

4. What is the difference in the role of electrons in an ionic bond as compared to a covalent bond?

5. What is the electrical charge on an anion as compared to a cation?

6. What is the most important characteristic of a mineral?

7. Explain why time is important to the growth of minerals?

8. What chemical feature is used in the classification of minerals into groups?

9. Name the mineral group for the following minerals:

calcite		biotite		pyrite	
gypsum		galena		orthoclase	
hematite		graphite		magnetite	
quartz		fluorite		olivine	

10. What is the net charge on an unbonded silica tetrahedron?

11. What allows magnesium to substitute freely for iron in olivine?

12. What is the silica tetrahedron structural difference between pyroxene and amphibole?

13. Why is biotite called ferromagnesian, while muscovite is not?

14. What are the two end-members of the plagioclase series?

15. Why does quartz have no additional cations (other than Si^{+4})?