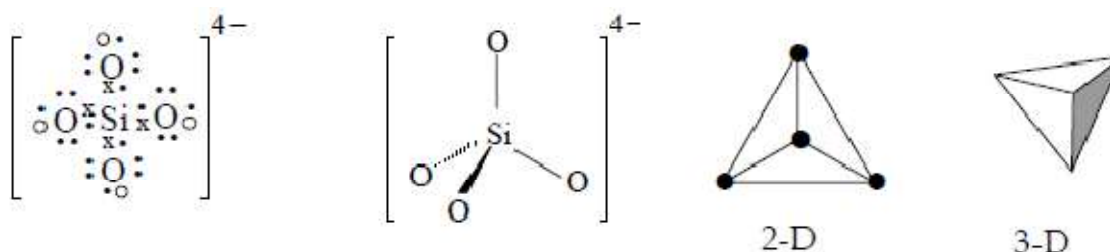


SILICATES

Silicates are salts containing anions of silicon (Si) and oxygen. There are many types of silicates, because the silicon-to-oxygen ratio can vary widely. In all silicates, however, silicon atoms are found at the centres of tetrahedrons with oxygen atoms at the corners. The silicon is always tetravalent (i.e., has an oxidation state of +4). The variation in the silicon-to-oxygen ratio occurs because the silicon-oxygen tetrahedrons may exist as discrete, independent units or may share oxygen atoms at corners, edges, or in rarer instances faces in several ways. Thus, the silicon-to-oxygen ratio varies according to the extent to which the oxygen atoms are shared by silicon atoms as the tetrahedrons are linked together. The linkage of these tetrahedrons provides a rather convenient way of classifying silicates. Seven different classifications are commonly recognized.

The building block of the silicate minerals

All silicate minerals are built up from the basic unit of silicate(IV) ion, SiO_4^{4-} , which has the following structural representations:



The Si atom is covalently bonded to 4 oxygen atoms. Each oxygen atom possesses a formal negative charge. Hence each tetrahedral unit has a formal charge of -4 . When linked together, the extended units are also negatively charged. Presence of other metallic ions such as Ca^{2+} or Mg^{2+} are necessary for electrical neutrality. The covalent Si-O bond, having a bond enthalpy of 466 kJ mol^{-1} , is particularly strong compared with the C-C bond which has a bond enthalpy of 347 kJ mol^{-1} . The linkage $-\text{Si-O-Si-O}-$ is very stable and instead of existing as discrete units of SiO_4^{4-} ions, the silicates tend to form chains, sheets or networks.

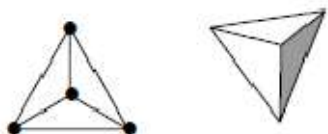
Classification of silicate

- Orthosilicate
- Pyrosilicate

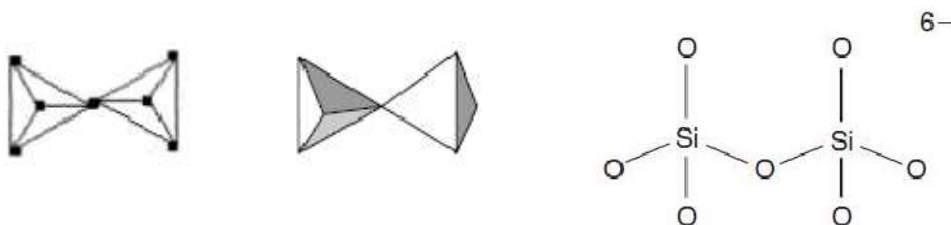
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- Cyclic silicate
- Chain silicate
- Sheet silicate
- 3D silicate

(i) Orthosilicate: If the corner oxygens are not shared with other SiO_4^{4-} tetrahedrons, each tetrahedron will be isolated. Thus, this group is often referred to as the island silicate group. The basic structural unit is then SiO_4^{4-} . In this group the oxygens are shared with octahedral groups that contain other cations like Mg^{+2} , Zr^{+2} , or Ca^{+2} . Simple silicate containing discrete SiO_4^{4-} tetrahedral. Silicates of magnesium (Mg_2SiO_4) and zirconium (ZrSiO_4) are examples.



