

If the number of BO_2 groups in the ring is increased indefinitely we reach in the limit the infinitely extended open chain of composition $[\text{BO}_2]_n^{n-}$ shown in fig. 11.01 e. Such an arrangement differs fundamentally from all the other complex anions so far described in that it is no longer possible to point to any discrete radical. The repeat period in the crystal may extend over several units of the chain, at different points of which different atoms may be attached, so that in chemical terminology such a

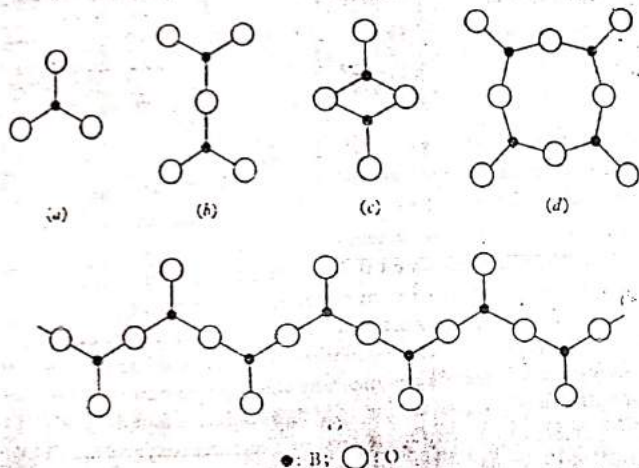


Fig. 11.01. Some actual or hypothetical boron-oxygen groupings in borates. (a) Isolated triangles, BO_3^{3-} , e.g. orthoborates. (b) Triangles sharing one oxygen atom, $\text{B}_2\text{O}_4^{4-}$, e.g. pyroborates. (c-e) Triangles sharing two oxygen atoms to form closed rings or an open chain, $[\text{BO}_2]_n^{n-}$, e.g. metaborates.

chain ion is indefinitely polybasic. An infinite ion of this type (but somewhat distorted from the idealized form shown at (e)) is found in the crystal structure of calcium metaborate, CaB_2O_4 . The ions extend parallel to one another through the structure and are linked together by ionic bonds between the calcium and the unshared oxygen atoms.

11.03. Although boron is normally 3-co-ordinated by oxygen there are also structures in which 4-co-ordination is found, as, for example, in the heteropolyacids (§ 10.24). The same co-ordination is found in a limited number of borate ions. Thus in borax, normally formulated as $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, the anion has the configuration shown in fig. 11.02, in

which two of the boron atoms are 3-co-ordinated and two are 4-co-ordinated by oxygen. The boron atoms are linked by shared oxygen atoms and the unshared oxygen atoms belong to hydroxyl groups. These hydroxyl groups are essential constituents of the complex anion, the composition of which is $\text{B}_4\text{O}_7(\text{OH})_4^{2-}$, so that the formula of the salt should more properly be written $\text{Na}_2[\text{B}_4\text{O}_7(\text{OH})_4] \cdot 8\text{H}_2\text{O}$. Examples such as this, and many others which could be quoted, serve to emphasize that the peculiar complexity of the chemistry of borates stems from the multiplicity of possible configurations for the complex ion, and that many of the difficulties which have arisen in discussing these compounds

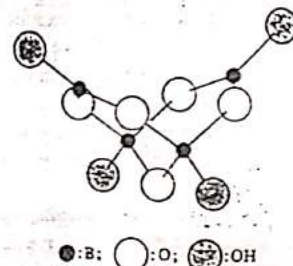


Fig. 11.02. Clinographic projection of the (idealized) structure of the $[\text{B}_4\text{O}_7(\text{OH})_4]^{2-}$ ion in borax, $\text{Na}_2[\text{B}_4\text{O}_7(\text{OH})_4] \cdot 8\text{H}_2\text{O}$.

have been due to attempts to interpret them as the salts of acids which often have no existence. We shall not, however, pursue the question further at this stage because the same point is illustrated even more strikingly by the structures of the silicates, to which we now turn.

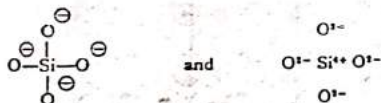
SILICATES

11.04. From both a structural and a chemical point of view the silicates are of far greater importance than the borates, and, on account of their great petrological interest as the most abundant component of the Earth's crust, they have been more exhaustively studied by X-ray methods than any other class of ionic crystals. The peculiar complexity of the chemistry of silicates has long been recognized, the enormous variety of composition, the difficulty of assigning significant formulae, and the close morphological association of seemingly quite unrelated compounds all being characteristics difficult to interpret in terms of conventional chemical principles. Structural studies have thrown much light on these topics, and, in fact, in the structures of the silicates we find

not only some of the most elegant examples of the general principles of structural chemistry but also what is perhaps, as yet, the most impressive illustration of the power of such studies in rationalizing a previously intractable field of investigation. A discussion at some length is therefore justified, but, even so, it will be possible for us to describe only a limited number of the many known silicate structures, and our choice of examples will be confined to those which advance our arguments by the general principles which they exemplify. Many structures of which the interest is primarily mineralogical will have to be ignored, but the reader who is particularly concerned with this aspect of silicate chemistry will find an exhaustive and readily accessible account in the work by Bragg and Claringbull quoted in appendix 1.

General principles of silicate structures

11.05. The fundamental characteristic of all silicate structures is the tetrahedral co-ordination of silicon by oxygen. The nature of the Si-O bond has already been discussed (§8.33) and we have seen that this bond has a considerable degree of ionic character. The SiO₄ group can therefore be regarded as having a structure to which both the extreme configurations



make a contribution, and it is for this reason that silicates occupy a position in respect of their structures intermediate between the salts and the complex oxides. If we picture a simple silicate such as Mg₂SiO₄ (to be described shortly) as consisting of the ions Mg²⁺ and SiO₄⁴⁻ it would be regarded as a salt, but if we think of it in terms of the separate ions Mg²⁺, Si⁴⁺ and O²⁻ it would more properly be classified as a complex oxide. Either view is equally acceptable provided that we understand the implication that neither alone is wholly adequate.

Although in a limited number of silicates isolated SiO₄⁴⁻ ions are found, just as isolated SO₄²⁻ ions occur in sulphates, the great majority of these compounds contain SiO₄ groups linked together through common oxygen atoms to form complex polynuclear anions of finite or infinite extent. The silicates may therefore be classified in a manner formally analogous to that used for the borates in terms of the way in which the co-ordinating tetrahedra are united. The higher co-ordination

of silicon, however, leads to a greater number of structural types, while at the same time additional complexities due to other causes arise.

In the first place the isomorphous replacement of cations by others of the same charge and similar size, or even the replacement of several different cations by others of different valencies but with the same aggregate charge, although possible in many ionic structures, is particularly common among the silicates. We give in table 11.01 a list of the ions of most frequent occurrence in silicate minerals, together with their radii and the oxygen co-ordination numbers—commonly observed. Within wide limits we may say that those ions which have the same oxygen co-ordination (e.g. Mg²⁺, Fe²⁺; Na⁺, Ca²⁺; etc.) are readily interchangeable, and it is this isomorphous replacement which confers on silicate structures their variable and indefinite composition, the chemical interpretation of which presented many difficulties before its structural origin was understood. It is, moreover, not only the cations in silicate structures which can experience isomorphous replacement; the anions O²⁻, OH⁻ and F⁻ are closely comparable in size and they, too, can replace each other statistically.

