Previous Page

determined[41] and various crystalline methyl and ethyl esters of cyclic silicic acids have been isolated.[42]

9.3.5 Silicate minerals [24,43,44]

The earth's crustal rocks and their breakdown products — the various soils, clays and sands — are composed almost entirely (~95%) of silicate minerals and silica. This predominance of silicates and aluminosilicates is reflected in the abundance of O, Si and Al, which are the commonest elements in the crust (p. 329). Despite the great profusion of structural types and the widely varying stoichiometries which are unmatched elsewhere in chemistry, it is possible to classify these structures on the basis of a few simple principles. Almost invariably Si is coordinated tetrahedrally by 4 oxygen atoms and these $\{SiO_4\}$ units can exist either as discrete structural entities or can combine by corner sharing of O atoms into larger units. The resulting O lattice is frequently close-packed, or approximately so, and charge balance is achieved by the presence of further cations in tetrahedral, octahedral, or other sites depending on their size. Typical examples are as follows (radii in pm):[†]

CN 4 : Li^I (59) Be^{II} (27) Al^{III} (39) Si^{IV} (26)
CN 6 : Na^I (102) Mg^{II} (72) Al^{III} (54) Ti^{IV} (61) Fe^{II} (78)
CN 8 : K^I (151) Ca^{II} (112)
CN 12: K^I (164)

The quoted radii, which in turn depend on the CN, are the empirical "effective ionic radii" deduced by R. D. Shannon (and C. T. Prewitt)[45] and do not imply full charge separation such as $\{Si^{4+}(O^{2-})_4\}$, etc. Note that Al^{III} can occupy either 4- or 6-coordinate sites so that it can replace either Si or M in the lattice — this is particularly important in discussing the structures of the aluminosilicates. Several other cations can occupy sites of differing CN, e.g. Li (4 and 6), Na (6 and 8), K (6–12), though they are most commonly observed in the CN shown.

As with the borates (p. 205) and to a lesser extent the phosphates (p. 526), the $\{SiO_4\}$ units can build up into chains, multiple chains (or ribbons), rings, sheets and three-dimensional networks as summarized below and elaborated in the following paragraphs.

Neso-silicates	discrete $\{SiO_4\}$	no O atoms shared
soro-silicates	discrete $\{Si_2O_7\}$	1 O atom shared
cyclo-silicates	closed ring structures	2 O atoms shared
ino-silicates	continuous chains or ribbons	
phyllo-silicates	continuous sheets	3 O atoms shared
tecto-silicates	continuous 3D frameworks	all 4 O atoms shared

Silicates with discrete units

Discrete $\{SiO_4\}$ units occur in the orthosilicates $M^{II}_2SiO_4$ (M = Be, Mg, Mn, Fe and Zn) and in $ZrSiO_4$ as well as in the synthetic orthosilicates Na_4SiO_4 and K_4SiO_4.[46] In phenacite, Be_2SiO_4, both Be and Si occupy sites of CN 4 and the structure could equally well be described as a 3D network M_3O_4. When octahedral sites are occupied, isomorphous replacement of M^{II} is often extensive as in olivine, $(Mg,Fe,Mn)_2SiO_4$ which derives its name from its olive-green colour (Fe^{II}). In zircon, $ZrSiO_4$, the stoichiometry

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[41] M. H. Chisholm, T. A. Budzichowski, F. J. Feher and J. W. Ziller, *Polyhedron* **11**, 1575–9 (1992).

[42] H. C. Marsmann and E. Meyer, *Z. anorg. allg. Chem.* **548**, 193–203 (1987).

[43] W. A. Deer, R. A. Howie and J. Zussman, *An Introduction to the Rock-forming Minerals*, Longmans, London, 1966, 528 pp. B. Mason and L. G. Berry, *Elements of Mineralogy*, W. H. Freeman, San Francisco, 1968, 550 pp.

[44] F. Liebau, Silicon, element 14, in K. H. Wedepohl (ed.), *Handbook of Geochemistry*, Vol. II-2, Chap. 14, Springer-Verlag, Berlin, 1978. F. Liebau, *Structural Chemistry of Silicates*, Springer-Verlag, Berlin, 1985, 347 pp.

[†] The metals which form silicate and aluminosilicate minerals are the more electropositive metals, i.e. those in Groups 1, 2 and the 3d transition series (except Co), together with Y, La and the lanthanoids, Zr, Hf, Th, U and to a much lesser extent the post-transition elements Sn^{II}, Pb^{II}, and Bi^{III}.

[45] R. D. Shannon, *Acta Cryst.* **A32**, 751–67 (1976).

[46] M. G. Barker and P. G. Good, *J. Chem. Research (S)*, 1981, 274, and references cited therein.

of the crystal and the larger radius of Zr (84 pm) dictate eightfold coordination of the cation. Another important group of orthosilicates is the garnets, $[\text{M}_3^{\text{II}}\text{M}_2^{\text{III}}(\text{SiO}_4)_3]$, in which M^{II} are 8-coordinate (e.g. Ca, Mg, Fe) and M^{III} are 6-coordinate (e.g. Al, Cr, Fe).(47) Orthosilicates are also vital components of Portland cement (p. 252): β-Ca_2SiO_4 has discrete $\{\text{SiO}_4\}$ groups with rather irregularly coordinated Ca in sixfold and eightfold environments (the α-form has the K_2SO_4 structure and the γ-form has the olivine structure). Again alite, Ca_3SiO_5, which is intimately involved in the "setting" process, has individual Ca, $\{\text{SiO}_4\}$ and O as the structural units.

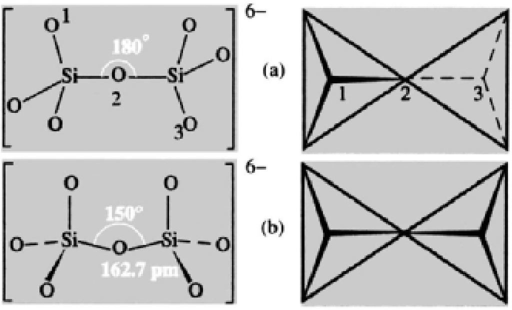

Figure 9.4 (a) Two representations of the $\{\text{Si}_2\text{O}_7\}$ unit in $\text{Sc}_2\text{Si}_2\text{O}_7$ showing the linear Si–O–Si link between the two tetrahedra and the D_{3d} (staggered) conformation, and (b) eclipsed (C_{2v}) conformation of the $\{\text{Si}_2\text{O}_7\}$ unit in hemimorphite, $[\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2].\text{H}_2\text{O}$.

Disilicates, containing the discrete $\{\text{Si}_2\text{O}_7{}^{6-}\}$ unit, are rare. One example is the mineral thortveitite, $\text{Sc}_2\text{Si}_2\text{O}_7$, which features octahedral Sc^{III} (r 75 pm) and a linear Si–O–Si bond between staggered tetrahedra (Fig. 9.4a). There is also a series of lanthanoid disilicates $\text{Ln}_2\text{Si}_2\text{O}_7$ in which the Si–O–Si angle decreases progressively from 180° to 133° and the CN of Ln increases from 6 through 7 to 8 as the size of Ln increases from 6-coordinated Lu^{III} (86 pm) to 8-coordinated Nd^{III} (111 pm). In the Zn mineral hemimorphite the angle is 150° but the conformation of the 2 tetrahedra is eclipsed (C_{2v}) rather than staggered (Fig. 9.4b); the mineral was originally formulated as $\text{Zn}_2\text{SiO}_4.\text{H}_2\text{O}$ or $\text{H}_2\text{Zn}_2\text{SiO}_5$, but X-ray studies showed that the correct formula was $[\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7].\text{H}_2\text{O}$, i.e."$2\text{H}_2\text{Zn}_2\text{SiO}_5$". Two further features of importance also emerged. The first was that there was no significant difference between the Si–O distances to "bridging" and "terminal" O atoms as would be expected for isolated $\{\text{Si}_2\text{O}_7{}^{6-}\}$ groups, and the structure is best considered as a 3D framework of $\{\text{ZnO}_3(\text{OH})\}$ and $\{\text{SiO}_4\}$ tetrahedra linked in threes to form 6-atom rings $\overline{\text{Zn}-\text{O}-\text{Si}-\text{O}-\text{Zn}-\text{OH}}$. The rings are linked into infinite sheets in the (010) planes which are themselves linked via Zn–O(H)–Zn or Si–O–Si bonds. The 3D framework so generated leaves large channels which open into large cavities that accommodate the removable H_2O molecules. The structure is thus very similar in principle to that of the framework aluminosilicates (p. 354) and its conventional description in terms of discrete $\text{Si}_2\text{O}_7{}^{6-}$ ions is rather misleading and uninformative.

Structures having triple tetrahedral units are extremely rare but they exist in aminoffite, $\text{Ca}_3(\text{BeOH})_2(\text{Si}_3\text{O}_{10})$, and kinoite, $\text{Cu}_2\text{Ca}_2(\text{Si}_3\text{O}_{10}).2\text{H}_2\text{O}$. The first chain-tetrasilicate, $[\text{O}_3\text{Si}(\text{OSiO}_2)_2\text{OSiO}_3]^{10-}$, was synthesized as recently as 1979:(48) $\text{Ag}_{10}\text{Si}_4\text{O}_{13}$ was prepared as stable vermilion crystals by heating AgO and SiO_2 for 1–3 days at 500–600°C under a pressure of 2–4.5 kbar of O_2. At lower temperatures (<470°C) the bright red mixed silicate $[\text{Ag}_{18}(\text{SiO}_4)_2(\text{Si}_4\text{O}_{13})]$ crystallizes.(49)

When every $\{\text{SiO}_4\}$ shares 2 O with contiguous tetrahedra, metasilicates of empirical

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[47] See p. 500 of ref. 24 for a description of the garnet structure which is also adopted by many synthetic and non-silicate compounds; these have been much studied recently because of their important optical and magnetic properties, e.g. ferrimagnetic yttrium iron garnet (YIG), $\text{Y}_3^{\text{III}}\text{Fe}_2^{\text{III}}(\text{Al}^{\text{III}}\text{O}_4)_3$.

[48] M. Jansen and H.-L. Keller, *Angew. Chem. Int. Edn. Engl.* **18**, 464 (1979).

