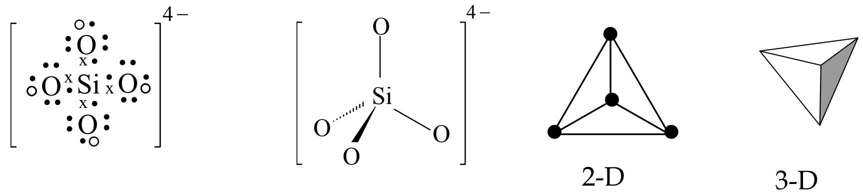
Silicates

1. Introduction

Silicon and oxygen make up most of the Earth's crust. They form the basis of a class of minerals called silicates. All silicates and analogues are derived from the silicate ion, SiO_4^{4-}. The silicon atoms can be replaced by other metals to form analogous compounds, notably the aluminosilicates in which aluminium atoms partially replace the silicon atoms.

2. 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:



"Dot-and-cross" 3-dimensional representation Simplified representation

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 -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.

3. Similarities and differences between silicon and carbon

Unlike elements in the other groups which show a general trend of variation in properties down a group, elements of Group IV show similarities as well as differences down the group, especially the first two and the last two members. The first two members, i.e. C and Si are generally similar in chemical properties. However, their behaviour is not the same as those of the last two typical metallic members, i.e. Sn and Pb.

Although both C and Si atoms tend to form covalent bonds, $Si_{sp^3} - Si_{sp^3}$ overlap is not as effective as $C_{sp^3} - C_{sp^3}$ overlap and as a result, bond enthalpy of C-C bond is 347 kJ mol^{-1} whereas Si-Si bond is just 226 kJ mol^{-1}. Hence, the fact that carbon is capable of forming long -C-C- chains does not mean silicon also forms stable -Si-Si- chains. On the other hand, $Si_{sp^3} - O_{sp^3}$ overlap is of the right order to form strong Si-O bonds, as reflected by a high Si-O bond enthalpy of 466 kJ mol^{-1}. Thus, similar to carbon which forms -C-C-C-C- chains and hence polymers, silicon forms -Si-O-Si-O- chains and hence polymeric silicates.

4. The silicates

Silicate Structures				
Structure	Figure	Corners shared at each tetrahedron	Repeat unit	Example
Tetrahedra	1	0	SiO_4^{4-}	*Olivines,* $(Mg/Fe)_2SiO_4$
Pairs of tetrahedra	2	1	$Si_2O_7^{6-}$	*Thortveitite,* $Sc_2(Si_2O_7)$
Closed rings	3	2	SiO_3^{2-}	*Beryl,* $Be_3Al_2(Si_6O_{18})$
Single chains	4	2	$SiO_3^{2-}/Si_2O_6^{4-}$	*Pyroxenes,* $CaMg(Si_2O_6)$
Double chains	5	2.5	$Si_4O_{11}^{6-}$	*Amphibole,* $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$
Sheets	6	3	$Si_2O_5^{2-}$	*Talc,* $Mg_3(Si_4O_{10})(OH)_2$
Three-dimensional network	7	4	SiO_2	*Quartz,* $(SiO_2)_n$

Table 1

Notes: Photographs of silicates can be found at http://www.mindat.org.

(a) Tetrahedra / pairs of tetrahedra

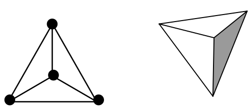


Fig. 1

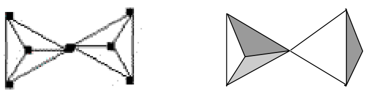


Fig. 2

The cations are arranged around the tetrahedral units on a regular crystalline lattice.