Table 11.01. Some common ions in silicate structures

Ion	Radius (Å)	Oxygen co-ordination	Ion	Radius (Å)	Oxygen co-ordination
Be ²⁺	0.31	4	Fe ²⁺	0.80	6, 8
Si ⁴⁺	0.41	4	Mn ²⁺	0.80	6, 8
Al ³⁺	0.50	4, 6	Na ⁺	0.95	6, 6
Cr ³⁺	0.63	6	Ca ²⁺	0.99	8
Fe ³⁺	0.64	6	K ⁺	1.33	6-12
Mg ²⁺	0.65	6, 8	F ⁻	1.36	—
Ti ⁴⁺	0.68	6	O ²⁻	1.40	—
Zn ²⁺	0.74	4	OH ⁻	1.53	—

A second feature of silicate crystal chemistry is peculiar to silicates alone, and arises accidentally from the particular value of the radius of the aluminium ion. The Al:O radius ratio of 0.36 is so close to the critical value of 0.3 for transition from 6- to 4-co-ordination that this ion can occur in both conditions, sometimes in the same structure. When 4-co-ordinated the aluminium ion replaces silicon, and such replacement is purely random and may be of indefinite extent. For every aluminium ion so introduced a corresponding substitution of Ca²⁺ for Na⁺, Al³⁺ for Mg²⁺ or Fe³⁺ for Fe²⁺ must simultaneously occur else,

where in the structure to preserve neutrality. The appearance of aluminium in one structure in two entirely different roles is a feature of the silicates which chemical analysis alone cannot reveal, and which has given rise to many difficulties in the interpretation of such systems.

The classification of silicates

11.06. The classification of silicate structures is immediately analogous to that of the borates, and is most conveniently made in terms of the way in which the silicon tetrahedra are linked together. Such a classification, originally proposed by Machatschki, must be regarded as one of the most valuable contributions to silicate chemistry, for it has introduced order in a field where previous classifications, based on hypothetical acids of which the silicates were supposed to be salts, led to considerable confusion; and it is interesting to find that this new classification supports in almost every detail that developed by the mineralogist from purely morphological and physical properties. We shall now proceed to discuss briefly a number of silicate structures in order to make clear the basis of the classification and to illustrate the characteristic features which these structures show.

Isolated SiO_4 groups: orthosilicates

11.07. The simplest possible structural arrangement is that in which isolated SiO_4^{4-} groups of the form shown in fig. 11.03a are linked together only through the medium of other cations. Such groups are found in the *orthosilicates*, and correspond to an oxygen:silicon ratio of 4:1 or greater.

Olivine

11.08. A typical structure of this kind is that of the olivine series of minerals, of which forsterite, Mg_2SiO_4 , may be taken as an example. A somewhat idealized form of this structure is shown in fig. 11.04, in which, for clarity, the SiO_4 tetrahedra have been outlined although the lines shown do not of course represent bonds between oxygen atoms. The silicon atoms at the centres of these tetrahedra are not shown in the figure.

The main points of importance to note in this structure are:

- (1) The SiO_4 tetrahedra are isolated and occur pointing alternately up and down.
- (2) The tetrahedra are linked together only by O-Mg-O bonds.

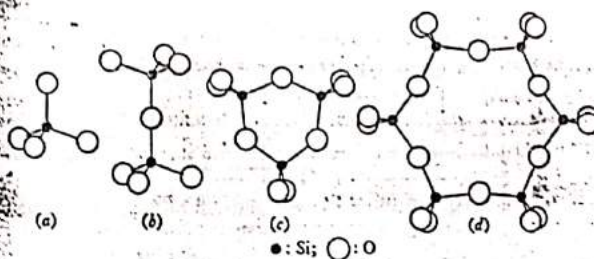


Fig. 11.03. Some possible closed silicon-oxygen groupings in silicates. (a) Isolated tetrahedra, SiO_4^{4-} , e.g. orthosilicates. (b) Tetrahedra sharing one oxygen atom, $\text{Si}_2\text{O}_7^{6-}$, e.g. thortveitite. (c) Tetrahedra sharing two oxygen atoms to form a three-membered ring, $\text{Si}_3\text{O}_9^{6-}$, e.g. benitoite. (d) Tetrahedra sharing two oxygen atoms to form a six-membered ring, $\text{Si}_6\text{O}_{18}^{12-}$, e.g. beryl.

¹³ In some of the diagrams superimposed oxygen atoms have been displaced slightly for clarity.

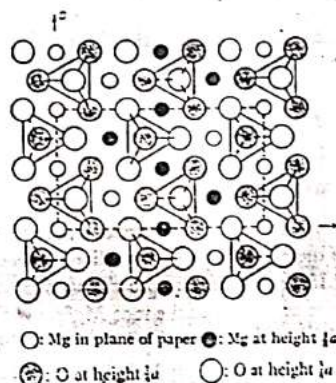


Fig. 11.04. Plan of the idealized orthorhombic structure of forsterite, Mg_2SiO_4 , projected on a plane perpendicular to the x axis. The silicon atoms lie at the centres of the tetrahedra of oxygen atoms, and are not shown.

- (3) The magnesium ions are co-ordinated by six oxygen ions lying at the corners of a very nearly regular octahedron, so that the whole structure can be described as a packing together of tetrahedra and octahedra.
- (4) The disposition of the oxygen ions alone is approximately that of hexagonal close packing. A close-packed arrangement of oxygen ions is

a characteristic feature of many silicate structures and results from the large size of these ions compared with that of most others of common occurrence.

11.09. Other members of the olivine group have the same structure, but with Mg^{2+} ions partly or wholly replaced by Fe^{2+} or Mn^{2+} . In olivine itself about 10 per cent of the Mg^{2+} ions of forsterite are replaced by Fe^{2+} ; fayalite and tephroite have the idealized compositions Fe_2SiO_4 and Mn_2SiO_4 , respectively.

Chondrodite

11.10. The minerals of the chondrodite series are closely related to olivine, and illustrate a type of mixed structure of frequent occurrence among silicates. These minerals may be represented by the general formula $Mg(F, OH)_2 \cdot nMg_2SiO_4$, and members are known for all values of n from 1 to 4. The exact details of the structures will not be considered here, but briefly they may be described as formed by the superposition of sheets of the forsterite structure and of that of $Mg(OH)_2$. The structure of $Mg(OH)_2$ is the same as that of cadmium iodide, with the OH^- ions arranged in hexagonal close packing, and it is the similarity of the arrangement of the oxygen ions in olivine and of the hydroxyl groups in $Mg(OH)_2$ which enables a 'fit' to be achieved.

Phenacite and willemite

11.11. The structure of phenacite, Be_2SiO_4 , is of interest in that in spite of its similarity in composition to forsterite the atomic arrangement is entirely different, and a relatively complex rhombohedral structure obtains in which the oxygen atoms are far from close packed. In this structure both the silicon and beryllium atoms are tetrahedrally co-ordinated, and each oxygen atom is common to two BeO_4 tetrahedra and to one SiO_4 group; the complexity of the resulting structure is merely an expression of the difficulty of linking these tetrahedra together in a manner satisfying this condition.

The difference between the structures of forsterite and phenacite can readily be attributed to the difference in size of the Mg^{2+} and Be^{2+} ions, the radii of which are appropriate to oxygen co-ordination of 6 and 4, respectively. It is not, however, possible in this way to explain why willemite, Zn_2SiO_4 , has the phenacite structure rather than that of olivine, for the radii of the Zn^{2+} and Mg^{2+} ions are very nearly the same,

and it seems likely that in both phenacite and willemite the tetrahedral co-ordination of the metal atoms is due to a considerable degree of covalent character in the metal-oxygen bonds. The difference between the structures of Mg_2SiO_4 and Zn_2SiO_4 may therefore be compared with that between the structures of MgO and ZnO ; the former has the sodium chloride structure with 6-co-ordination of magnesium, whereas in the latter the more covalent character of the bonding gives rise to the 4-co-ordinated wurtzite arrangement.

Garnets

11.12. The garnets comprise a wide range of minerals of very variable composition which may be represented by the general formula $A_2^{2+} B_2^{3+} Si_3 O_{12}$, where A^{2+} is Ca^{2+} , Mg^{2+} , Fe^{2+} or Mn^{2+} , and B^{3+} is Al^{3+} , Fe^{3+} or Cr^{3+} . They are typical orthosilicates, with independent SiO_4 groups, and the co-ordinations of the A and B ions are in accordance with their relative sizes; the larger A ions are 8- and the smaller B ions 6-co-ordinated by oxygen. The readiness with which the garnets form solid solution with each other, and the variable composition which thus results, are clearly to be attributed to the closely comparable sizes of most of the alternative substituent A and B ions. In this connexion however, it is noteworthy that the calcium garnets differ from the others in showing only a limited range of solid solution, owing to the significantly larger radius of the Ca^{2+} ion in comparison with the ions Mg^{2+} , Fe^{2+} and Mn^{2+} . We have already quoted the garnet $Ca_3Al_2Si_3O_{12}$ as an illustration of the application of Pauling's rules to silicate structures (§9.10).