[49] K. Heidebrecht and M. Jansen, *Z. anorg. allg. Chem.* **597**, 79–86 (1991).

formula SiO_3^{2-} are formed. Cyclic metasilicates $[(SiO_3)_n]^{2n-}$ having 3, 4, 6 or 8 linked tetrahedra are known, though 3 and 6 are the most common. These anions are shown schematically in Fig. 9.5 and are exemplified by the mineral benitoite $[BaTi\{Si_3O_9\}]$, the synthetic compound $[K_4\{Si_4O_8(OH)_4\}]$, and by beryl $[Be_3Al_2\{Si_6O_{18}\}]$ (p. 107) and murite $[Ba_{10}(Ca,Mn,Ti)_4\{Si_8O_{24}\}(Cl,OH,O)_{12}].4H_2O$.

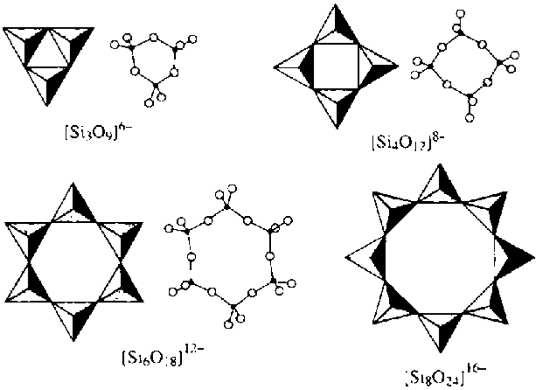

Figure 9.5 Schematic representations of the structures of cyclic metasilicate anions with $n = 3, 4, 6$, and 8.

Silicates with chain or ribbon structures

Chain metasilicates $\{SiO_3^{2-}\}_\infty$ formed by corner-sharing of $\{SiO_4\}$ tetrahedra are particularly prevalent in nature and many important minerals have this basic structural unit (cf. polyphosphates, p. 528). Despite the apparent simplicity of their structure motif and stoichiometry considerable structural diversity is encountered because of the differing conformations that can be adopted by the linked tetrahedra. As a result, the repeat distance along the *c*-axis can be (1), 2, 3, ..., 7, 9 or 12 tetrahedra (T), as illustrated schematically in Fig. 9.6. The most common conformation for metasilicates is a repeat after every second tetrahedron (2T) with the chains stacked parallel so as to provide sites of 6- or 8-coordination for the cations; e.g. the pyroxene minerals enstatite $[Mg_2Si_2O_6]$, diopside $[CaMgSi_2O_6]$, jadeite $[NaAlSi_2O_6]$, and spodumene $[LiAlSi_2O_6]$ (p. 69). The synthetic metasilicates Li_2SiO_3 and Na_2SiO_3 are similar; for the latter compound Si–O–Si is 134° and the Si–O distance is 167 pm within the chain and 159 pm for the other two O. The minerals wollastonite $[Ca_3Si_3O_9]$ and pectolite $[Ca_2NaHSi_3O_9]$ have a 3T repeat unit, haradaite $[Sr_2(VO)Si_4O_{12}]$ is 4T, rhodonite $[CaMn_4Si_5O_{15}]$ has a 5T repeat, etc.[24,44]

In the next stage of structural complexity the single $\{SiO_3^{2-}\}_\infty$ chains can link laterally to form double chains or ribbons whose stoichiometry depends on the repeat unit of the single chain (Fig. 9.7). By far the most numerous are the amphiboles or asbestos minerals which adopt the $\{Si_4O_{11}^{6-}\}$ double chain, e.g. tremolite $[Ca_2Mg_5(Si_4O_{11})_2(OH)_2]$; the structure of this compound is very similar to that of diopside (above) except that the length of the *b*-axis of the unit cell is doubled. The fibrous nature of the asbestos minerals thus finds a ready interpretation on the basis of their crystal structures (see Panel on p. 351). In addition to these well-established double chains of linked $\{SiO_4\}$ tetrahedra, examples of infinite one-dimensional structures consisting of linked triple, quadruple and even sextuple chains have been discovered in nephrite jade by means of electron microscopy,[50] and these form a satisfying link between the pyroxenes and amphiboles, on the one hand, and the sheet silicates (to be described in the next paragraph), on the other.

Silicates with layer structures

Silicates with layer structures include some of the most familiar and important minerals known to man, particularly the clay minerals [such as kaolinite (china clay), montmorillonite (bentonite, fuller's earth), and vermiculite], the micas (e.g. muscovite, phlogopite, and biotite), and others such as chrysotile (white asbestos),

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[50] L. G. MALLINSON, J. L. HUTCHINSON, D. A. JEFFERSON and J. M. THOMAS, *J. Chem. Soc., Chem. Commun.*, 910–11 (1977).

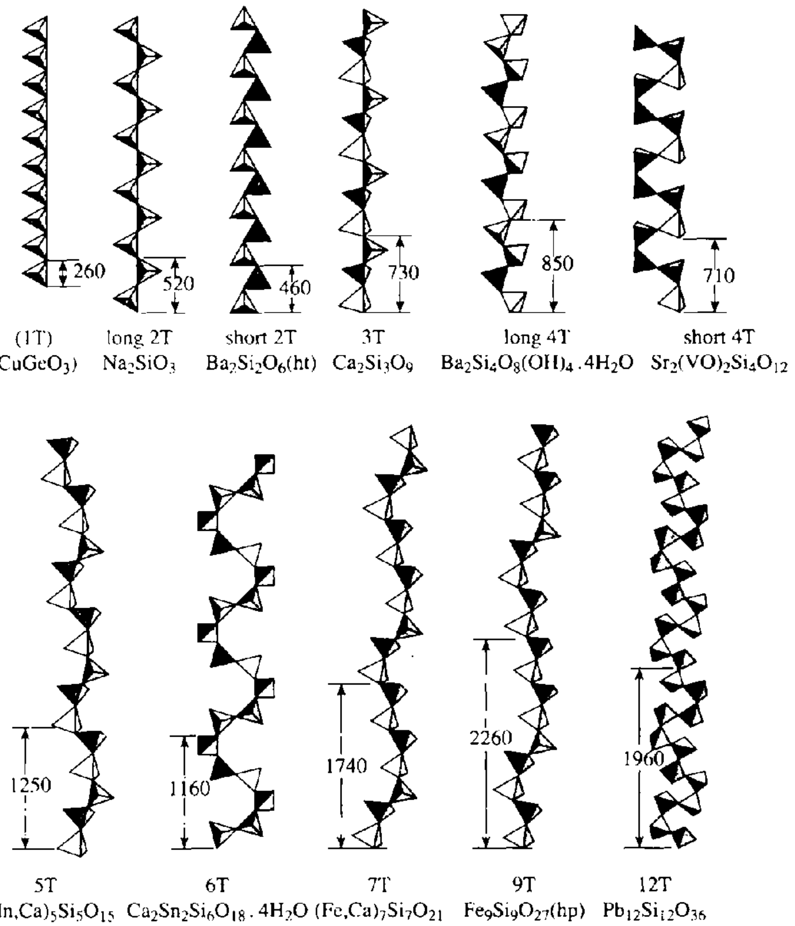


Figure 9.6 Schematic representation and examples of various chain metasilicates $\{SiO_3^{2-}\}_\infty$ with repeat distances (in pm) after 1, 2, ..., 7, 9 or 12 tetrahedra (T), [(ht) high-temperature form; (hp) high-pressure form].

talc, soapstone, and pyrophyllite. The physical and chemical properties of these minerals, which have made many of them so valued for domestic and industrial use for several milleniums (p. 328), can be directly related to the details of their crystal structure. The simplest silicate layer structure can be thought of as being formed either by the horizontal cross-linking of the 2T metasilicate chain $\{Si_2O_6^{4-}\}$ in Fig. 9.6 or by the planar condensation of the $\{Si_6O_{18}^{12-}\}$ unit in Fig. 9.5 to give a 6T network of composition $\{Si_2O_5^{2-}\}$ in which 3 of the 4 O atoms in each tetrahedron are shared; this is shown in both plan and elevation in Fig. 9.8. In fact, such a structure with a completely planar arrangement is extremely rare though closely related puckered 6T networks are found in $M_2Si_2O_5$ (M=Li, Na, Ag, H) and in petalite ($LiAlSi_4O_{10}$, p. 69). More complex arrangements are also found in which the 6T rings forming the network are replaced by alternate 4T and 8T rings, or by equal numbers of 4T, 6T, and 8T rings, or even by a network of 4T, 6T and 12T rings.(24,44)

Double layers can be generated by sharing the fourth (apical) O atom between pairs of tetrahedra as in Fig. 9.9(a). This would give a stoichiometry SiO_2 (since each O atom is shared between 2 Si atoms) but if half the Si^{IV} were replaced by

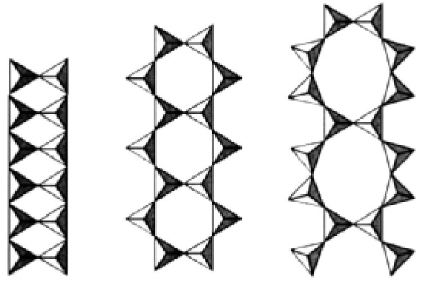
Production and Uses of Asbestos

The fibrous silicate minerals known collectively as asbestos (Greek ἄσβεστος, unquenchable) have been used both in Europe and the Far East for thousands of years. In ancient Rome the wicks of the lamps of the vestal virgins were woven from asbestos, and Charlemagne astounded his barbarian guests by throwing the festive table cloth into the fire whence, being woven asbestos, it emerged cleansed and unburnt. Its use has accelerated during the past 100 y and it is now an important ingredient in over 3000 different products. Its desirable characteristics are high tensile strength, great flexibility, resistance both to heat and flame and also to corrosion by acids or alkalis, good thermal insulation properties and low cost.

Asbestos is derived from two large groups of rock-forming minerals — the serpentines and the amphiboles. Chrysotile, or white asbestos [$Mg_3(Si_2O_5)(OH)_4$], is the sole representative of the serpentine layer silicate group (p. 352) but is by far the most abundant kind of asbestos and constitutes more than 98% of world production. The amphibole group includes the blue asbestos mineral crocidolite [$Na_2Fe^{II}_3Fe^{III}_2Si_8O_{22}(OH)_2$] (<1% of world production) and the grey-brown mineral amosite [$(Mg,Fe)_7Si_8O_{22}(OH)_2$}. (<1%). Annual production in 1989 was 4.3 million tonnes having fallen from a maximum of 5 Mt in 1979.(51) The main producing countries are Russia (55%), Canada (20%), South Africa (4.7%) and Zimbabwe, China, Italy and Brazil (3–4% each).

