**1.4.2 Structure of Silicates**

Silicates are also oxides, but they contain two or more oxides, out of which one is essentially silica. Earth’s crust contains 48% by weight O2, 26% Si, 8% Al, 5% Fe, and 11% Ca, Na, K, and Mg combined. Thus, the earth’s crust and also mantle consist mainly of silicates. In silicates, two types of oxygens can be seen. They are bridging and nonbridging oxygens (NBOs). Oxygen atoms are bonded to two Si atoms in the case of bridging oxygens, whereas they are bonded to only one in the case of nonbridging oxygens. NBOs are formed by the addition of either alkali or alkaline earth metal oxides to silica, as shown in Figure 1.18. In this, O− denotes an NBO. NBOs are negatively charged. Local neutrality is maintained by having cations end up adjacent to the NBOs. The following are the salient points in the formation of NBOs:

1. The number of NBOs are proportional to the number of moles of alkali or alkaline earth metal oxides added. 2. Addition of alkali or alkaline earth metal oxides to silica increases the overall O/Si ratio of the silicate.

3. Increasing the number of NBOs results in the progressive breakdown of the silicate structure into smaller units.

***FIGURE 1.18 Formation of nonbridging oxygen by the addition of an alkali oxide to silica.***

A critical parameter that determines the structure of silicate is the number of

NBOs per tetrahedron, which, in turn, is determined by the O/Si ratio. The principals involved in the formation of silicate structures are the following:

1. The basic building block is the SiO4 tetrahedron. The Si–O bond is partly covalent, and tetrahedron satisfies both the bonding requirements of covalent directionality and the relative size ratio for ionic structures.

2. Because of the high charge on the Si4+ ion, the tetrahedral units are rarely joined edge-to-edge, and never face to face, but usually share the corners. The reason was first stated by Pauling, and it is illustrated by Figure 1.19. The reason is that the cation separation distance decreases in going from the corner to the edge to the face sharing. This in turn results in cation–cation repulsions and a decrease in stability of structure.

The relationship between the O/Si ratio, which can vary between 2 and 4, and the structure of silicate, is given in Table 1.2.



***FIGURE 9.10 Effect of corner edge and face sharing on cation–cation separation. The distances S1:S2:S3 are in the ratio 1:0.58:0.33; that is, cation–cation repulsion increases on going from left to right, which tends to destabilize the structure***.

**1- Silica**

As already stated, the basic building block of silicates are (SiO4)4− tetrahedra. This building block is possessed by the silica structure. When this block is joined to the neighboring tetrahedra, the four negative charges on each block is balanced, and the structure becomes neutral. This gives rise to the O/Si ratio of 2 and the chemical formula of silica as SiO2. In this structure, each O is linked to two Si, and each Si is linked to four O. Since the tetrahedron is a three-dimensional structure, the network formed by the combination of the tetrahedra also becomes a three-dimensional network. Examples for this kind of structure are the different allotropes of silica that, depending on the exact arrangement of the tetrahedra, include quartz, tridymite, and cristobalite. When the long-range order is lacking, the resulting solid is called amorphous silica or fused quartz.

***TABLE 1.2 Relationship between Silicate Structure and O/Si Ratio***

**2- Sheet Silicates**

When three out of four oxygens are shared, with an O/Si ratio of 2.5, the sheet structure results. Examples for this structure are clays, talc [Mg3(OH)2 (Si2O5)2], and mica [KAl2(OH)2(AlSi3O10)]. Kaolinite [Al2(OH)4(Si2O5)] is a clay (Figure 1.20a). In this, (Si2O5)2− sheets are held together by the positively charged sheets of octahedral (Figure 1.20b). This structurehelps explain why clays absorb water so readily; the polar water molecule is easily absorbed between the top of positive sheets and the bottom of silicate sheets. This is shown in Figure 1.1.21. In mica (Figure 1.22), Al ions substitute for one-fourth of Si atoms in sheets, requiring an alkali ion such as K+ in order for structure to remain electrically neutral. Alkali ions fit in holes of silicate sheets and bond sheets together with an ionic bond that is stronger than that in clays.

**** The resulting structure is shown in Figure 1.23. Mica does not absorb water as readily as clays do. Little effort is required to flake off a very thin chip of the material.

****

***FIGURE 1.20 Structure of kaolinite (a) shows the different layers in the structure; (b) shows the composition of the two layers.***

***FIGURE 1.21 Structure of hydrated clay.***

**3- Chain Silicates**

For an O/Si ratio of 3, infinite chains or ring structures result. An example for a silicate material having this structure is asbestos. Chains are held together by weak electrostatic forces.

****

***FIGURE 1.22 Structure of mica.***

****

***FIGURE 1.23 Structure of mica showing the position of alkali ions.***

**4- Island Silicates**

When the O/Si ratio is 4, the structural units are isolated (SiO4)4− tetrahedra. These units are connected by positive ions. The resulting structure gives rise to what is called an island silicate. In garnets (Mg,Fe2+,Mn,Ca)3(Cr,Al, Fe3+)2(SiO4)3 and olivines (Mg,Fe2+)2(SiO4), (SiO4)4− becomes the anion. These anions are bonded ionically by the metallic cations.

**5- Aluminosilicates**

Aluminosilicates are formed by the combination of Al2O3 and SiO2. We have seen in mica that Al ions substitute for Si4+ ions. For each of this substitution, the resulting negative charge has to be compensated for by an additional cation. In clays, Al ions occupy the holes in the silicate network. When Al substitutes for Si in the network, the appropriate ratio for determining the structure is the O/(Al+ Si) ratio. For albite (NaAlSi3O8), anorthite (CaAl2Si2O8), eucryptite (LiAlSiO4), orthoclase (KAlSi3O8), and spodune (LiAlSi2O6), the ratio becomes 2. The structure is three dimensional, corresponding to the three-dimensional tetrahedral units. As the bonds are both covalent and ionic primary bonds, the melting points of these aluminosilicates are the highest among all the silicates. In aluminosilicates in general, bonding can be mixed within the silicate network. Si–O–Si bonds are different from those bonds holding the units together, which can be ionic or weak secondary bonds.