Other orthosilicates

11.13. Many other orthosilicates with an oxygen:silicon ratio of 4:1 and isolated SiO_4 groups are known, but they are mostly among substances of primarily mineralogical interest. When the oxygen:silicon ratio exceeds 4:1 some oxygen atoms are necessarily not linked to silicon at all, and such atoms may occur either as isolated O^{2-} ions co-ordinated only by metallic cations, as in cyanite, Al_2SiO_5 , or as hydroxyl ions OH^- , as in topaz, $(F, OH)_2Al_2SiO_5$. In either case these oxygen atoms must be ignored in deriving the oxygen:silicon ratio, for otherwise the value of this ratio characteristic of the isolated SiO_4 tetrahedra will be concealed. Thus the formula of euclase is often given as $HBeAlSiO_4$, but X-ray analysis has shown that it is actually a normal orthosilicate and therefore to be regarded as $(OH)BeAlSiO_4$.

Structures with Si_2O_7 groups*Thortveitite and melilite*

11.14. When the SiO_4 groups in a silicate are not separate, but occur linked together through one or more shared oxygen ions, the number of possible arrangements is very large. The simplest of these is that shown in fig. 11.03b, where two such groups share a single oxygen ion to form the composite group $\text{Si}_2\text{O}_7^{6-}$. Such an arrangement is found in thortveitite, $\text{Sc}_2\text{Si}_2\text{O}_7$, melilite and a number of other minerals. The idealized composition of melilite may be represented as $\text{Ca}_2\text{MgSi}_2\text{O}_7$, but the mineral frequently contains considerable quantities of aluminium and is our first example of a structure in which aluminium replaces silicon in 4-co-ordination. For every Si^{4+} ion thus replaced by Al^{3+} a compensatory change must be made elsewhere in the structure to maintain electrical neutrality, and this is achieved by the replacement of one Mg^{2+} ion by an Al^{3+} ion in 6-co-ordination. The composition of the aluminium-containing mineral may thus be represented as $\text{Ca}_2(\text{Mg}_{1-x}\text{Al}_x)(\text{Si}_{2-x}\text{Al}_x\text{O}_7)$, and such a formula emphasizes the importance of distinguishing between the aluminium atoms in their two different roles and the difficulty in assigning a significant formula on the basis of chemical analysis alone.

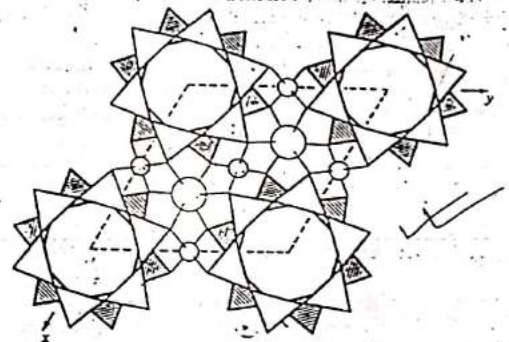
Hemimorphite and vesuvianite

11.15. A further interesting structure containing Si_2O_7 groups is that of hemimorphite. On the basis of chemical analysis this mineral is usually represented by the formula $\text{H}_2\text{Zn}_2\text{Si}_2\text{O}_7$. The structure analysis reveals, however, that the mineral is not an orthosilicate and that the oxygen ions are of three kinds, those co-ordinating the silicon ions, those contained in hydroxyl groups and those in water molecules. The true arrangement is made clear by writing the formula $(\text{OH})_2\text{Zn}_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$ so that the characteristic oxygen:silicon ratio is revealed. In vesuvianite a combination of independent SiO_4 tetrahedra and Si_2O_7 groups is found: $(\text{OH})_4\text{Ca}_{10}\text{Al}_4(\text{Mg}, \text{Fe})_2 \{(\text{Si}_2\text{O}_7)_2 \cdot (\text{SiO}_4)_3\}$. On the basis of Pauling's fifth rule, however, such a combination of two different types of co-ordination is not likely to be of common occurrence.

Ring structures: metasilicates

11.16. (Closed ring-groups of composition $(\text{SiO}_2)_n^{2n-}$ containing an indefinite number of members are formed when two oxygen ions are shared between neighbouring SiO_4 tetrahedra.) Such groups occur in

the metasilicates, and correspond to an oxygen:silicon ratio of 3:1. In view of the partially ionic character of the Si-O bond the two-membered ring Si_2O_6 is unlikely to be found in any structure because it would involve an edge common to the two tetrahedra; of the other possible ring anions only those with $n = 3$ and $n = 6$ have so far been observed. The three-membered ring (fig. 11.03c) occurs in benitoite, $\text{BaTiSi}_3\text{O}_{11}$, and the ring of six SiO_4 groups (fig. 11.03d) is found in beryl,



○: Be; ○: Al

Fig. 11.05. Plan of the unit cell of the hexagonal structure of beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, projected on the basal plane. The Si_6O_{18} rings (see fig. 11.03d) at two different heights are represented as rings of shaded and unshaded tetrahedra. The beryllium and aluminium ions lie in a plane midway between the two sets of rings.

$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, a structure which we may describe in somewhat more detail as a particularly beautiful illustration of many of the principles of silicate crystal chemistry.

Beryl and cordierite

11.17. A plan of the beryl structure is shown in fig. 11.05. For clarity the SiO_4 groups are here shown as solid tetrahedra, and only the beryllium and aluminium ions are separately indicated. The Si_6O_{18} rings are clearly revealed and it will be seen that these rings are bound together

On the other hand, it will be remembered that in the structure of SiS_2 (§8.39) the SiS_4 tetrahedra do, indeed, share edges, and that this fact was used as an argument pointing to the covalent character of the Si-S bond.

by the metallic cations. The oxygen co-ordination of these cations is that demanded by the radius ratio, and each beryllium ion is tetrahedrally surrounded by four oxygen ions belonging to four different rings. Similarly, the aluminium ions occur between six different rings and are octahedrally co-ordinated by oxygen. The separate rings are thus bound together both laterally and vertically by the oxygen-cation bonds. The strength of each of these bonds, both from the aluminium and beryllium, is $\frac{1}{2}$, and the electrostatic valency rule is therefore satisfied in detail, since every oxygen ion not shared between two SiO_4 tetrahedra is linked to one silicon, one beryllium and one aluminium ion. A characteristic feature of the beryl structure is the wide, empty tunnels passing through the centres of the rings. No ions can be placed in these tunnels, since the valencies of the surrounding oxygen ions are already completely expended on their silicon neighbours, but it is possible that the helium so often found physically occluded in beryl is here accommodated. Such occluded helium may be expelled by heat without damage to the structure.