(b) Closed rings

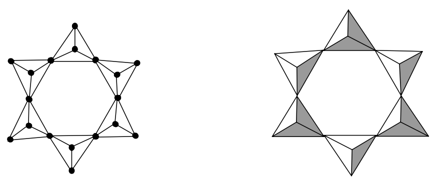


Fig. 3: Beryl, $(Si_6O_{18}^{12-})$

(c) Single chains

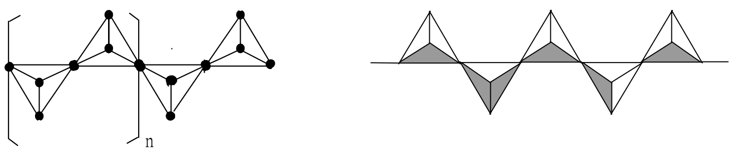


Fig. 4: Pyroxenes, $(Si_2O_6^{4-})_n$

(d) Double chains

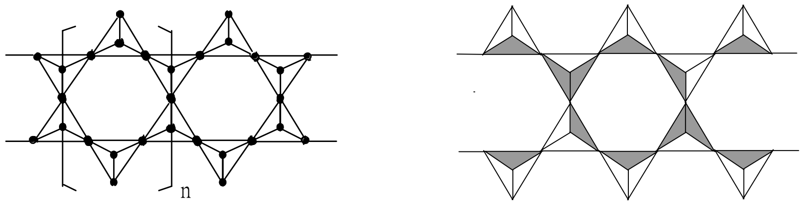


Fig. 5: Amphibole, $(Si_4O_{11}^{6-})_n$

Asbestos is a generic term for a group of naturally occurring hydrated silicates that can be processed mechanically into long fibres. It refers to two kinds of minerals: serpentines and amphiboles. Serpentines, the most common of which is chrysotile, $Mg_3Si_2O_5(OH)_4$, account for almost 90% of worldwide asbestos production. Chrysotile has a sheet structure of Fig. 6 while Tremolite (amphibole), $Ca_2Mg_5(Si_4O_{11})_2(OH)_2$, possesses the double chain structure of Fig. 5. Both chain and sheet structures are held together by the electrostatic attraction between the cations and the negative silicate structures. Crystal cleavage is expected to occur along the chain direction because the non-directional ionic links are comparatively weaker than the strong Si-O covalent bonds. Hence asbestos minerals are fibrous.

(e) Sheets

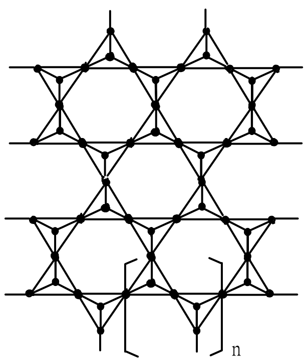


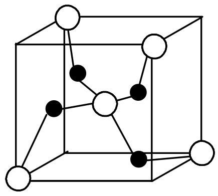
Fig. 6: Talc, $(Si_2O_5^{2-})_n$

Talc, $Mg_3(Si_4O_{10})(OH)_2$**,** 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.

A VRML (Virtual Reality Modelling Language) image of talc is available at http://www.ill.fr/dif/3D-crystals. The double layers of silica tetrahedra sandwiching a single layer of MgO octahedra (contributed by Mg^{2+} and OH^- ions) is apparent. H atoms play no role in the sandwiched layers.

The website provides three-dimensional diagrams of numerous crystal structures, including the silicates. A special viewing technique, called the VRML is employed in which viewers can manipulate the diagrams as if he is handling a real object and can look at it at various angles by performing operations such as rotation, roll, zoom and panning. VRML viewer can be downloaded from the following website: http://www.parallelgraphics.com/products/cortona/download/iexplore.

(f) Three-dimensional network



● – O atom
○ – Si atom

Fig. 7: Quartz, $(SiO_2)_n$

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.

Exercises:

By referring to Table 1, predict the structure of each of the following silicate minerals (double chains, sheets, networks, and so forth).

1. $Ca_3Fe_2(SiO_4)_3$
2. $Na_2ZrSi_4O_{10}$
3. $Ca_2ZnSi_2O_7$
4. $Mg_3Si_2O_5(OH)_4$

Answers:

1. Tetrahedra 2. Sheets 3. Pairs of tetrahedra 4. Sheets

5. 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 $KMg_3(AlSi_3O_{10})(OH)_2$. 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 $NaAlSi_3O_8$ 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.

Exercises:

By referring to Table 1, predict the structure of each of the following aluminosilicate minerals (double chains, sheets, networks, and so forth). In each case, the aluminum atoms grouped with the silicon and oxygen in the formula substitute for Si atoms in tetrahedral sites.

1. $Li(AlSi_2O_6)$
2. $KAl_2(AlSi_3O_{10})(OH)_2$
3. $Al_3Mg_2(AlSi_5O_{18})$

Answers:

1. Network 2. Sheets 3. Closed ring or single chains

6. 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 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.

References

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http://www.mindat.org

http://ccp14.minerals.csiro.au/ccp/web-mirrors/xtaldraw/crystal/silicate.htm