Asbestos-reinforced cements (~12.5% asbestos) absorb nearly two-thirds of the world's annual production of chrysotile: it is used in corrugated and flat roofing sheets, pressure pipes and ducts, and many other hard-wearing, weather-proof, long-lasting products. About 8% is used in asbestos papers and a further 7% is used for making vinyl floor tiles. Other important uses include composites for brake linings, clutch facings, and other friction products. Long-fibred chrysotile (fibre length >20 mm) is woven into asbestos textiles for fire-fighting garments and numerous fire-proofing and insulating applications.

Prolonged exposure to airborne suspensions of asbestos fibre dust can be very dangerous and there has been increasing concern at the incidence of asbestosis (non-malignent scarring of lung tissue) and lung carcinoma among certain workers in the industry. Unfortunately, there is an extended latent period (typically 20–30 y) before these diseases are manifest. Stringent precautions are now enforced in many countries and the incidence of the disease appears to be falling steadily. There is also general (though not universal) agreement that white asbestos (chrysotile), which is the overwhelmingly predominant type of asbestos in use, is not implicated in the incidence of asbestosis and lung carcinoma which seems to be confined mainly (perhaps exclusively) to the blue crocidolite and brown amosite amphibole varieties. Asbestosis is dose-related and the best form of control is to reduce the level of dust exposure in places where the mineral is mined, processed or fabricated.



(a) [$Si_2O_5^{2-}$] (b) [$Si_4O_{11}^{6-}$] (c) [$Si_6O_{17}^{10-}$]

Figure 9.7 Double chains of {SiO_4} tetrahedra: (a) the double chain based on the 1T metasilicate structure, stoichiometry {$Si_2O_5^{2-}$} -- it is found in the aluminosilicate sillimanite [$Al(AlSiO_5)$]; (b) {$Si_4O_{11}^{6-}$} chain based on the 2T metasilicate occurs in the amphiboles (see text); and (c) the rare 3T double chain $Si_6O_{17}^{10-}$ occurs in xonotlite [$Ca_6Si_6O_{17}(OH)_2$]. More complex 3T, 4T and 6T double chains are also known.(44)

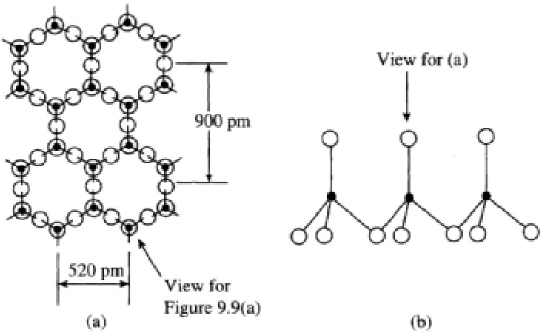


Figure 9.8 Planar network formed by extended 2D condensation of rings of 6 {SiO_4} tetrahedra to give {$Si_2O_5^{2-}$}. (a) Plan as seen looking down the O-Si direction, and (b) side elevation.

Al^{III} then the composition would be {$Al_2Si_2O_8^{2-}$} as found in $Ca_2Al_2Si_2O_8$ and $Ba_2Al_2Si_2O_8$ (Fig. 9.9b). Another way of building up double layers involves the interleaving of layers of the

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[51] Reference 1, 4th edn., Asbestos 3, 659-88 (1992).

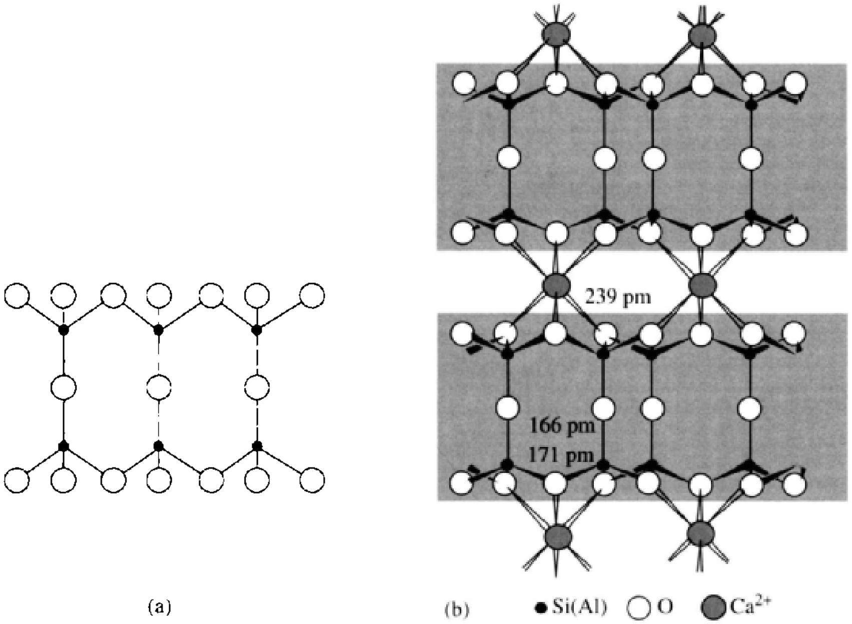
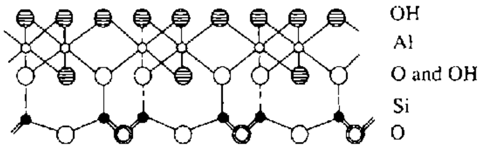


Figure 9.9 (a) Side elevation of double layers of formula $\{Al_2Si_2O_8^{2-}\}$ formed by sharing the fourth (apical) O in Fig. 9.9(b). Sites marked • are occupied by equal numbers of Al and Si atoms. (b) Structure of $Ca_2Al_2Si_2O_8$ formed by interleaving 6-coordinated Ca^{II} atoms between the double layers depicted in (a).

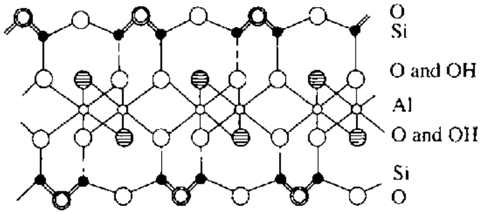
gibbsite $Al(OH)_3$ or brucite $Mg(OH)_2$ structure (pp. 243–5, 121) which happen to have closely similar dimensions and can thus share O atoms with the silicate network. This leads to the china-clay mineral kaolinite $[Al_2(OH)_4Si_2O_5]$ illustrated in Figs. 9.10(a) and 9.11(a). [The mineral was so-named in 1867 from "kaolin", a corruption of the Chinese *kauling*, or high-ridge, the name of the hill where this china clay was found some 300 miles north of Hong Kong.]

Repetition of the process on the other side of the Al/O layer leads to the structure of pyrophyllite $[Al_2(OH)_2Si_4O_{10}]$ (Fig. 9.10b,c). Replacement of $2Al^{III}$ by $3Mg^{II}$ in kaolinite $[Al_2(OH)_4Si_2O_5]$ gives the serpentine asbestos mineral chrysotile $[Mg_3(OH)_4Si_2O_5]$ and a similar replacement in pyrophyllite gives talc $[Mg_3(OH)_2Si_4O_{10}]$. The gibbsite series is sometimes called dioctahedral and the brucite series trioctahedral in obvious reference to the number of octahedral sites occupied in the "non-silicate" layer.

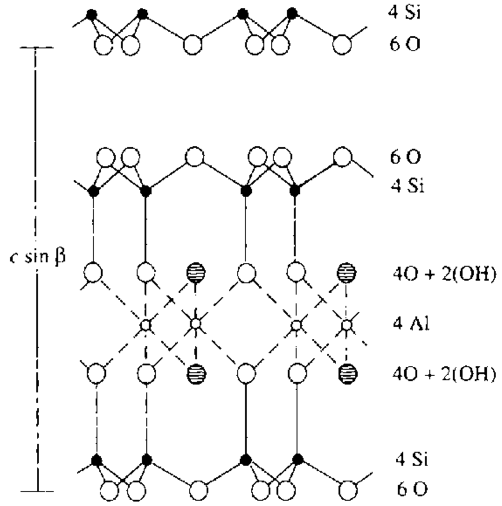
Alternative representations of the structures are given in Fig. 9.11, and it is well worth while looking carefully at these various diagrams since they have the pleasing property of becoming simpler and easier to understand the longer they are contemplated. It should be stressed that the formulae given are ideal limiting compositions and that Al^{III} or Mg^{II} can be replaced by several other cations of appropriate size. The stoichiometry is further complicated by the possibility that Si^{IV} can be partly replaced by Al^{III} in the tetrahedral sites thereby giving rise to charged layers. These layers can be interleaved with M^{I} or M^{II} cations to give the micas or by layers of hydrated cations to give montmorillonite. Alternatively, charge balance can be achieved by interleaving positively charged $(Mg,Al)(OH)_2$ layers as in the chlorites. These possibilities are shown schematically in Figs. 9.12 and 9.13 (p. 355) and elaborated in the following paragraphs.



(a) Kaolinite, $[Al_2(OH)_4Si_2O_5]$



(b) Pyrophyllite, $[Al_2(OH)_2Si_4O_{10}]$



(c) Pyrophyllite, $[Al_4(OH)_4Si_8O_{20}]$

Figure 9.10 (a) Schematic representation of the structure of kaolinite (side elevation) showing $\{SiO_3O\}$ tetrahedra (bottom) sharing common O atoms with $\{Al(OH)_2O\}$ to give a composite layer of formula $[Al_2(OH)_4Si_2O_5]$. The double lines and double circles in the tetrahedra indicate bonds to 2 O atoms (one in front and one behind). (b) Similar representation of the structure of pyrophyllite, showing shared $\{SiO_3O\}$ tetrahedra above and below the $\{Al(OH)O_2\}$ layer to give a composite layer of formula $[Al_2(OH)_2Si_4O_{10}]$. (c) Alternative representation of pyrophyllite to be compared with (b), and showing the stoichiometry of each layer.

The technological importance of the clay minerals is outlined in the Panel on p. 356.