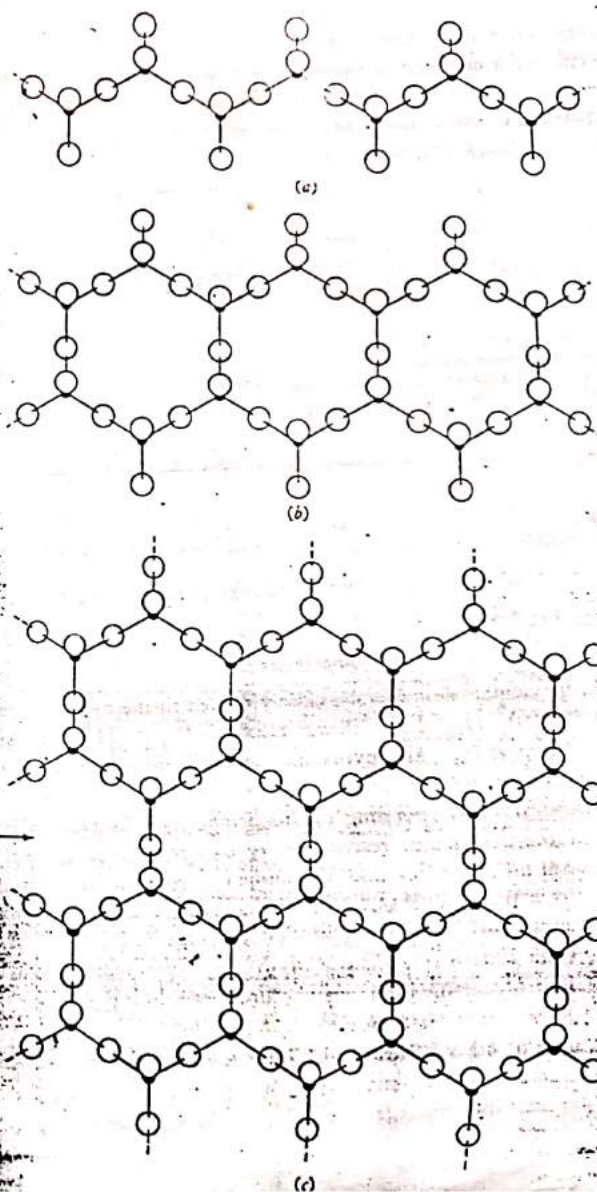
Cordierite, $\text{Al}_3\text{Mg}_2(\text{Si}_3\text{Al})\text{O}_{16}$, has a similar structure to beryl. One-sixth of the silicon atoms in the anion are replaced by aluminium to give the ion $[(\text{Si}_3\text{Al})\text{O}_{18}]^{12-}$, and the balance of charge is maintained by replacing $(3\text{Be}^{2+} + 2\text{Al}^{3+})$ by $(3\text{Al}^{3+} + 2\text{Mg}^{2+})$. In this case all the aluminium ions are 4-co-ordinated, but the distinction between their two roles, as cations and as constituents of the anion, must still be recognized and should be represented in the formula, as indicated above.

Chain structures

The pyroxenes

11.18. (When the closed rings of SiO_4 groups, each sharing two oxygen ions, contain an infinite number of members, they degenerate into indefinitely extended straight chains of the type shown in fig. 11.06a) Chains of this kind are found in the important group of pyroxene minerals, the structure of the simplest of which, diopside, $\text{CaMg}(\text{SiO}_3)_2$ is illustrated in an idealized form in fig. 11.07. Here the chains are seen

Fig. 11.06. Some possible open silicon-oxygen groupings in silicates. (a) Tetrahedra sharing two oxygen atoms to form open chains, $[\text{SiO}_3]_n^{2n-}$, e.g. pyroxenes. (b) Tetrahedra sharing alternately two and three oxygen atoms to form open chains, $[\text{Si}_4\text{O}_{11}]_n^{4n-}$, e.g. amphiboles. (c) Tetrahedra sharing three oxygen atoms to form open sheets, $[\text{Si}_2\text{O}_6]_n^{4n-}$, e.g. talc. Some oxygen atoms have been displaced slightly to reveal the silicon atoms.



end-on, and it will be noticed that they are arranged with the vertices of the tetrahedra pointing alternately in opposite directions. In the two directions normal to their length the chains are linked together by the oxygen-cation bonds. Each magnesium ion is 6- and each calcium ion 8-co-ordinated by oxygen.

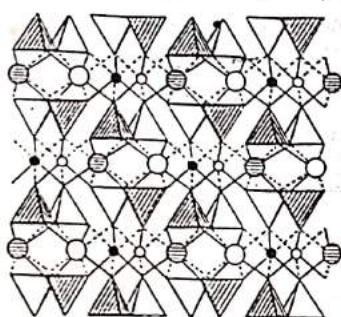
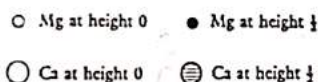


Fig. 11.07. Plan of the idealized monoclinic structure of diopside, $\text{CaMg}(\text{SiO}_3)_2$, projected on a plane perpendicular to the z axis. The chains of fig. 11.06a are here seen end-on.



The amphiboles

11.19. In the amphibole minerals, closely related to the pyroxenes, a double chain of the type shown in fig. 11.06b is found. This may be regarded as derived from the pyroxene chain by the operation of a reflexion plane passing through the outermost oxygen ions. The oxygen:silicon ratio corresponding to this arrangement is 11:4. The structures of the amphiboles resemble very closely in their general features those of the pyroxenes, and will not be discussed in detail here. They differ from the pyroxenes, however, in containing hydroxyl or fluorine as an essential constituent, so that the idealized formula of tremolite may be written $(\text{OH}, \text{F})_2\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}$. The hydroxyl and fluorine ions in such structures can never occur directly linked to silicon, since the single Si-OH or Si-F bond would completely saturate their valency and leave no other bonds available for their attachment to the rest of the structure. Accordingly, oxygen atoms contained in the hydroxyl group must be disregarded in deducing the characteristic oxygen:silicon ratio.

The crystal chemistry of pyroxenes and amphiboles

11.20. It is instructive to compare the now accepted formula of tremolite, $(\text{OH}, \text{F})_2\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}$, with the composition $\text{CaMg}_5(\text{SiO}_3)_8$, $\text{Ca}_2\text{Mg}_6\text{Si}_8\text{O}_{24}$ previously assigned on the basis of chemical analysis. The latter formula not only ignores the small quantity of water found as an essential constituent of the mineral, but also indicates a considerable excess of magnesium compared with the amount usually observed. Nevertheless, six magnesium ions are necessary to achieve electrical neutrality. In the light of the structure analysis it at once becomes clear that the characteristic oxygen:silicon ratio is 22:8 and not 24:8, and that there are only five magnesium ions present. We cannot, however, express the composition in the form $\text{O}_2\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}$, since such a structure, containing two oxygen ions other than those in the silicon chains, is not neutral. Only if these oxygen ions occur as hydroxyl groups is the electrostatic valency rule satisfied and neutrality preserved.

The pyroxenes and amphiboles are characterized by the very extensive isomorphous substitution which they show. In the amphiboles we find another example of the replacement of silicon by aluminium in 4-co-ordination, and in hornblende this occurs up to the extent of about $\text{Si}_4\text{Al}_2\text{O}_{22}$ compared with Si_8O_{22} in tremolite. The corresponding balance of charge is achieved either by the replacement of some Mg^{2+} ions by Al^{3+} in 6-co-ordination; or by the introduction of additional alkali or alkaline earth metal ions into the crystal. There is sufficient space between the chains in the structure to accommodate these additional ions. Even when no replacement of silicon occurs, extensive substitution of cations by others of the same charge and comparable size may take place. Thus Fe^{2+} or Mn^{2+} may replace Mg^{2+} , the ions Fe^{2+} , Mg^{2+} or 2Na^+ may replace Ca^{2+} , and F^- may replace OH^- . In view of the complexities of these structures it is not surprising that their interpretation in terms of chemical analysis alone presented great difficulties. Even when we know what characteristic oxygen:silicon ratios to expect, care must be taken in deducing such ratios to exclude from the oxygen ions any which occur in hydroxyl groups or as water, and to include with the silicon ions those aluminium ions which are in 4- but not those in 6-co-ordination.

Sheet structures

11.21. If SiO_4 tetrahedra are linked together in such a way that three of the four oxygen atoms are shared with neighbouring tetrahedra a two-dimensional network of the type shown in fig. 11.06c is one of a number of possible arrangements which may result. Such a network corresponds to an oxygen:silicon ratio of 10:4, and is found in talc and the micas.

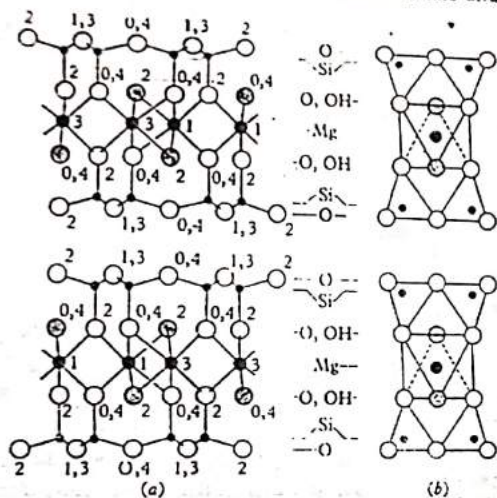


Fig. 11.08. (a) Plan of the idealized monoclinic structure of talc, $\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$, projected on a plane perpendicular to the x axis. The sheets of fig. 11.06c are here seen edge-on, as viewed in the direction of the arrow. For clarity only one ring of each sheet is drawn and only some of the magnesium atoms are shown, but the sheets do, of course, extend indefinitely. The numbers indicate the heights of the various atoms above the plane of projection, expressed in units of $\frac{1}{4}a$. The heights of the silicon atoms are not marked; they are the same as those of the unshared oxygen to which they are attached. (b) Schematic representation of the same structure, showing the co-ordinating tetrahedra about the silicon atoms and the co-ordinating octahedra about the magnesium atoms.