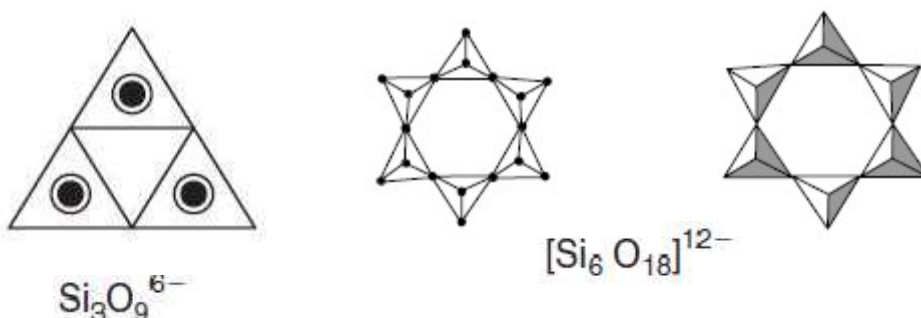
(ii) Pyrosilicate: one of the corner oxygens is shared with another tetrahedron, this gives rise to this group. It is often referred to as the double island group because there are two linked tetrahedrons isolated from all other tetrahedrons. Two SiO_4 tetrahedrons share one corner oxygen atom to form discrete $\text{Si}_2\text{O}_7^{6-}$ ions. Two compounds with this type of linkage are $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ and $\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$.



(iii) Cyclic silicate (ring silicate): If two of the oxygens are shared and the structure is arranged in a ring, such as that shown here, we get the basic structural unit of the cyclosilicates or ring silicates. Shown here is a six membered ring forming the structural group $\text{Si}_6\text{O}_{18}^{-12}$. Three membered rings, $\text{Si}_3\text{O}_9^{-6}$, four membered rings, $\text{Si}_4\text{O}_{12}^{-8}$, and five membered rings $\text{Si}_5\text{O}_{15}^{-10}$ are

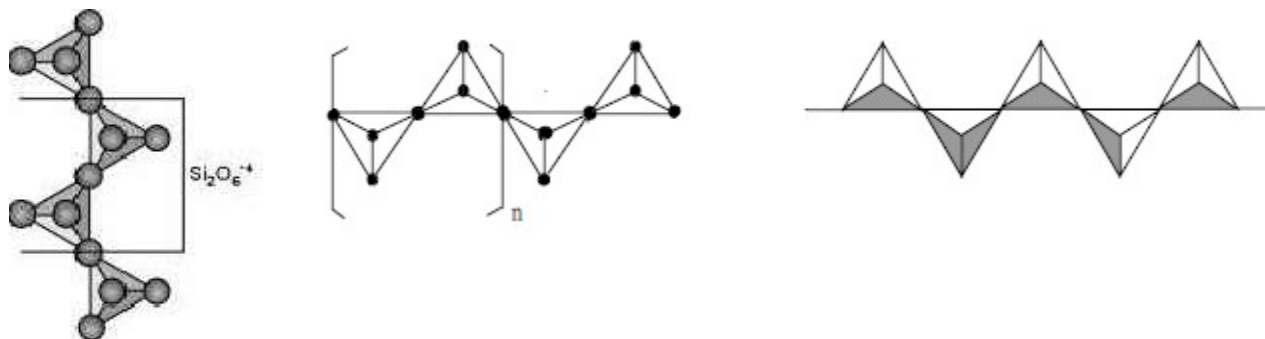
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also possible. In $\text{BaTiSi}_3\text{O}_9$, three SiO_4 tetrahedrons share corners, whereas in $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ (beryl), six tetrahedrons share corners to form a closed ring.



(iv) Chain silicate:

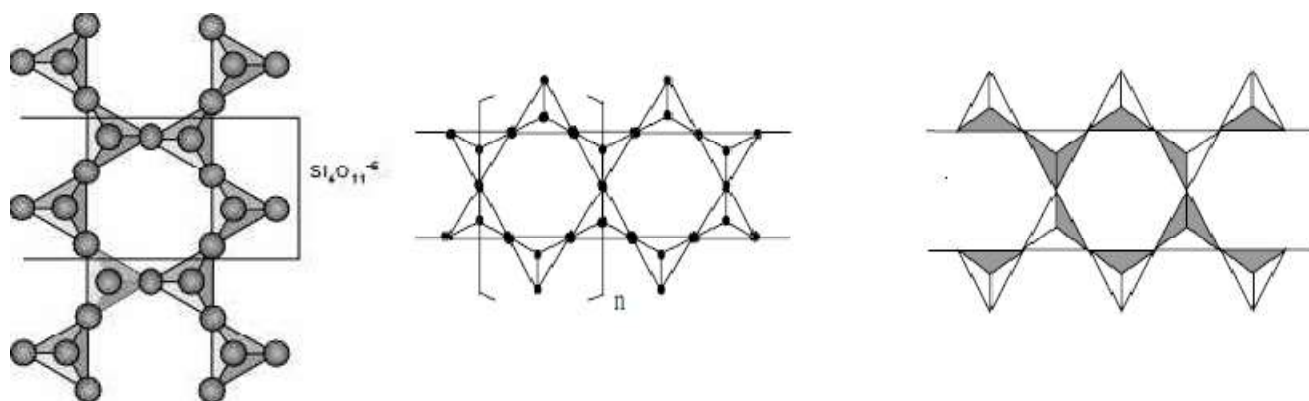
Single Chain Silicates: If two of the oxygens are shared in a way to make long single chains of linked SiO_4 tetrahedra, we get the single chain silicates or inosilicates. In this case the basic structural unit is $\text{Si}_2\text{O}_6^{-4}$ or SiO_3^{-2} . This group is the basis for the pyroxene group of minerals, like the orthopyroxenes $(\text{Mg,Fe})\text{SiO}_3$, $\text{CaMg}(\text{SiO}_3)_2$.