Micas are formed when one-quarter of the Si^{IV} in pyrophyllite and talc are replaced by Al^{III} and the resulting negative charge is balanced by K^I:

$$\text{pyrophyllite } [Al_2(OH)_2Si_4O_{10}] \longrightarrow$$
$$[KAl_2(OH)_2(Si_3AlO_{10})] \text{ muscovite (white mica)}$$
$$\text{talc } [Mg_3(OH)_2Si_4O_{10}] \longrightarrow$$
$$[KMg_3(OH)_2(Si_3AlO_{10})] \text{ phlogopite}$$

The OH can be partly replaced by F and, in phlogopite, partial replacement of Mg^{II} by Fe^{II} gives biotite (black mica) $[K(Mg,Fe^{II})_3(OH,F)_2(Si_3AlO_{10})]$. The presence of K^I between the layers makes the micas appreciably harder than pyrophyllite and talc but the layers are still a source of weakness and micas show perfect cleavage parallel to the layers. With further substitution of up to half the Si by Al charge balance can be restored by the more highly charged Ca^{II} and brittle micas result, such as margarite $[CaAl_2(OH)_2(Si_2Al_2O_{10})]$ which is even harder than muscovite.

Another set of minerals, the montmorillonites, result if, instead of replacing tetrahedral Si^{IV} by Al^{III} in phlogopite, the octahedral Al^{III} is *partially* replaced by Mg^{II} (not *completely* as in talc). The resulting partial negative charge per unit formula can be balanced by incorporating hydrated M^I or M^{II} between the layers; this leads to the characteristic swelling, cation exchange and thixotropy of these minerals (see Panel, p. 356). A typical sodium montmorillonite might be formulated $Na_{0.33}[Mg_{0.33}Al_{1.67}(OH)_2(Si_4O_{10})].nH_2O$, but more generally they can be written as $M_x[(Mg,Al,Fe)_2(OH)_2(Si_4O_{10})].nH_2O$ where M = H, Na, K, $\frac{1}{2}$Mg or $\frac{1}{2}$Ca. Simultaneous altervalent substitution in both the octahedral and tetrahedral sites in talc leads to the vermiculites

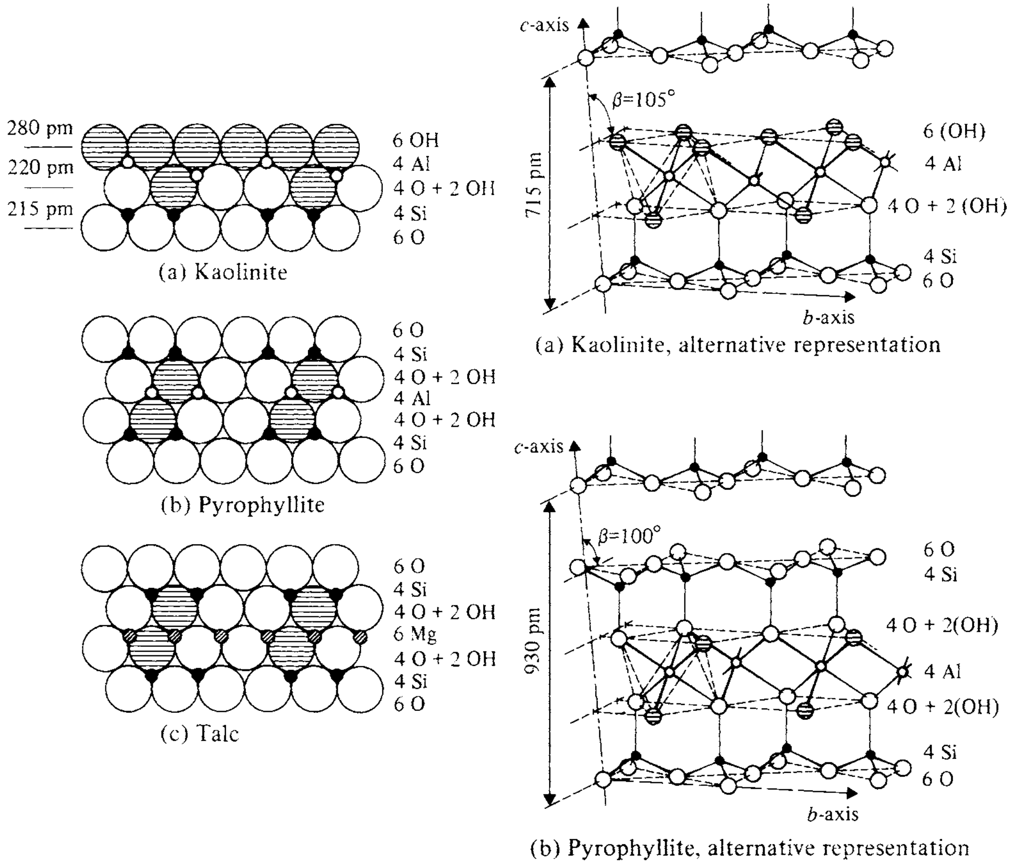


Figure 9.11 Alternative representations of the layer structures of (a) kaolinite, (b) pyrophyllite, and (c) talc. (After H. J. Emeléus and J. S. Anderson, 1960 and B. Mason and L. G. Berry, 1968.)

of which a typical formula is

$$[Mg_{0.32}(H_2O)_{4.32}]^{0.64+} + [(\underbrace{Mg_{2.36}Al_{0.16}Fe^{III}_{0.48}}_{\text{total } 3.00})(OH)_2(Si_{2.72}Al_{1.20}O_{10})]^{0.64-}$$

When these minerals are heated they dehydrate in a remarkable way by extruding little worm-like structures as indicated by their name (Latin *vermiculus*, little worm); the resulting porous light-weight mass is much used for packing and insulation. The relationship between the various layer silicates is summarized with idealized formulae in Table 9.10 (on page 357).

Silicates with framework structures

The structural complexity of the 3D framework aluminosilicates precludes a detailed treatment here, but many of the minerals are of paramount importance. The group includes the feldspars (which are the most abundant of all minerals, and comprise ~60% of the earth's crust), the zeolites (which find major applications as molecular sieves, desiccants, ion exchangers and water softeners), and the ultramarines which, as their name implies, often have an intense blue colour. All are constructed from SiO_4 units in which each O atom is shared by 2 tetrahedra (as in the various forms of SiO_2 itself), but up to one-half of the Si

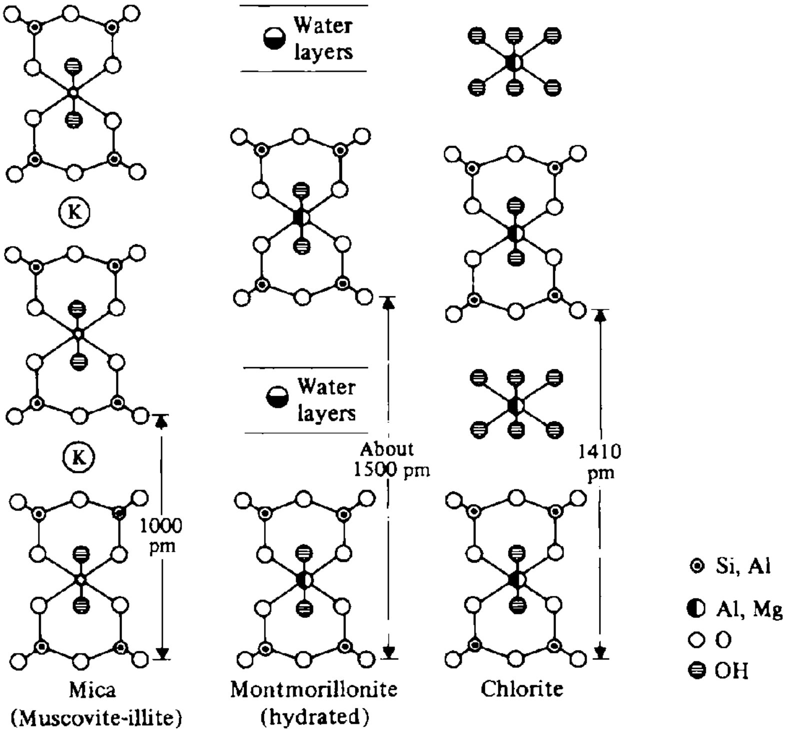
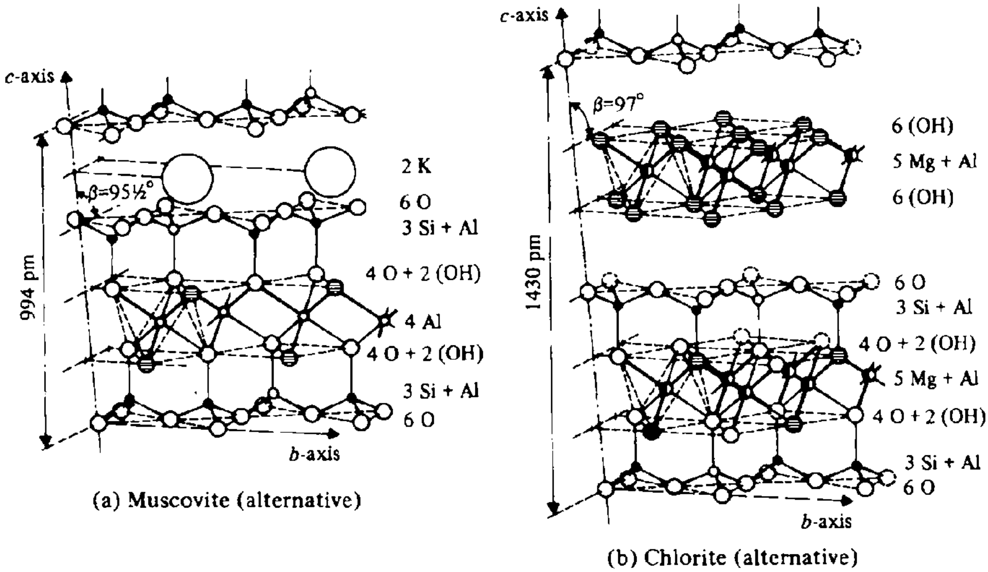


Figure 9.12 Schematic representation of the structures of muscovite mica, $[K_2Al_4(Si_6Al_2)O_{20}(OH)_4]$, hydrated montmorillonite, $[Al_4Si_8O_{20}(OH)_4].xH_2O$ and chlorite, $[Mg_{10}Al_2(Si_6Al_2)O_{20}(OH)_{16}]$, see text.



(a) Muscovite (alternative)

(b) Chlorite (alternative)

Figure 9.13 Alternative representations of muscovite and chlorite (after B. Mason and L. G. Berry[43]).