11.22. The structure of talc, $\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$, is illustrated in idealized form in fig. 11.08a. Here the sheets of SiO_4 tetrahedra are seen edge-on, and it will be observed that they are arranged in pairs with the vertices and bases of the tetrahedra alternately adjacent. The bases of the sheets are held together only by weak van der Waals forces, but the unshared oxygen atoms at the vertices are strongly cross-linked by magnesium

ions, each of which is octahedrally co-ordinated by four of these oxygen atoms (two from each sheet) and by two hydroxyl ions. These hydroxyl ions lie at the centres of the hexagonal rings of unshared oxygen atoms and, with them, form a close-packed (O + OH) layer. If the distinction between O and OH is ignored, the magnesium ions are co-ordinated in the same manner as in $\text{Mg}(\text{OH})_2$. The structure can thus alternatively be regarded as consisting of sheets of $\text{MgO}_4(\text{OH})_2$ octahedra sandwiched between sheets of SiO_4 tetrahedra and bound to them by the common oxygen atoms which they share, an arrangement conveniently represented, purely conventionally, in the way shown in fig. 11.08b.

The micas

11.23. The structure of muscovite mica, $\text{KAl}_2(\text{OH})_2(\text{Si}_3\text{Al})\text{O}_{10}$, is related to that of talc in the manner shown in fig. 11.09. One-quarter of the silicon atoms in the sheets are replaced by aluminium in tetrahedral co-ordination and the three magnesium ions are replaced by two aluminium ions octahedrally co-ordinated. To maintain electrical neutrality one potassium ion is introduced for every silicon atom replaced by aluminium, and these potassium ions are located between the faces of the sheets, where they are co-ordinated by twelve oxygen neighbours.

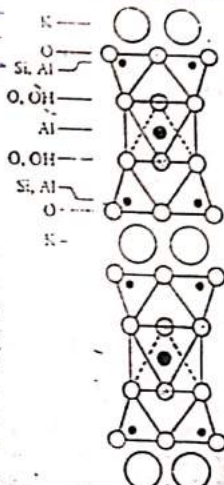


Fig. 11.09. Schematic representation of the structure of muscovite mica, $\text{KAl}_2(\text{OH})_2(\text{Si}_3\text{Al})\text{O}_{10}$.

11.24. The structure of other common micas may be readily derived from that described for muscovite. In phlogopite, $\text{KMg}_3(\text{OH})_2(\text{Si}_3\text{Al})\text{O}_{10}$, the 4-co-ordinated aluminium of muscovite is preserved but the 6-co-ordinated sites are now occupied by magnesium, as in talc. In margarite, $\text{CaAl}_2(\text{OH})_2(\text{Si}_2\text{Al}_2)\text{O}_{10}$, two instead of only one of the silicon atoms are replaced by aluminium and the divalent Ca^{2+} ion is therefore required in place of K^+ to restore neutrality. As with the pyroxenes and amphiboles, however, isomorphous substitution in the micas is very common, and idealized compositions of the type just considered are rarely realized. Thus the extent to which silicon is replaced by aluminium is very variable, while the cations which may occur in 6-co-ordination include

Al³⁺, Fe³⁺, Fe²⁺, Mg²⁺, Mn²⁺ and Li⁺. The alkali metal, although most commonly K⁺, may be Na⁺ or Ca²⁺, while finally OH⁻ may be replaced by considerable quantities of F⁻. In spite of this complexity of composition, however, the structures can all be interpreted in terms of the simple idealized formula provided only that the primary significance of co-ordination number rather than valency is clearly appreciated. This point may be most readily illustrated by considering a number of typical analyses.

11.25. In table 11.02, the chemical analyses of some specimens of talc and of muscovite mica are shown. In the first column the composition is given in the conventional form as oxides, and in the second column the analyses are recalculated to show the relative number of atoms of each kind present, expressed on a basis of 10 atoms of oxygen. Oxygen in the hydroxyl group, which appears as water in the chemical analysis, is excluded from these 10 oxygen atoms and expressed separately as OH.

Table 11.02. Analyses of talc and muscovite mica*

Composition by oxides		Composition by atoms	
Talc			
MgO	30.22	Mg	2.92
FeO	2.66	Fe	0.14
SiO ₂	62.24	Si	4.05
H ₂ O	4.94	OH	2.14
	100.06	O	10.00
Muscovite I			
Na ₂ O	0.90	Na	0.12
K ₂ O	10.70	K	0.91
MgO	0.38	Mg	0.05
Al ₂ O ₃	37.15	Al	2.90
SiO ₂	45.54	Si	3.03
H ₂ O	4.80	OH	2.13
	99.47	O	10.00
Muscovite II			
Na ₂ O	1.01	Na	0.12
K ₂ O	6.05	K	0.49
MgO	0.50	Mg	0.05
CaO	0.27	Ca	0.02
Al ₂ O ₃	34.70	Al	2.61
SiO ₂	53.01	Si	3.40
H ₂ O	4.67	OH	1.99
	100.21	O	10.00

* Idealized formulae: talc (OH)₂Mg₃Si₄O₁₀; mica (OH)₂KAl₃(Si₃Al)O₁₀.

11.25

The figures in the second column are therefore immediately comparable with the idealized formulae of the minerals.

The analysis of the talc shows that this particular specimen corresponds closely to the ideal composition (OH)₂Mg₃Si₄O₁₀. The O:Si ratio of 10:4 is closely satisfied, but there is some replacement of magnesium by iron. The total of (Mg + Fe) slightly exceeds 3 and the resulting excess of positive charge is compensated by a corresponding excess of OH.

The analysis of muscovite I may be compared with the formula (OH)₂KAl₃(Si₃Al)O₁₀. The number of silicon ions is 3.03, so that 0.97 of the 2.90 aluminium ions must occur in tetrahedral co-ordination. The remaining 1.93 aluminium ions, together with 0.05 magnesium, are 6-co-ordinated. The loss of 0.97 unit of positive charge, brought about by the substitution of Al³⁺ for Si⁴⁺, is compensated by the introduction of (Na + K), and there is therefore a close correspondence between the amount of aluminium in 4-co-ordination and the total alkali content. In muscovite II an unusually low replacement of silicon occurs and only 0.60 aluminium ion is found in tetrahedral co-ordination. Corresponding to this the total alkali content is only 0.61 ion of (Na + K).

The chlorite minerals

11.26. The minerals of the chlorite group closely resemble the micas in many of their physical properties, but differ from them chemically in that they contain a very much larger proportion of hydroxyl and no alkali or alkaline earth metal; a typical member has the approximate empirical composition Al₂Mg₅Si₂O₁₀(OH)₈. The structure of these minerals can most easily be described by starting from the structure of muscovite shown in fig. 11.09, which, however, for our present purpose may now be considered to represent phlogopite, KMg₃(OH)₂(Si₃Al)O₁₀.

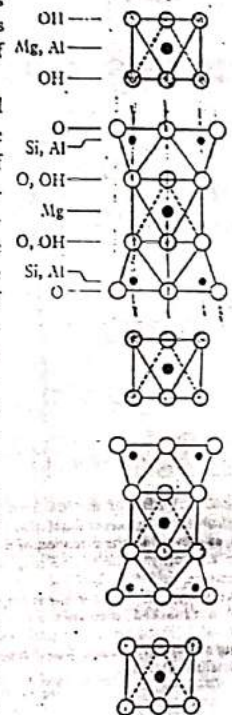
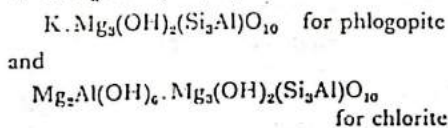


Fig. 11.10. Schematic representation of the structure of chlorite, Mg₅Al(OH)₈(Si₂Al)O₁₀.