Double Chain Silicates: If two chains are linked together so that each tetrahedral group shares 3 of its oxygens, we can form double chains, with the basic structural group being $\text{Si}_4\text{O}_{11}^{-6}$. When SiO_4 tetrahedrons in single chains share oxygen atoms, double silicon-oxygen chains form. Metal cations link the parallel chains together. Many of these silicates are fibrous in nature, because the ionic bonds between the metal cations and the silicate anions are not as strong as the silicon-oxygen bonds within the chains. A class of fibrous silicate minerals that belong to this group is

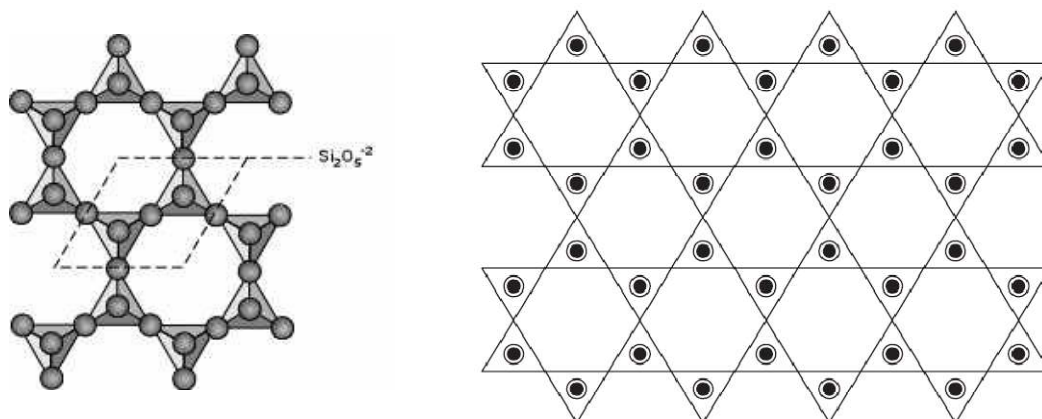
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collectively called asbestos. The amphibole group of minerals are double chain silicates, for example the tremolite – ferroactinolite series - $\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$.



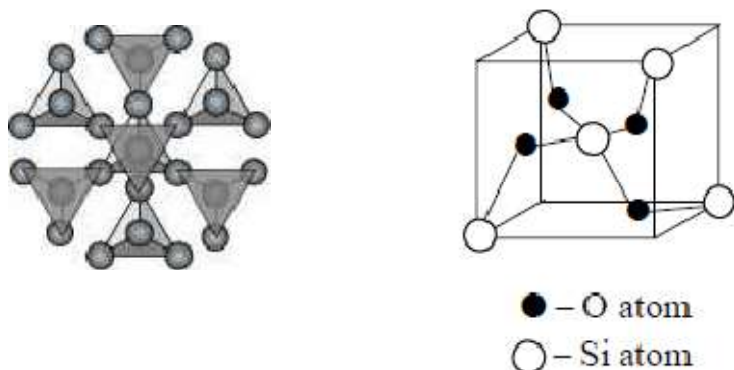
(v) Sheet silicate: If 3 of the oxygens from each tetrahedral group are shared such that an infinite sheet of SiO_4 tetrahedra are shared we get the basis for the phyllosilicates or sheet silicates. In this case the basic structural group is $\text{Si}_2\text{O}_5^{2-}$. The micas, clay minerals, chlorite, talc, and serpentine minerals are all based on this structure. A good example is biotite - $\text{K}(\text{Mg,Fe})_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$.

Talc, $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$, has a structure consisting of layers and parallel sheets. All of the strong bonding interactions among the atoms occur within the layers. Two parallel sheets have the unshared oxygen atoms of the tetrahedra pointing toward each other. In the middle of this sandwich are the magnesium and hydroxide ions, which serve to bind the two silicate sheets together. Only weak van der Waals forces hold the sandwiches (layers) together. Thus layers can slip easily across one another and accounts for the ease for it to be pulverized to make talcum powder, a soft and fine powder to make one's skin feel smooth and dry.