Clay Minerals and Related Aluminosilicates(1,52)

Clays are an essential component of soils, to which we owe our survival, and they are also the raw materials for some of mankind's most ancient and essential artefacts: pottery, bricks, tiles, etc. Clays are formed by the weathering and decomposition of igneous rocks and occur typically as very fine particles: e.g. kaolinite is formed as hexagonal plates of edge ~0.1–3 μm by the weathering of alkaline feldspar:

$$2[KAlSi_3O_8] + CO_2 + H_2O \xrightarrow{\text{idealized}} [Al_2(OH)_4Si_2O_5] + 4SiO_2 + K_2CO_3$$

When mixed with water, clays become soft, plastic and mouldable; the water of plasticity can be removed at ~100° and the clay then becomes rigid and brittle. Further heating (~500°) removes structural water of crystallization and results in the oxidation of any carbonaceous material or Fe^{II} (600–900°). Above about 950° mullite ($Al_6Si_2O_{13}$) begins to form and glassy phases appear. Common clay is mined on a huge scale (28 million tonnes in USA alone in 1991) and is used principally in the manufacture of bricks (12 Mt), portland cement (10 Mt) and concrete (2.4 Mt), as well as for paper filling and coating (3.7 Mt).

China clay or kaolin, which is predominantly kaolinite, is particularly valuable because it is essentially free from iron impurities (and therefore colourless). World production in 1991 was 24.7 Mt (USA 39%, UK 13%, Colombia, Korea and USSR ~7% each). In the USA over half of this vast tonnage is used for paper filling or paper coating and only 130 000 tonnes was used for china, crockery, and earthenware, which is now usually made from ball clay, a particularly fine-grained, highly plastic material which is predominantly kaolinite together with clay-mica and quartz. Some 800 000 tonnes of ball clay is used annually in the USA for white ware, table ware, wall and floor tiles, sanitary ware, and electrical porcelain.

Fuller's earth is a montmorillonite in which the principal exchangeable cation is calcium. It has a high absorbance and adsorptive capacity, and pronounced cation exchange properties which enable it to be converted to sodium-montmorillonite (bentonite). Nomenclature is confusing and, in American usage, the fibrous hydrated magnesium aluminosilicate attapulgite is also called fuller's earth. World production (1991) was 4.0 million tonnes (USA 68%, Germany 19%, UK 5%). Of the 2.74 Mt produced in the USA, two-thirds was used for what government statisticians coyly call "pet absorbant" and about one-eighth was for oil and grease absorbance.

Bentonite (sodium-montmorillonite) is extensively used as a drilling mud, but this apparently mundane application is based on the astonishing thixotropic properties of its aqueous suspensions. Thus, replacement of Ca by Na in the montmorillonite greatly enhances its ability to swell in one dimension by the reversible uptake of water; this effectively cleaves the clay particles causing a separation of the lamellar units to give a suspension of very finely divided, exceedingly thin plates. These plate-like particles have negative charges on the surface and positive charges on the edges and, even in a suspension of quite low solid content, the particles orient themselves negative to positive to give a jelly-like mass or gel; on agitation, however, the weak electrical bonds are broken and the dispersion becomes a fluid whose viscosity diminishes with the extent of agitation. This indefinitely reversible property is called thixotropy and is widely used in civil engineering applications, in oil-well drilling, and in non-drip paints. The plasticity of bentonite is also used in mortars, putties, and adhesives, in the pelletizing of iron ore and in foundry sands. World production was 9.3 Mt in 1991 (USA 37%, USSR 26% Greece 11%).

Micas occur as a late crystallization phase in igneous rocks. Usually the crystals are 1–5 mm on edge but in pegmatites (p. 108) they may considerably exceed this to give the valuable block mica. Uses of muscovite mica depend on its perfect basal cleavage, toughness, elasticity, transparency, high dielectric strength, chemical inertness and thermal stability to 500°. Phlogopite (Mg-mica) is less used except when stability to 850–1000° is required. Sheet mica is used for furnace windows, for electrical insulation (condensers, heating elements, etc.) and in vacuum tubes. Ground mica is used as a filler for rubber, plastics and insulating board, for silver glitter paints, etc. World production (excluding China) was ~240 000 tonnes in 1974 (USA 53%, India 20%, USSR 17%).

Talc, unlike the micas, consists of electrically neutral layers without the interleaving cations. It is valued for its softness, smoothness and dry lubricating properties, and for its whiteness, chemical inertness and foliated structure. Its most important applications are in ceramics, insecticides, paints and paper manufacture. The more familiar use in cosmetics and toilet preparations accounts for only 3% of world production which is about 5 Mt per annum. Half of this comes from Japan and the USA, and other major producers are Korea, the former Soviet Union, France and China. Talc and its more massive mineral form soapstone or steatite are widely distributed throughout the world and many countries produce it for domestic consumption either by open-cast or underground mining.

atoms have been replaced by Al, thus requiring the addition of further cations for charge-balance.

Most feldspars can be classified chemically as members of the ternary system $NaAlSi_3O_8–KAlSi_3O_8–CaAl_2Si_2O_8$. This is illustrated in Fig. 9.14, which also indicates the names of the mineral phases. Particularly notable

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[52] *Minerals Yearbook Vol. 1, 1991*, US Dept of the Interior, Bureau of Mines, Washington DC, pp. 403–45 (1991).

Table 9.10 Summary of layer silicate structures (idealized formulae)[44]

Dioctahedral (with gibbsite-type layers)	Trioctahedral (with brucite-type layers)
Two-layer structures	
Kaolinite, nacrite, dickite $[Al_4(OH)_8(Si_4O_{10})]$	Antigorite (platy serpentine) $[Mg_6(OH)_8(Si_4O_{10})]$
Halloysite $[Al_4(OH)_8(Si_4O_{10})]$	Chrysotile (fibrous serpentine) $[Mg_6(OH)_8(Si_4O_{10})]$
Three-layer structures	
Pyrophyllite $[Al_2(OH)_2(Si_4O_{10})]$	Talc $[Mg_3(OH)_2(Si_4O_{10})]$
Montmorillonite $[Al_2(OH)_2(Si_4O_{10})].xH_2O$[a]	Vermiculite $[Mg_3(OH)_2(Si_4O_{10})].xH_2O$[b]
Muscovite (mica) $[KAl_2(OH)_2(AlSi_3O_{10})]$	Phlogopite (mica) $[KMg_3(OH)_2(AlSi_3O_{10})]$
Margarite (brittle mica) $[CaAl_2(OH)_2(Al_2Si_2O_{10})]$	Clintonite $[CaMg_3(OH)_2(Al_2Si_2O_{10})]$
	Chlorite $[Mg_5Al(OH)_8(AlSi_3O_{10})]$[c]

[a] With partial replacement of octahedral Al by Mg and with adsorbed cations.

[b] With partial replacement of octahedral Mg by Al and with adsorbed cations.

[c] That is, regularly alternating talc-like and brucite-like sheets.

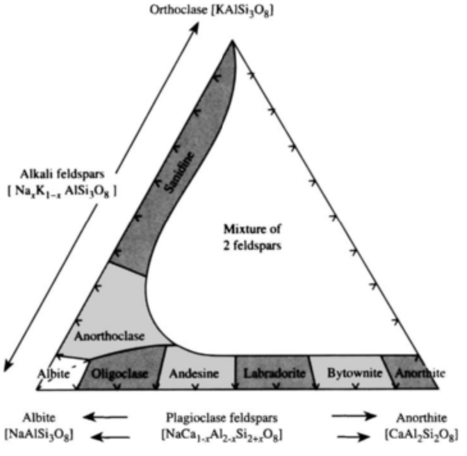

Figure 9.14 Ternary phase diagram for feldspars. The precise positions of the various phase boundaries depend on the temperature of formation.

is the continuous plagioclase series in which Na^I (102 pm) is replaced by Ca^{II} (100 pm) on octahedral sites, the charge-balance being maintained by a simultaneous substitution of Al^{III} for Si^{IV} on the tetrahedral sites. K^I (138 pm) is too disparate in size to substitute for Ca^{II} and 2-phase mixtures result, though orthoclase does form a continuous series of solid solutions with the Ba feldspar celsian $[BaAl_2Si_2O_8]$ (Ba^{II} 136 pm). Likewise, most of the alkaline feldspars are not homogeneous but tend to contain separate K-rich and Na-rich phases unless they have crystallized rapidly from solid solutions at high temperatures (above ~600°). Feldspars have tightly constructed aluminosilicate frameworks that generate large interstices in which the large M^I or M^{II} are accommodated in irregular coordination.[43] Smaller cations, which are common in the chain and sheet silicates (e.g. Li^I, Mg^{II}, Fe^{III}), do not occur as major constituents in feldspars presumably because they are unable to fill the interstices adequately.

Pressure is another important variable in the formation of feldspars and at sufficiently high pressures there is a tendency for Al to increase its coordination number from 4 to 6 with consequent destruction of the feldspar lattice.† For example:

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† In some compounds of course, octahedrally coordinated Al is stable at normal atmospheric pressure, e.g. in Al_2O_3,

$$\underset{\text{albite (feldspar)}}{\mathrm{NaAl_tSi_3O_8}} \xrightarrow{\text{pressure}} \underset{\text{jadeite (clinopyroxene)}}{\mathrm{NaAl_oSi_2O_6}} + \underset{\text{quartz}}{\mathrm{SiO_2}}$$

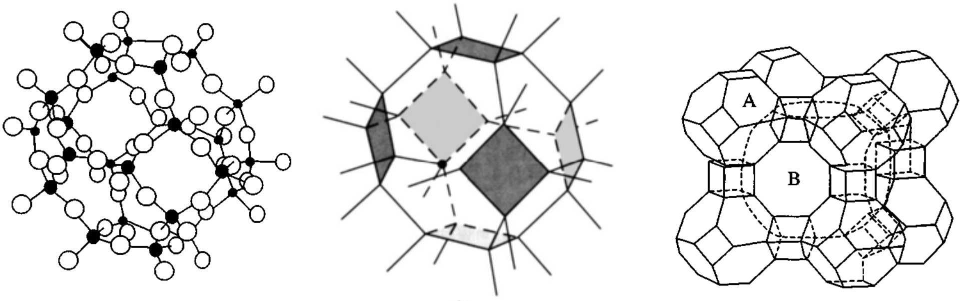
$$\underset{\text{albite}}{\mathrm{NaAl_tSi_3O_8}} + \underset{\text{nepheline}}{\mathrm{NaAl_tSiO_4}} \xrightarrow{\text{pressure}} \underset{\text{jadeite}}{\mathrm{2NaAl_oSi_2O_6}}$$

$$\underset{\text{anorthite (feldspar)}}{\mathrm{3Ca(Al_t)_2Si_2O_8}} \xrightarrow{\text{pressure}} \underset{\text{grossular (Ca garnet)}}{\mathrm{Ca_3(Al_o)_2(SiO_4)_3}} + \underset{\text{kyanite}}{\mathrm{2(Al_o)_2SiO_5}} + \underset{\text{quartz}}{\mathrm{SiO_2}}$$

$$\underset{\text{anorthite}}{\mathrm{Ca(Al_t)_2Si_2O_8}} + \underset{\text{gehlenite}}{\mathrm{Ca_2(Al_t)_2SiO_7}} + \underset{\text{wollastonite}}{\mathrm{3CaSiO_3}} \xrightarrow{\text{pressure}} \underset{\text{grossular}}{\mathrm{2Ca_3(Al_o)_2(SiO_4)_3}}$$

Such reactions marking the disappearance of plagioclase feldspars may be responsible for the Mohorovicic discontinuity between the earth's crust and mantle: this implies that the crust and mantle are isocompositional, the crustal rocks above having phases characteristic of gabbro rock (olivine, pyroxene, plagioclase) whilst the mantle rocks below are an eclogite-containing garnet, Al-rich pyroxene and quartz. Not all geochemists agree, however.