As we have seen, this structure may be regarded as consisting of two-dimensional 'sandwich' anions $[Mg_3(OH)_2(Si_3Al)O_{10}]^-$ held together by potassium cations. In the chlorites the same anions are found, but now the cations themselves are also complex two-dimensional units the structure of which is closely related to that of $Mg(OH)_2$. In the $Mg(OH)_2$ structure (§§.30) $Mg(OH)_6$ octahedra are linked together in the form of layers, and the layers are, of course, electrically neutral. If, however, we replace one-third of the Mg^{2+} ions by Al^{3+} we obtain a positively charged layer of empirical composition $[Mg_2Al(OH)_6]^+$, and it is this layer which constitutes the cation in the chlorites. The structure is therefore as represented schematically in fig. 11.10, which is drawn in such a way as to emphasize the relationship to mica. This same relationship may also be made clear by expressing the formulae in analogous styles, e.g.



It will be seen how much more illuminating is this formulation of chlorite than the empirical formulation given earlier; not only does it express the correct O:(Si, Al) ratio of 10:4 but it also shows that Mg^{2+} , Al^{3+} and OH^- ions all appear in the structure in two distinct roles. Few more striking examples could be given of the value of X-ray structural studies in resolving the complex problems of silicate chemistry.

The clay minerals

11.27. The clay minerals comprise a series of complex silicates which again resemble the micas in some of their physical properties but which differ from them in forming sizeable crystals only with extreme difficulty. As an example, the structure of kaolinite, $Al_2(OH)_4Si_2O_7$, may be described. (In this structure, illustrated in fig. 11.11, there is no replacement of silicon by aluminium and we find single sheets of SiO_4 tetrahedra linked by three corners, just as in talc. These sheets, however, are no

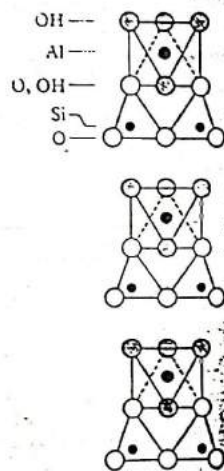


Fig. 11.11. Schematic representation of the structure of kaolinite, $Al_2(OH)_4Si_2O_7$.

longer grouped in pairs, but instead all point the same way. Hydroxyl groups lie inside the hexagonal ring of unshared oxygen atoms at the vertices of the SiO_4 tetrahedra to form a close-packed (O+OH) layer, again as in talc, and above this layer is a complete close-packed sheet of hydroxyl groups. Aluminium ions occupy positions of octahedral coordination between these two sheets so that each Al^{3+} ion is co-ordinated by four hydroxyl groups and two oxygen atoms. The structure may therefore be regarded as made up by the superposition of composite layers each consisting of a sheet of SiO_4 tetrahedra and a sheet of $AlO_2(OH)_4$ octahedra united by the common oxygen atoms. (These layers are, of course, electrically neutral and are therefore held together only by van der Waals forces.) It will be noted, however, that they are unsymmetrical in character, and therefore probably polar, and it may be this fact which is responsible for the reluctance of the clay minerals to form large crystals.)

The physical properties of the sheet structures

11.28. Many of the very distinctive physical properties of the micas and related minerals find a ready explanation in their structures. The pseudo-hexagonal symmetry is an immediate consequence of the hexagonal form of the separate sheets, and the eminent cleavage results from the weakness of the bonds by which these sheets are held together. These bonds, however, are not uniformly weak, and corresponding to gradations in strength we find gradations in hardness and in quality of cleavage. Thus in talc and the clay minerals the binding is due only to van der Waals forces, and these minerals are extremely soft and cleave readily; talc is in fact the softest of all known minerals and its cleavage finds application in the use of French chalk as a lubricant. In muscovite mica, on the other hand, the bonds are ionic links through the K^+ ion, and these forces, although still weak compared with the other bonds in the structure, are strong enough to occasion a marked increase in hardness. Finally, in margarite and the other so-called brittle micas, the bonds are yet stronger, owing to the presence of Ca^{2+} or other doubly charged ions between the layers, and a further increase in hardness, accompanied by less perfect cleavage, is observed.

Framework structures

11.29. (The final class of silicate structures is that which arises when the SiO_4 tetrahedra are so linked that every oxygen ion is shared between

two tetrahedra. Such an arrangement gives rise to an indefinitely extended three-dimensional framework with an oxygen:silicon ratio of 2:1, and is, of course, found in its simplest form in the various modifications of silica already discussed. It is clear that no metallic silicate can be based on such a structure unless some of the silicon is replaced by aluminium, for only then does the framework acquire the negative charge required to balance that of the cations introduced.

In contrast to the other types of tetrahedron linkage already described, the three-dimensional frameworks commonly exist in a number of entirely different forms which give rise to several quite distinct families of petrologically important minerals. A few silicates have structures based on the frameworks found in the various forms of silica. Thus the structures of kalsilite, $K(AlSi_3)O_8$, and nepheline, $Na_3K(Al_3Si_4)O_{16}$, can be regarded as derived from that of tridymite by the replacement of one-half of the silicon ions by aluminium and the introduction of the appropriate number of alkali ions to restore neutrality. The structures of carnegieite, $Na(AlSi_3)O_8$, and eukryptite, $Li(AlSi_3)O_8$, are similarly related to those of cristobalite and quartz, respectively. It will be noted that in all these minerals aluminium is, of course, always present and that the O:(Si, Al) ratio is always 2:1.

In the majority of the framework silicates, however, the framework is far more open than that found in silica, and this open character, coupled with the intrinsic rigidity of the three-dimensional network, confers on these structures a quite exceptional degree of flexibility of composition. The framework silicates are also notably less dense, as a class, than those (such as olivine and the micas) in which the oxygen atoms are more nearly close packed. We shall confine our discussion to three important groups of such structures:

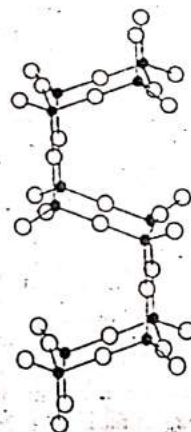
The feldspars

11.30. Mineralogically by far the most important framework silicates, and indeed the most important of all rock-forming minerals, are the feldspars, the structures of which are based on the framework shown in fig. 11.12. It will be seen that the $(Si, Al)O_4$ tetrahedra are grouped in rings of four members and that these rings in their turn form links of a kinked chain running vertically in the diagram. This appearance is, however, somewhat deceptive, for it must be remembered that all the oxygen atoms of the tetrahedra are shared so that the bonding in the structure extends not only vertically, as shown, but also transversely to build up a three-dimensional network.

In orthoclase, $K(AlSi_3)O_8$, one-quarter of the silicon is substituted by aluminium, and for each silicon ion thus replaced one potassium ion is introduced. The potassium is accommodated in large interstices in the structure and is surrounded by ten oxygen atoms; the co-ordination is, however, irregular and the structure cannot conveniently be regarded as based on a packing of polyhedra. In albite, $Na(AlSi_3)O_8$, sodium replaces the potassium of orthoclase (and in anorthite, $Ca(Al_2Si_2)O_8$, two of the silicon ions are replaced by aluminium and a divalent cation is therefore required to restore neutrality). Complete solid solution occurs between albite and anorthite, on account of the close correspondence between the radii of the Na^+ and Ca^{2+} ions (0.95 and 0.99 Å, respectively), but not between albite and orthoclase, despite their closer chemical similarity, owing to the difference in size between the Na^+ and K^+ ions (0.95 and 1.33 Å, respectively). The close morphological and physical association between albite and anorthite has long been recognized by mineralogists as more significant than their chemical dissimilarity, and the structural justification for this association provides us with another elegant example of the geometrical principles determining the structures of ionic crystals.

The zeolites

11.31. A second group of minerals based on a framework structure is the zeolite family of hydrated silicates, but (here the framework is very much more open than that found in the feldspars and is intersected by wide channels in which the cations and water molecules are located. These water molecules, however, are very loosely bound in the crystal and it is a distinctive feature of the zeolites that they can be readily expelled by heat without destroying the structure; they can, moreover, be reversibly replaced or even substituted by other neutral molecules such as those of ammonia, mercury, alcohol or iodine provided that these molecules are not too large to penetrate the interstices of the framework. Zeolites therefore possess the remarkable property of acting as 'molecular sieves' permeable only to small molecules.)