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(vi) **3D silicate:** If all of the corner oxygens are shared with another SiO_4 tetrahedron, then a framework structure develops. The basic structural group then becomes SiO_2 . The minerals quartz, cristobalite, and tridymite all are based on this structure. If some of the Si^{+4} ions are replaced by Al^{+3} then this produces a charge imbalance and allows for other ions to be found coordinated in different arrangements within the framework structure. Thus, the feldspar and feldspathoid minerals are also based on the tectosilicate framework.



Quartz: The mineral Quartz is one form of silica. In quartz, all the four vertices of each tetrahedron are linked to other tetrahedra. The quartz network carries no charge and there are no cations in its structure. The three-dimensional network silicates such as quartz are much harder than their linear or layer counterparts. As the silica structure consists of a giant network of strong covalent bonds. Melting points of quartz and silica (sand) are very high.

Zeolite: A most interesting class of silicates consists of the zeolites. These compounds are three-dimensional silicon-oxygen networks with some of the tetravalent silicon ions replaced by trivalent aluminum (Al^{3+}) ions. The negative charge that results—because each Al^{3+} ion has one fewer positive charge than the Si^{4+} ion it replaces—is neutralized by a distribution of positive ions throughout the network. An example of a zeolite is $\text{Na}_2(\text{Al}_2\text{Si}_3\text{O}_{10}) \cdot 2\text{H}_2\text{O}$. Zeolites are characterized by the presence of tunnels and systems of interconnected cavities in their structures. Zeolites are used as molecular sieves to remove water and other small molecules from mixtures, and they can also be employed to separate molecules for which the molecular masses are the same or similar but the molecular structures are different. In addition, they are used as

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solid supports for highly dispersed catalysts and to promote specific size-dependent chemical reactions.

The aluminosilicates

Very often the silicon atoms are replaced by aluminium atoms to form the silicate analogue, the aluminosilicates. When an aluminium atom replaces a silicon atom, it contributes only three electrons to the bonding framework in place of the four electrons of silicon atoms. The remaining electron is supplied by the ionization of a metal atom such as sodium or potassium.

a) Sheets

Mica belongs to a family in which one of the four silicon atoms in the structural unit of talc is replaced by an aluminium atom and inserting a potassium atom to supply the fourth electron needed for electrical neutrality. Mica has a composition of $\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$. Micas are harder than talc and their layers slide less readily over one another. Like talc, crystals of mica cleave easily into sheets. The cations occupy sites between the sheets. The van der Waals attraction between sheets is increased by the presence of extra ionic charge and accounts for the overall hardness of mica over talc.

(b) Three-dimensional network

The feldspars, in which albite $\text{NaAlSi}_3\text{O}_8$ is an example, are the most abundant aluminosilicate minerals in the Earth surface. The silicon atoms and aluminum atoms occupy the centers of interlinked tetrahedra of SiO_4^{4-} and AlO_4^{5-} . These tetrahedra connect at each corner to other tetrahedra forming an intricate, three-dimensional, negatively charged framework. The sodium cations sit within the voids in this structure.

Daily life importance of some of the silicate minerals

(a) Silicates

(i) Asbestos (double chains or sheets): Asbestos is an excellent thermal insulator that is non-combustible, acid-resistant, and strong. In the past, it was used extensively in construction work to make cement floor tiles, roof covers and ducts. It can also be woven into fabric to make fire-resistant blankets. Its use has been decreased greatly in recent years because inhalation of small

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asbestos fibres during mining and manufacturing or during the removal of frayed and crumbled building materials can cause the lung disease called **asbestosis**.

(ii) Talc (sheets): The common use of talc crystals is to make talcum powder which is a soft and fine powder to make one's skin feel smooth and dry . Its resistance to heat and electricity makes it ideal for surfacing benches and switchboards. It is also an important filler for paint and rubber

(iii) Quartz (three-dimensional network): The hardness of quartz is widely made use of in construction work as sandstones. Quartz/silica tubing are used for high temperature heating. Quartz possesses piezoelectric property which enables it to make crystal oscillators used in watches and electronic circuits and also as pressure sensor in electronic balances. Quartz is also widely used in jewelry and ornamental decorations.

(b) Aluminosilicates

(i) Feldspar (three-dimensional network): In glassmaking, feldspar provides alumina for improving hardness, durability, and resistance to chemical corrosion. In ceramics, feldspar is used as a flux, lowering the vitrifying temperature of a ceramic body during firing and forming a glassy phase.

(ii) Mica (sheets): Mica possesses excellent electrical insulation and is widely used in electronic products such as capacitors, washers for transistors and radar high tension coils. It also has excellent heat insulation and is used in soldering irons and jet engines.