Zeolites have much more open aluminosilicate frameworks than feldspars and this enables them to take up loosely bound water or other small molecules in their structure. Indeed, the name zeolite was coined by the mineralogist A. F. Cronstedt in 1756 (ζειν *zein*, to boil; λιθος *lithos*, stone) because the mineral appeared to boil when heated in the blow-pipe flame. Zeolite structures are characterized by the presence of tunnels or systems of interconnected cavities; these can be linked either in one direction giving fibrous crystals, or more usually in two or three directions to give lamellar and 3D structures respectively. Figure 9.15a shows the construction of a single cavity from 24 linked $\{SiO_4\}$ tetrahedra and Fig. 9.15b shows how this can be conventionally represented by a truncated cubo-octahedron formed by joining the Si atom positions. Several other types of polyhedron have also been observed. These are then linked in three dimensions to build the aluminosilicate framework. A typical structure is shown in Fig. 9.15c for the synthetic zeolite "Linde A" which has the formula $[Na_{12}(Al_{12}Si_{12}O_{48})].27H_2O$.(53) Other cavity frameworks are found in other zeolites such as faujasite, which has the idealized formula $[NaCa_{0.5}(Al_2Si_5O_{14})].10H_2O$, and chabazite $[Ca(Al_2Si_4)O_{12}].6H_2O$. There is great current interest in this field since it offers scope for the reproducible synthesis of structures having cavities, tunnels and pores of precisely defined dimensions on the atomic scale.(54) By



(a) (b) (c)

Figure 9.15 (a) 24 $\{SiO_4\}$ tetrahedra linked by corner sharing to form a framework surrounding a truncated cubo-octahedral cavity; (b) conventional representation of the polyhedron in (a); and (c) space-filling arrangement of the polyhedra A which also generates larger cavities B.

$Al(OH)_3$, and spinels such as $MgAl_2O_4$. Much higher pressures still are required to transform 4-coordinated Si to 6-coordinated (p. 343).

[53] J. M. THOMAS, L. A. BURSILL, E. A. LODGE, A. K. CHEETHAM and C. A. FYFE, *J. Chem. Soc., Chem. Commun.*, 276–7 (1981).

[54] G. GOTTARD and E. GALLI, *Natural Zeolites*, Springer-Verlag, Berlin, 1985, 400 pp. P. A. JACOBS and

appropriate design such molecular sieves can be used to selectively remove water or other small molecules, to separate normal from branched-chain paraffins, to generate highly dispersed metal catalysts, and to promote specific size-dependent chemical reactions.(55) Zeolites are made commercially by crystallizing aqueous gels of mixed alkaline silicates and aluminates at 60–100°. Zeolite-A is being increasingly used as a detergent builder to replace sodium tripolyphosphate (p. 528).

The final group of framework aluminosilicates are the ultramarines which have alternate Si and Al atoms at the corners of the polyhedra shown in Fig. 9.15a and b and, in addition, contain substantial concentrations of anions such as Cl^-, SO_4^{2-} or S_2^{2-}. These minerals tend to be anhydrous, like the feldspars, and in contrast to the even more open zeolites. Examples are sodalite $[Na_8Cl_2(Al_6Si_6O_{24})]$, noselite $[Na_8(SO_4)(Al_6Si_6O_{24})]$ and ultramarine $[Na_8(S_2)(Al_6Si_6O_{24})]$. Sodalite is colourless if the supernumerary anions are all chloride, but partial replacement by sulfide gives the brilliant blue mineral lapiz lazuli. Further replacement gives ultramarine which is now manufactured synthetically as an important blue pigment for oil-based paints and porcelain, and as a "blueing" agent to mask yellow tints in domestic washing, paper making, starch, etc.[†] The colour is due to the presence of the sulfur radical anions S_2^- and S_3^- and shifts from green to blue as the ratio S_3^-/S_2^- increases; in ultramarine red the predominant species may be the neutral S_4 molecule though S_3^- and S_2^- are also present.(56)

9.3.6 Other inorganic compounds of silicon

This section briefly considers compounds in which Si is bonded to elements other than hydrogen, the halogens or oxygen, especially compounds in which Si is bonded to S, N or P. Silicon burns in S vapour at 100° to give SiS_2 which can be sublimed in a stream of N_2 to give long, white, flexible, asbestos-like fibres, mp 1090°, sublimation 1250°C. The structure consists of infinite chains of edge-shared tetrahedra (like W-silica, p. 343) and these transform at high temperature and pressure to a (corner-shared) cristobalite modification. The structural complexity of SiO_2 is not repeated, however. SiS_2 hydrolyses rapidly to SiO_2 and H_2S and is completely ammonolysed by liquid NH_3 to the imide

$$SiS_2 + 4NH_3 \longrightarrow Si(NH)_2 + 2NH_4SH$$

Sulfides of Na, Mg, Al and Fe convert SiS_2 into metal thiosilicates, and ethanol yields "ethylsilicate" $Si(OEt)_4$ and H_2S.[‡] Volatile

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J. A. MARTENS, *Synthesis of High-Silica Aluminosilicate Zeolites*, Elsevier, Amsterdam, 1987, 390 pp. M. L. OCCELLI and H. E. ROBSON (eds.), *Zeolite Synthesis*, ACS Symposium Series No. 398, 1989, 664 pp. J. KLINOWSKI and P. J. BARRIE (eds.) *Recent Advances in Zeolite Science*, Elsevier, Amsterdam, 1990, 310 pp. G. V. TSITSISHVILI, T. G. ANDRONIKASHVILI, G. M. KIROV and L. D. FILIZOVA, *Natural Zeolites*, Ellis Horwood, Chichester, 1990, 274 pp.

[55] D. W. BRECK, *Zeolite Molecular Sieves (Structure, Chemistry, and Uses)*, Wiley, New York, 1974, 771 pp. K. SEFF, *Acc. Chem. Res.* **9**, 121–8 (1976). R. M. BARRER, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London, 1978, 496 pp. W. HÖLDERICH, M. HESSE and F. NÄUMANN, *Angew. Chem. Int. Edn. Engl.* **27**, 226–46 (1988). G. A. OZIN, A. KUPEMAN and A. STEIN, *Angew. Chem. Int. Edn. Engl.* **28**, 359–76 (1989). See also K. B. YOON and J. K. KOCHI, *J. Chem. Soc., Chem. Commun.*, 510–11 (1988) for the novel synthesis of ionic clusters $[Na_4^{3+}]$, and P. A. ANDERSON, R. J. SINGER and P. P. EDWARDS, *J. Chem. Soc., Chem. Commun.*, 914–5 (1991) for the synthesis of $[Na_5^{4+}]$, $[Na_6^{5+}]$ and $[K_3^{2+}]$ by reaction of alkali metal vapours with zeolites.

[†] According to H. Remy the artificial production of ultramarine was first suggested by J. W. von Goethe in his *Italian Journey* (1786–8); it was first accomplished by L. Gmelin in 1828 and developed industrially by the Meissen porcelain works in the following year. It can be made by firing kaolin and sulfur with sodium carbonate; various treatments yield greens, reds and violets, as well as the deep blue, the colours being reminiscent of the highly coloured species obtained in nonaqueous solutions of S, Se and Te (pp. 664, 759).

[56] R. J. H. CLARK and D. G. COBBOLD, *Inorg. Chem.* **17**, 3169–74 (1978).

[‡] $Si(OEt)_4$ is an important industrial chemical that is made on the kilotonne scale by the action of EtOH on $SiCl_4$. It has mp −77°, bp 168.5°, and d_{20} 0.9346 g cm^{-3}. Almost all uses depend on its controlled hydrolysis to produce silica in an adhesive or film-producing form. It is also a source of

thiohalides have been reported from the reaction of SiX_4 with H_2S at red heat; e.g. $SiCl_4$ yields $S(SiCl_3)_2$, cyclic $Cl_2Si(\mu\text{-}S)_2SiCl_2$ and crystalline $(SiSCl_2)_4$. The first normal thiocyanate derivative of Si, $RMe_2Si{-}SCN$, [R = $-C(SiMe_3)_2\{SiMe_2(OMe)\}$] was prepared from the corresponding chloride by treatment with AgSCN; it is more readily solvolysed than its isothiocyanate isomer, $RMe_2Si{-}NCS$.(57)

The elusive Si=S grouping has been synthesized by reaction between solid Si and H_2S at 1200°C to give monomeric SiS; this high-temperature molecule can itself be reacted with Cl_2 or HCl in an argon matrix to yield monomeric $S{=}SiCl_2$ and $S{=}SiHCl$.(58) Synthesis of stable organosilanethiones, $RR'Si{=}S$ has been achieved by using the strategem of imparting additional stabilization through intramolecular coordination via an amine function; e.g. [(α-naphthyl)(8-$Me_2\overline{NCH_2C_{10}H_8)Si}{=}S$] was prepared by heating the corresponding silane $RR'SiH_2$ with S_8; the Si=S distance of 201.3 pm was noticeably shorter than the normal single bond Si–S distance of 216 pm.(59)

The most important nitride of Si is Si_3N_4; this is formed by direct reaction of the elements above 1300° or more economically by heating SiO_2 and coke in a stream of N_2/H_2 at 1500°. The compound is of considerable interest as an engineering material since it is almost completely inert chemically, and retains its strength, shape and resistance to corrosion and wear even above 1000°.(60) Its great hardness (Mohs 9), high dissociation temperature (1900°, 1 atm) and high density (3.185 g cm^{-3}) can all be related to its compact structure which resembles that of phenacite (Be_2SiO_4, p. 347). It is an insulator with a resistivity at room temperature $\sim 6.6 \times 10^{10}$ ohm cm. Another refractory, Si_2N_2O, is formed when Si + SiO_2 are heated to 1450° in a stream of Ar containing 5% N_2. The structure comprises puckered hexagonal nets of alternating Si and N atoms interlinked by nonlinear Si–O–Si bonds to similar nets on either side; the Si atoms are thus each 4-coordinate and the N atoms 3-coordinate.