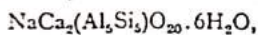


●: Si, Al; ○: O

Fig. 11.12. Clinographic projection of the (idealized) silicate-oxygen framework in feldspars.

Another distinctive characteristic of the zeolites is that the cations, too, can be readily and reversibly exchanged without damage to the structure as a whole, often by simply immersing the crystal in a solution of the appropriate salt, and it is, of course, this base-exchange property which is the foundation of the permutite system of water softening.

Naturally, if ions are removed they must be replaced by others of equal aggregate charge, but it is not necessary that they should be equal in number since the interstices in the structure are large enough to accommodate additional ions if required. Thus one-half of the calcium ions in thomsonite,



can be replaced by pairs of sodium ions, the total number of cations being thereby increased from three to four.

11.32. Although the above-mentioned properties are common to zeolites as a whole, the structures of these minerals differ in their detailed features and in the nature of the framework which they contain. Those which have been most extensively studied are the so-called fibrous

zeolites, which tend to grow as needles or as fibrous aggregates. In these minerals the $(\text{Si}, \text{Al})\text{O}_4$ tetrahedra are linked in the manner shown in fig. 11.13 to form chains extending indefinitely through the structure with a repeat unit of length 6.6 Å made up of five such tetrahedra. It is therefore a characteristic of all fibrous zeolites (of which thomsonite is an example) that the anion contains the unit $(\text{Si}, \text{Al})_5\text{O}_{10}$ and that one dimension of the unit cell is 6.6 Å or a multiple of this distance. As with the feldspars, the description in terms of chains of tetrahedra is in part deceptive, for these chains are, of course, cross-linked through the unshared oxygen atoms in fig. 11.13 to form coherent three-dimensional frameworks. Nevertheless, these cross-links are relatively few in

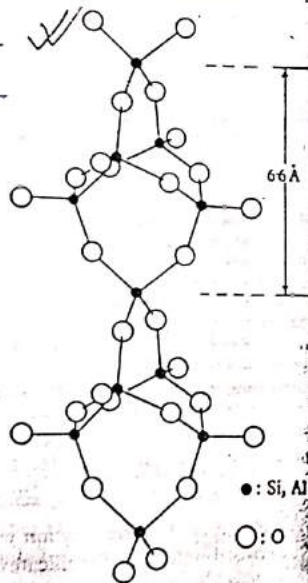


Fig. 11.13. The silicon-oxygen framework in the fibrous zeolites.

number, so that the structures are bonded more firmly along the lengths of the chains than transversely. In this respect they resemble the amphiboles and pyroxenes, and their fibrous character may be ascribed to the ease with which cleavage parallel to the chains can occur.

The ultramarines

11.33. The ultramarines comprise a group of naturally occurring and artificial framework silicates which differ from all silicate structures so far considered in that they contain not only the $(\text{Si}, \text{Al})\text{O}_4$ complex anion but also the negative ions Cl^- , SO_4^{2-} or S_2^{2-} . Ultramarine itself has the idealized formula $\text{Na}_3(\text{Al}_6\text{Si}_6)\text{O}_{24} \cdot \text{S}_2$, and sodalite and noselite have analogous compositions with the S_2^{2-} groups replaced respectively by 2Cl^- and by SO_4^{2-} . The ultramarines differ from the zeolites in being anhydrous, but they resemble these minerals in the readiness with which ion exchange can be achieved. Nor is this ion exchange confined to the cations, for the ions Cl^- , SO_4^{2-} and S_2^{2-} can also be interchanged, and sodalite, for example, can be artificially transformed into noselite. Moreover, other ions, both positive and negative, not found in the naturally occurring silicates may be readily introduced, giving an extensive series of synthetic ultramarines containing the elements Li, Ca, Ag, Tl, Se, Te and others. Wide variations in colour, ranging throughout the spectrum from red to blue, accompany these substitutions, and the artificial ultramarines accordingly find extensive use as pigments.

In spite of the complexity of the ultramarines their structures are basically quite simple. The minerals are all cubic, and contain basket-like frameworks of $(\text{Si}, \text{Al})\text{O}_4$ tetrahedra of the form shown in fig. 11.14a. This representation may appear complex but in fact it can be very simply described as consisting of rings of four tetrahedra on the faces of the cubic unit cell and rings of six tetrahedra encircling its corners, a description which is perhaps more easily seen in the alternative presentation of fig. 11.14b. Here the structure is shown in plan projected on the base of the unit cell and the tetrahedra in the lower half of the cell have been omitted. The four tetrahedra in the top face of the cell and the four groups of six about the corners of this face, are clearly visible. The 'baskets' in the structure are not, of course, isolated but are linked with their neighbours into a very open three-dimensional framework in the cavities of which the remaining ions are located. As with the zeolites, it is the large size of these cavities, coupled with the rigidity of the framework, which makes ion exchange possible without destruction of the crystal.

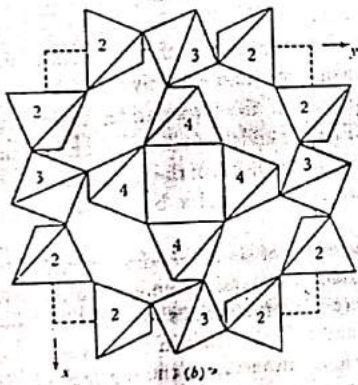
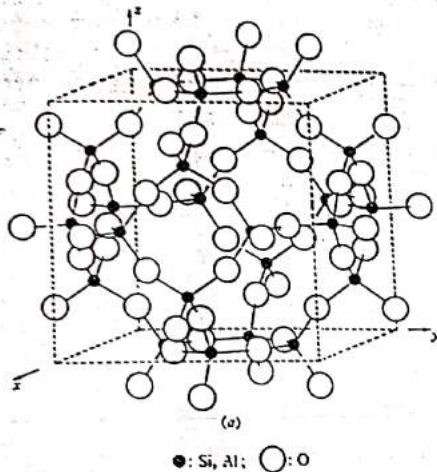


Fig. 11.14 (a) The silicon-oxygen framework in the ultramarines shown in clinographic projection. (b) The same, represented as a plan projected on the base of the cubic unit cell. Only the SiO₄ tetrahedra in the upper part of the cell are shown, and these have been displaced slightly to reveal more clearly the linkage between them. The numbers indicate the heights of the centres of the tetrahedra above the plane of projection, expressed in units of *l*c.

11.34. This concludes our systematic description of silicate structures, and for reference we give in table 11.03 a summary of the several classes which we have considered, together with the corresponding O:(Si, Al) ratios. Before we pass on to other topics there remain a number of general points common to all silicates which call for brief consideration.

Table 11.03. Some silicate structure types

Structural arrangement	Examples	O:(Si, Al) ratio
Independent tetrahedra	Orthosilicates, e.g. olivine, garnets	4:1
Two tetrahedra sharing one oxygen atom	Thortveitite	7:2
Closed rings of tetrahedra each sharing two oxygen atoms	Metasilicates, e.g. benitoite, beryl	3:1
Infinite chains of tetrahedra each sharing two oxygen atoms	Pyroxenes	3:1
Infinite double chains of tetrahedra sharing alternately two and three oxygen atoms	Amphiboles	11:4
Infinite sheets of tetrahedra each sharing three oxygen atoms	Micas, chlorites, clays	5:2
Infinite framework of tetrahedra each sharing all four oxygen atoms	Feldspars, zeolites, ultramarines	2:1

The crystal chemistry of the silicates

The replacement of silicon by other ions

11.35. Although Al³⁺ is the only ion which commonly replaces Si⁴⁺ in tetrahedral co-ordination in the silicates, other ions occasionally appear in the same role. The most important of these is As⁵⁺, which is found in berzeliite, Mg₂(Ca₂Na)As₃O₁₂. This mineral is isomorphous with the orthosilicate garnet, of ideal composition Al₂Ca₃Si₃O₁₂, and it is seen from a comparison of the formulae that the three units of positive charge acquired by the substitution of As⁵⁺ for Si⁴⁺ are compensated by the replacement of 2Al³⁺ by 2Mg²⁺ and of Ca²⁺ by Na⁺. Small but appreciable quantities of silicon are often found replacing arsenic in berzeliite. In the ultramarine helvite, (Mn, Fe, Zn)₃Be₆Si₆O₂₄·S₂, one-half of the tetrahedrally co-ordinated sites in the framework are occupied by beryllium.

