

and the arrangement of one kind of atom around another is determined by the orientations of the covalent bonds in space. This is the case in some metal sulphides, many of which are semiconductors. The properties of the solids are then best considered in terms of electron energy levels rather than individual bonds between atoms.

### 1.2.2. *Silicate Structures*

The earth's crust is made up almost entirely of silicates and silica, the rock forming minerals and the breakdown products of them which result from the weathering of rocks. The basis of the structure of silicates is the  $\text{SiO}_4^{4-}$  group in which four oxygen atoms are arranged tetrahedrally around the silicon atoms, the Si–O distance being about 1.6 Å and the distance between centres of oxygen atoms about 2.6 Å. There are some minerals which are orthosilicates, with lattices built up from simple  $\text{SiO}_4^{4-}$  ions and cations. Most silicates however are based on polymeric silicate groups, the simplest of which is  $\text{Si}_2\text{O}_7^{6-}$ , and which proceed to rings, chains, doubled chains (bands) and sheets, some of which are illustrated in Fig. 1.1. In addition there are the three dimensional frameworks, in the various forms of silica. The tetrahedral group  $\text{AlO}_4$  has very nearly the same size as the  $\text{SiO}_4$  group and so aluminium can replace silicon in the silicate anion structure, giving rise to the aluminosilicates.

Silicate and aluminosilicate lattices can be looked upon as being tetrahedra of oxide ions containing silicon or aluminium ions in the tetrahedral holes, packed together so as to form polyhedra which contain holes of different coordination numbers and sizes. These latter contain cations having appropriate ionic radii, in sufficient number to neutralise the ionic charge of the anionic silicate structure. Clearly as aluminium replaces some silicon more cationic charge is necessary. There are a number of ions of similar size which can occupy octahedral holes in silicate structures. Many metals were present in the magma from which silicate minerals crystallised so that isomorphous substitution is common in silicate minerals. This is the reason why many of them do not have the “ideal” composition of a chemical compound. Aluminium cannot only replace silicon in tetrahedral holes but also occupy octahedral holes and it is this dual role which makes the compositions of some aluminosilicates appear to be exceedingly confusing.

If aluminium replaces some silicon in a three dimensional framework silica structure, the composition remaining  $(\text{Si}, \text{Al})\text{O}_2$ , the solid becomes negatively

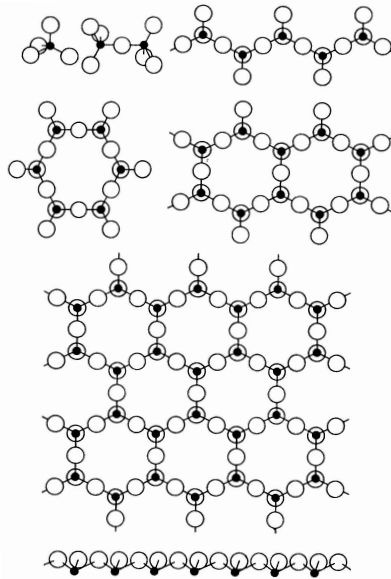


Fig. 1.1. Silicate structures, from top left. (1) Orthosilicate ( $\text{SiO}_4$ ) $^{4-}$  ion. (2) Pyrosilicate ( $\text{Si}_2\text{O}_7$ ) $^{6-}$  ion. (3) Chain structure ( $\text{SiO}_3$ ) $^{2n-}$ . (4) Ring ( $\text{Si}_6\text{O}_{18}$ ) $^{12-}$  group structure, present in beryl. (5) Doubled chain (band) structure based on ( $\text{Si}_4\text{O}_{11}$ ) $^{6-}$  groups. (6) Sheet structure silicon–oxygen network with cross section of the sheet below.

charged and positive ions must be present in holes in the structure. Zeolites and feldspars are examples of such materials. If there are suitable diffusion paths in a zeolite for metal ions to pass into and out of the structure when it is fully wetted by water then ion exchange can occur. In other cases a metal present in a silicate can only be extracted by breaking up the silicate structure. This occurs naturally during weathering under certain conditions, resulting in silicate species as well as metals passing into solution in any water present if chemical conditions are suitable. If reprecipitation occurs due to the water passing to a region where the chemical conditions, for example pH or redox potential, change a silicate of indeterminate composition and containing several metals may form. This may subsequently crystallise, usually to give a poorly crystalline solid which can have a wide range of composition because of substitution of one metal in the “ideal” composition of the mineral by others present which have suitable ionic radii. This occurs during the laterisation process which forms the “oxide ores” of nickel.

Olivine, an important mineral in the basic, or mafic, rock peridotite is the first silicate to crystallise from magma of appropriate composition and tends to preferentially incorporate  $\text{Ni}^{2+}$  ions into its lattice if nickel is present. The regions in which this occurred to a significant extent became nickel provinces. Olivine and related minerals have the general formula  $\text{M}_2\text{SiO}_4$  where M is a divalent metal having a suitable ionic radius to allow it to be accommodated in holes between six oxygen atoms. The “ideal” composition of olivine itself may be written  $9\text{Mg}_2\text{SiO}_4 \cdot \text{Fe}_2\text{SiO}_4$ , a representation which can lead to confusion. The crystal lattice of olivine contains discrete  $\text{SiO}_4^{4-}$  tetrahedra packed together with  $\text{Mg}^{2+}$  ions between them in octahedral holes between oxygen atoms. Approximately one in ten of the  $\text{Mg}^{2+}$  ions is replaced by  $\text{Fe}^{2+}$ . Olivine is not a “double salt” or mixture of two silicates. Zircon,  $\text{ZrSiO}_4$ , is also an orthosilicate and because the ionic radii of Zr and Hf are very similar, due to the lanthanide contraction, the mineral always contains hafnium in its lattice also.

### 1.2.3. *Oxides*

Two types of oxide are important in hydrometallurgy, the binary oxides which contain only one metal and the complex oxides which contain two or more. The majority of structures of both types are essentially ionic and the metal atoms have large coordination numbers, often 6 or 8. The most important structures of binary oxides of interest here are given in Table 1.2. The coordination numbers of the rutile structure, taken as an example, indicate that each metal atom has a group of 6 oxygen atoms around it and each oxygen has 3 metal atoms.

Table 1.2.

Formula type	Name of structure	Coordination numbers		Examples
		M	O	
$\text{MO}_3$	$\text{ReO}_3$	6	2	$\text{WO}_3$
$\text{MO}_2$	Rutile	6	3	$\text{TiO}_2$ , $\text{MnO}_2$ , $\text{SnO}_2$
	Fluorite	8	4	$\text{ZrO}_2$ , $\text{ThO}_2$ , $\text{UO}_2$
$\text{MO}$	Sodium chloride	6	6	$\text{MgO}$ , $\text{CaO}$ , $\text{NiO}$
	Wurtzite	4	4	$\text{ZnO}$
$\text{M}_2\text{O}_3$	Corundum	6	4	$\text{Al}_2\text{O}_3$ , $\text{Fe}_2\text{O}_3$ , $\text{Cr}_2\text{O}_3$
$\text{M}_2\text{O}$	Cuprite	2	4	$\text{Cu}_2\text{O}$