Volatile silylamides are readily prepared by reacting a silyl halide with NH_3, RNH_2 or R_2NH in the vapour phase or in Et_2O, e.g.:

$$3SiH_3Cl + 4NH_3 \longrightarrow N(SiH_3)_3 + 3NH_4Cl$$

$$SiH_3Br + 2Me_2NH \longrightarrow SiH_3NMe_2 + Me_2NH_2Br$$

$$4SiH_3I + 5N_2H_4 \longrightarrow (SiH_3)_2NN(SiH_3)_2 + 4N_2H_5I$$

Silicon-substituted derivatives may require the use of lithio or sodio reagents, e.g.:

$$Me_3SiCl + NaN(SiMe_3)_2 \longrightarrow N(SiMe_3) + NaCl$$

$$Ph_3SiLi + R_2NH \longrightarrow Ph_3SiNR_2 + LiH$$

The N atom is always tertiary in these compounds and no species containing the SiH–NH group is stable at room temperature. Apart from this restriction, innumerable such compounds have been prepared including cyclic and polymeric analogues, e.g. [cyclo-$\{Me_2SiN(SiMe_3)_2\}$] and [cyclo-$(Me_2SiNH)_4$]. Interest has focused on the stereochemistry of the N atom which is often planar, or nearly so.(61) Thus $N(SiH_3)_3$ features a planar N atom and this has been ascribed to p_π-d_π interaction between the "nonbonding" pair of electrons on N and the "vacant" d_π orbitals on Si as shown schematically in Fig. 9.16. Consistent with this trisilylamines are notably weaker ligands than their tertiary amine analogues though replacement of one or two SiH_3 by CH_3 enhances the donor power again; e.g. $N(SiH_3)_3$ forms no adduct with BH_3 even at low temperature;

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metal-free silica for use in phosphors in fluorescent lamps and TV tubes. In partly hydrolysed form it is used as a paint vehicle, a protective coating for porous stone, and as a vehicle for zinc-containing galvanic corrosion-preventing coatings. Many other orthoesters $Si(OR)_4$ are known but none are commercially important.

[57] C. Eaborn and M. N. Romanelli, *J. Chem. Soc., Chem. Commun.*, 1616–7 (1984).

[58] H. Schnöckel, H. J. Göcke and R. Köppe, *Z. anorg. allg. Chem.* **578**, 159–65 (1989). R. Köppe and H. Schnöckel, *Z. anorg. allg. Chem.* **607**, 41–4 (1992).

[59] P. Arya, J. Boyer, F. Carré, R. Corriu, G. Lanneau, J. Lapasset, M. Perrot and C. Priou, *Angew. Chem. Int. Edn. Engl.* **28**, 1016–7 (1989).

[60] *Silicon Nitride and the SIALONS* World Business Publications Ltd., (two vols.), 1989, 285 pp.

[61] E. A. V. Ebsworth, *Volatile Silicon Compounds*, Pergamon Press, Oxford, 1963, 179 pp.

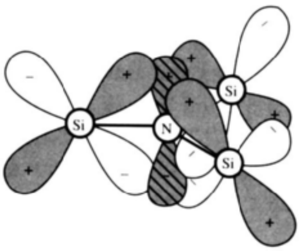
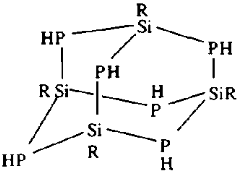


Figure 9.16 Symmetry relation between p_π orbital on N and d_π orbitals on the 3 Si atoms in planar $\{NSi_3\}$ compounds such as $N(SiH_3)_3$.

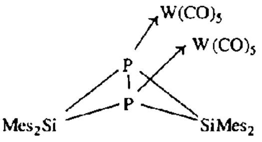
$MeN(SiH_3)_2$ forms a 1:1 adduct with BH_3 at −80° but this decomposes when warmed; $Me_2N(SiH_3)$ gives a similar adduct which decomposes at room temperature into Me_2NBH_2 and SiH_4 (cf. the stability of Me_3NBH_3, p. 165). The linear skeleton of H_3SiNCO and H_3SiNCS has also been interpreted in terms of $p_\pi{-}d_\pi$ $\mathrm{N}\overset{\rightharpoonup}{=}\mathrm{Si}$ bonding.

Compounds containing an Si=N double bond are of very recent provenance. The first stable silanimine, $Bu^t{}_2Si{=}N{-}SiBu^t{}_3$, was prepared in 1986 as pale yellow crystals, mp 85° (decomp.);(62) it features a short Si=N distance (156.8 pm, cf. Si–N 169.5 pm) and almost linear coordination about the N atom (177.8°), suggesting some electronic delocalization as described above. The compound was made by reacting the azidosilane $Bu^t{}_2SiCl(N_3)$ with $NaSiBu^t{}_3$ in Bu_2O at −78°. The related compound $Pr^i{}_2Si{=}NR$ ($R = 2,4,6\text{-}Bu^t{}_3C_6H_2{}^-$) forms stable orange crystals, mp 98°.(63)

Unusual Si/P compounds are also beginning to appear, for example, the tetrasilahexaphospha-adamantane derivative $[(Pr^iSi)_4(PH)_6]$ (1), which is made by reacting Pr^iSiCl_3 with $Li[Al(PH_2)_4]$.(64) Again, reaction of white phosphorus, P_4, with tetramesityldisilene, $Mes_2Si{=}SiMes_2$, in toluene at 40° gives an 87% yield of the yellow bicyclo $(Mes_2Si)_2P_2$: this has a "butterfly" structure in which the "hinge" P atoms retain electron donor properties to give adducts such as the bis-$W(CO)_5$ complex (2) (P–P 234.2 pm; Si–P 224.4, 226.7 pm; P–W 256.0 pm; Si···Si 324.4 pm; angle Si–P–Si 91.9°).(65) The now extensive field of phosphorus-rich silaphosphanes has been reviewed.(66) Silaphosphenes, RR′Si=PAr are also known.(67)



(1)



(2)

9.3.7 Organosilicon compounds and silicones

Well over 100 000 organosilicon compounds have been synthesized. Of these, during the past few decades, silicone oils, elastomers and resins have become major industrial products. Many organosilicon compounds have considerable thermal stability and chemical inertness; e.g. $SiPh_4$ can be distilled in air at its bp 428°, as can Ph_3SiCl (bp 378°) and Ph_2SiCl_2 (bp 305°). These, and innumerable similar compounds, reflect the considerable strength of the Si–C bond which is, indeed, comparable with that of the C–C bond (p. 338). A further illustration is the compound SiC which closely resembles diamond in its properties (p. 334). Catenation and the formation of multiple bonds are further similarities with carbon chemistry, though these features are less prominent in organosilicon chemistry and much of the work in these areas is of recent

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[62] N. WIBERG, K. SCHURZ, G. REBER and G. MÜLLER, *J. Chem. Soc., Chem. Commun.*, 591–2 (1986).

[63] M. HESSE and U. KLINGEBIEL, *Angew. Chem. Int. Edn. Engl.* **25**, 649–50 (1986).

[64] M. BAUDLER, W. OELERT and K.-F. TEBBE, *Z. anorg. allg. Chem.* **598/599**, 9–23 (1991).

[65] M. DRIESS, A. D. FANTA, D. R. POWELL and R. WEST, *Angew. Chem. Int. Edn. Engl.* **28**, 1038–40 (1989).

[66] G. FRITZ *Advances in Inorg. Chem.* **31**, 171–214 (1987).

[67] N. C. NORMAN, *Polyhedron* **12**, 2431–46 (1993) and references cited therein. M. DRIESS, *Adv. Organomet. Chem.* **39**, 193–229 (1996) — also deals with sila-arsenes containing Si=As bonds).

origin (e.g. pp. 338 and below). For example, although the word "silicone" was coined by F. S. Kipping in 1901 to indicate the similarity in *formula* of Ph_2SiO with that of the ketone benzophenone, Ph_2CO, he stressed that there was no chemical resemblance between them and that Ph_2SiO was polymeric.(68) It is now recognized that the great thermal and chemical stability of the silicones derives from the strength both of the Si–C bonds and of the Si–O–Si linkages. Many general reviews of the vast subject of organosilicon chemistry are available (e.g. refs 1, 2, 69–74) and only some of the salient or topical features will be touched on here. An interesting subset comprises the carbosilanes, that is compounds with a skeleton of alternating C and Si atoms.(75) These include chains, rings and polycyclic compounds, many of which can be made on a multigram or even larger scale by controlled thermolysis or by standard organometallic syntheses.

Transient reaction species containing Si=C bonds have been known since about 1966 and can be generated thermally, photolytically, or even chemically. A decade later $Me_2Si{=}CHMe$ was isolated in low-temperature matrices(76) but, despite concerted and well-planned attempts over many years, it was not until 1981 that a stable silene was reported.(77) A. G. Brook and his group prepared 2-adamantyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silaethene as very pale yellow needles, mp 92°:

$$(Me_3Si)_3SiC(O)(C_{10}H_{15}) \xrightleftharpoons{\text{ether}/h\nu} (Me_3Si)_2Si{=}C(OSiMe_3)(\text{adamantyl})$$

The solid silaethene was stable indefinitely at room temperature in the absence of air or other reagents but in solution it slowly reverted (over several days) to the isomeric acylsilane starting material. An X-ray analysis confirmed the structure and revealed a short >Si=C< bond (176.4 pm, cf. 187–191 pm for single-bonded Si–C) and a planar disposition of *ipso* atoms, the two planes being slightly twisted with respect to each other (14.6°). The use of bulky groups to enhance the stability of the silaethene is also notable, though this is not a necessary feature, at least at the Si centre, since $Me_2Si{=}C(SiMe_3)(SiMeBu^t_2)$ is stable as colourless crystals at room temperature (>Si=C< distance 170.2 pm, Si–C 189.0 pm and a planar $C_2Si{=}CSi_2$ skeleton).(78) The not unrelated planar heterocyclic compounds silabenzene, C_5SiH_6,(15) and silatoluene, C_5H_5SiMe,(16) should also be recalled.