Model structures of the silicates

11.36. We have already defined model structures as isostructural substances in which ions occur closely equivalent in size but different in charge. In this sense Li₂Bef₄ is a model of the structure of willemite,

Zn_2SiO_4 . The radii of the several ions in these two structures are

Li^+	0.60 Å	Be^{2+}	0.31 Å	F^-	1.36 Å
Zn^{2+}	0.74	Si^{4+}	0.41	O^{2-}	1.40

and the close correspondence between the two sets of radii results in isomorphous structures with closely similar cell dimensions and crystallographic properties. On the other hand, the increased strength of the polar binding in the silicate is reflected in the physical properties, as the following data show:

	Li_2BeF_4	Zn_2SiO_4
Hardness (Mohs scale)	3.8	5.5
Melting point (°C)	470	1509
Solubility in water	Readily soluble	Insoluble

The chemical classification of silicates

11.37. The purely structural classification of the silicates which we have here adopted naturally challenges comparison with older and more orthodox chemical classifications. Long before the application of X-ray structure analysis, the mineralogist had classed together, on purely morphological grounds, many silicates of very different constitution, while the chemical classification of substances of such uncertain and variable composition necessarily presented great difficulties. Nevertheless, we can now see that the failure of the chemical classification was due not so much to the inherent difficulty of the material as to the falsity of the principles on which it was based. On the one hand, the dual role of aluminium, which enables it to appear either as a normal metallic cation or in place of silicon, could be detected only by X-ray methods, and, on the other, the chemical classification sought always to refer all silicates to some corresponding acid. We cannot here emphasize too strongly that structurally there is no relation whatsoever between acids and their salts, and that in so far as acids exist it is a structural accident which does not represent any structural association. The properties of the strongly polarizing and vanishingly small H^+ ion are so entirely different from those of any other cation that they demand entirely separate treatment and we deliberately refrain until chapter 12 from discussing the structures of any acids or acid salts. In most of the silicates the disorganization of the structure which would result from the substitution of hydrogen for the other cations is so drastic that it is unthinkable that such an arrangement should be stable. The acids simply have no existence.

11.38. This concludes our account of the silicates. While we have tried to discuss the more important structural and chemical features of these minerals we would again emphasize that our treatment has been in no sense exhaustive from a mineralogical point of view; $(Si, Al)O_4$ tetrahedra can be linked together in many different ways and numerous types of silicate exist in addition to those which we have discussed. The reader who wishes for a more detailed account of these structures is referred to the work by Bragg and Claringbull already mentioned.

GERMANATES AND PHOSPHATES

11.39. Other oxy-salts in which large polynuclear anions are found are the germanates and phosphates. The radius of the Ge^{4+} ion, which is very nearly the same as that of Si^{4+} , again corresponds to tetrahedral co-ordination by oxygen, and GeO_2 (in one of its forms) has the quartz structure. A number of germanates are known with structures analogous to those of some of the silicates which we have discussed, but they have not been widely studied.

11.40. Phosphorus is characterized by the complexity of its oxygen chemistry (compared, say, with that of nitrogen), and the salts of many oxy-acids are known. X-ray structural studies have been concerned principally with the salts of quinquivalent phosphorus, in all of which the phosphorus atom is tetrahedrally co-ordinated by oxygen. Isolated PO_4^{3-} ions, analogous to SO_4^{2-} and SiO_4^{4-} ions, exist in many orthophosphates, some of which have structures closely related to those of orthosilicates when due allowance is made for the difference in valency. The PO_4 groups, however, may also be linked, by sharing one or more oxygen atoms, to give polynuclear complexes. Thus the $P_2O_7^{4-}$ ion (analogous to the $Si_2O_7^{6-}$ ion in thortveitite) is found in pyrophosphates, and four-membered ring-ions $P_4O_{12}^{4-}$, of the form shown in fig. 11.15, occur in aluminium metaphosphate, $Al_3(P_4O_{12})_3$. (This ring may be compared with the ions $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$ in benitoite and beryl.) The association of PO_4 groups into infinite chains (analogous to those in the pyroxenes) has not been established in any metaphosphate but may occur in metaphosphoric acid and be responsible for the fact that this acid normally exists only as a glass.

The possibility of more complex associations of PO_4 groups, analogous to those found in the micas and feldspars, does not arise in phosphates because any arrangement in which these groups share three of their four

oxygen atoms is already electrically neutral, while the sharing of all oxygen atoms would yield a positive ion of composition $[\text{PO}_2]_n^{+}$. In the various forms of phosphorus pentoxide, however, PO_4 groups are found united by sharing three oxygen atoms. In one form the association is into discrete P_4O_{10} molecules (fig. 11.16), bound to one another only by van der Waals forces, and in this form the compound is soft, volatile and reactive. In a second form, however, the PO_4 groups are linked into a coherent three-dimensional network extending throughout

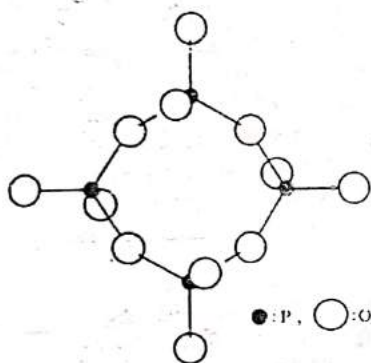


Fig. 11.15. Clinographic projection of the structure of the $\text{P}_4\text{O}_{12}^{4-}$ ion.

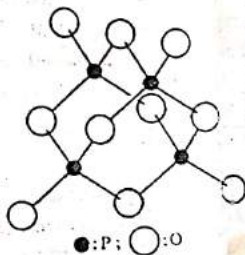


Fig. 11.16. Clinographic projection of the structure of one form of the P_4O_{10} molecule.

the structure to give a harder, less volatile and less reactive crystal. This latter arrangement may be regarded as the analogue of the various silica structures, but clearly no silica analogue of the molecular structure is possible since the union of SiO_4 groups by a sharing of all oxygen atoms can never yield a finite complex.

12 THE STRUCTURES OF SOME COMPOUNDS CONTAINING HYDROGEN

INTRODUCTION

12.01. We have already discussed the structures of a limited number of hydrogen-containing compounds, notably the hydrides of the metals, certain hydroxides and some ammonium salts. In the hydrides the hydrogen atom appears as the anion H^- , comparable in character with a halogen ion, and the structures of the hydroxides and of the ammonium salts which we have so far considered can similarly be described in terms of spherical OH^- and NH_4^+ ions. We now turn to discuss some structures in which the hydrogen atom plays a much more distinctive part and in most of which it appears as the positive ion H^+ . The peculiar characteristics of these structures arise from the unique position of the hydrogen cation as an ion of vanishingly small size and one lacking any extranuclear electronic structure. In terms of the simple geometric picture of ionic structures such an ion would be expected to be 2-coordinated, and in the majority of the structures to which we now turn we find two atoms X and Y linked by a hydrogen atom to form the group $X\text{-H-Y}$. Such a link is termed a hydrogen bond.

THE HYDROGEN BOND

The hydrogen bond in chemistry

12.02. The conception of a binding between two atoms as being possible through the medium of a hydrogen atom was first advanced some fifty years ago and has since been widely applied, especially in organic chemistry. Thus the fact that certain types of organic compound, such as the sugars, for example, are harder and more brittle, and melt at higher temperatures, than the majority of organic substances is attributed to hydrogen bonds between the molecules in the crystal stronger than the normal van der Waals forces. Similarly, the tendency to association shown by compounds containing the groups $-\text{NH}_2$, $-\text{OH}$, $-\text{COOH}$, $=\text{NOH}$, $=\text{NH}$, etc., may also be ascribed to hydrogen-bond formation between two or more molecules; the fact that association does not occur in these compounds when the hydrogen