Disilenes, containing the grouping >Si=Si<, can be isolated as thermally stable yellow or orange crystalline compounds provided that the substituents are sufficiently large to prevent

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[68] F. S. Kipping and L. L. Lloyd, *J. Chem. Soc. (Transactions)* **79**, 449–59 (1901).

[69] G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, Vol. 2 (1982): D. A. Armatage, Organosilanes, pp. 1–203; T. J. Barton, Carbocyclic Silanes, pp. 205–303; F. O. Stark, J. R. Falender and A. P. Wright, Silicones, pp. 305–63; R. West, Organopolysilanes, pp. 365–97.

[70] S. Pawlenko, *Organosilicon Chemistry*, de Gruyter, Berlin, 1986, 186 pp.

[71] J. Y. Corey, E. J. Corey and P. P. Gasper (eds.), *Silicon Chemistry*, Ellis Horwood, Chichester, 1988, 565 pp.

[72] M. Zeldin, K. J. Wynne and H. R. Alcock (eds.), *Inorganic and Organometallic Polymers*, ACS Symposium Series **360** (1988) 512 pp.

[73] S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds* (2 vols.), Wiley, Chichester, 1989, 892 pp. and 1668 pp.

[74] N. Auner, W. Ziche and R. West, *Heteroatom Chemistry* **2**, 335–55 (1991). This is a very readable account of current work, and includes an update of ref. 73 with a further 222 references.

[75] G. Fritz, *Angew. Chem. Int. Edn. Engl.* **26**, 1111–32 (1987).

[76] O. L. Chapman, C.-C. Chang, J. Kole, M. E. Jung, J. A. Lowe, T. J. Barton and M. L. Tumey, *J. Am. Chem. Soc.* **98**, 7844–6 (1976). M. R. Chedekel, M. Skoglund, R. L. Kreeger and H. Shechter, *ibid.*, 7846–8 (1976).

[77] A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst and R. K. Kallury, *J. Chem. Soc., Chem. Commun.*, 191–2 (1981). A. G. Brook and 8 others, *J. Am. Chem. Soc.*, **104**, 5667–72 (1982). For the most recent review of the chemistry of silenes see A. G. Brook and M. A. Brook, *Adv. Organomet. Chem.*, **39**, 71–158 (1996).

[78] N. Wiberg, G. Wagner and G. Müller, *Angew. Chem. Int. Edn. Engl.* **24**, 229–31 (1985). See also N. Wiberg *et al.*, *Organometallics* **6**, 32–5 and 35–41 (1987).

polymerization (e.g. mesityl, *t*-butyl, etc.)[79] The first such compound, $\mathrm{Si_2Mes_4}$, was isolated in 1981 as orange crystals, mp 176°, following photolysis of the trisilane $\mathrm{SiMes_2(SiMe_3)_2}$.[80] The Si=Si distance in several such compounds falls in the range 214–216 pm, which is about 10% shorter than the normal single-bonded Si–Si distance. Disilenes are chemically very reactive. Halogens and HX molecules give 1,2-addition products, e.g. $\mathrm{Mes_2Si(Cl)Si(Cl)Mes_2}$, whilst aldehydes and ketones undergo [2 + 2] cyclo-addition reactions to give 1,2,3-oxadisilenanes, $\overline{\mathrm{OSi(Mes)_2Si(Mes)_2C}}\mathrm{HR}$. Controlled oxidation gives predominantly the 1,2-dioxetane $\overline{\mathrm{OSiR_2SiR_2O}}$ (80%), plus the 1,3-cyclodisiloxane $\overline{\mathrm{OSiR_2OSi}}\mathrm{R_2}$ as a minor product. Numerous other novel heterocyles have been prepared by controlled reactions of disilenes with chalcogens, $\mathrm{N_2O}$, $\mathrm{P_4}$ and organic nitro-, nitroso-, azo- and azido-compounds.[81] Transition metal complexes can give η^2-disilene adducts such as $\mathrm{[Pt(PR_3)_2)(\eta^2\text{-}Si_2Mes_4)]}$.[79,82]

Another fertile area of current interest is the synthesis of stable homocyclic polysilane derivatives.[83] Typical examples are cyclo-$\mathrm{(SiMe_2)_7}$,[84] (cyclo-$\mathrm{Si_5Me_9}$)-$\mathrm{(SiMe_2)}_n$-(cyclo-$\mathrm{Si_5Me_9}$), $n = 2$–5,[85] and several new permethylated polycylic silanes such as the colourless crystalline compounds bicyclo[3.2.1]-$\mathrm{Si_8Me_{14}}$ (mp 245°), bicyclo[3.3.1]-$\mathrm{Si_9Me_{16}}$ (mp ≥330°) and bicyclo[4.4.0]-$\mathrm{Si_{10}Me_{18}}$ (mp 165°.[86] Analogues of cubane and tetrahedrane have also been synthesized. Thus, the one-step condensation of $\mathrm{Br_2RSiSiRBr_2}$ or even $\mathrm{RSiBr_3}$ with Na in toluene at 90° gave yields of up to 72% of the cubane $\mathrm{(SiR)_8}$ ($\mathrm{R = SiMe_2Bu^t}$) as bright yellow, air-sensitive crystals which are stable up to at least 400°C.[87] The synthesis of a molecular tetrasilatetrahedrane has also finally been achieved by the following ingenious route ($\mathrm{R = SiBu^t{}_3}$):[88]

$$\mathrm{2SiH_2Cl_2 \xrightarrow{2NaR} 2RSiH_2Cl \xrightarrow{2Na} RSiH_2SiH_2R \longrightarrow RSiBr_2SiBr_2R}$$

$$\mathrm{2RSiBr_2SiBr_2R + 4NaR \longrightarrow Si_4R_4 + 4RBr + 4NaBr}$$

The product, $\mathrm{Si_4(SiBu^t{}_3)_4}$, forms intensely orange crystals that are stable to heat, light, water and air, and do not melt below 350°. The Si–Si distances within the *closo*-$\mathrm{Si_4}$ cluster are 232–234 pm and the *exo* Si–Si distances are slightly longer, 235–237 pm (cf. Si–Si 235.17 in crystalline Si). Comparison with the *closo*-anion $\mathrm{Si_4{}^{4-}}$, which occurs in several metal silicides (p. 337) and is isoelectronic with the $\mathrm{P_4}$ molecule, is also appropriate.

There are three general methods for forming Si–C bonds. The most convenient laboratory method for small-scale preparations is by the reaction of $\mathrm{SiCl_4}$ with organolithium, Grignard or organoaluminium reagents. A second attractive route is the hydrosilylation of alkenes, i.e. the catalytic addition of Si–H across C=C double bonds; this is widely applicable except for the crucially important methyl and phenyl silanes. Industrially, organosilanes are made by the direct reaction of RX or ArX with a fluidized bed of Si in the presence of about 10% by weight of metallic Cu as catalyst (cf. the direct preparation of organo compounds of

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[79] R. WEST, *Angew. Chem. Int. Edn. Engl.* **26** 1201–11 (1987). R. OKAZAKI and R. WEST, *Adv. Organomet. Chem.* **39**, 232–73 (1996).

[80] R. WEST, M. J. FINK and J. MICHL, *Science* **214**, 1343–4 (1981). See also B. D. SHEPHERD, C. F. CAMPANA and R. WEST, *Heteroatom Chemistry*, **1**, 1–7 (1990).

[81] R. WEST, in R. STEUDEL (ed.), *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, 1992, pp. 35–50. See also M. WEIDENBRUCH, *ibid.*, pp. 51–74.

[82] C. ZYBILL, *Topics in Current Chemistry* **160**, 1–45 (1992).

[83] E. HENGGE and H. STÜGER, in H. W. ROESKY (ed.), *Rings, Clusters and Polymers of Main Group and Transition Metals*, Elsevier, Amsterdam, 1989, pp. 107–38.

[84] F. SHAFIEE, J. R. DAMEWOOD, K. J. HALLER and R. WEST, *J. Am. Chem. Soc.* **107**, 6950–6 (1985).

[85] E. HENGGE and P. K. JENKNER, *Z. anorg. allg. Chem.* **560**, 27–34 (1988).

[86] E. HENGGE and P. K. JENKNER, *Z. anorg. allg. Chem.* **606**, 97–104 (1991).

[87] H. MATSUMOTO, K. HIGUCHI, Y. HOSHINO, H. KOIKE, Y. NAOI and Y. NAGAI, *J. Chem. Soc., Chem. Commun.*, 1083–4 (1988).

[88] N. WIBERG, C. M. M. FINGER and K. POLBORN, *Angew. Chem. Int. Edn. Engl.* **32**, 1054–6 (1993).

Ge, Sn, and Pb, pp. 396ff). The method was patented by E. G. Rochow in 1945 and ensured the commercial viability of the now extensive silicone industry.(2,69,72)

$$2\text{MeCl} + \text{Si} \xrightarrow[\sim 300^\circ]{\text{Cu powder}} \text{Me}_2\text{SiCl}_2 \quad (70\% \text{ yield})$$

By-products are MeSiCl_3 (12%) and Me_3SiCl (5%) together with 1–2% each of SiCl_4, SiMe_4, MeSiHCl_2, etc. Relative yields can readily be altered by modifying the reaction conditions or by adding HCl (which increases MeSiHCl_2 and drastically reduces Me_2SiCl_2). The overall reaction is exothermic and heat must be removed from the fluidized bed. Because of their very similar bps, careful fractionation is necessary if pure products are required: Me_3SiCl 57.7°, Me_2SiCl_2 69.6°, MeSiCl_3 66.4°. Mixtures of ethylchlorosilanes or phenylchlorosilanes (or their bromo analogues) can be made similarly. All these compounds are mobile, volatile liquids (except Ph_3SiCl, mp 89°, bp 378°).

Innumerable derivatives have been prepared by the standard techniques of organic chemistry.(2,69–75) The organosilanes tend to be much more reactive than their carbon analogues, particularly towards hydrolysis, ammonolysis, and alcoholysis. Further condensation to cyclic oligomers or linear polymers generally ensues, e.g.:

$$\text{Ph}_2\text{SiCl}_2 \xrightarrow{\text{H}_2\text{O}} \text{Ph}_2\text{Si(OH)}_2 \text{ white crystals, mp} \sim 132^\circ \text{ (d)}$$

$$\xrightarrow{>100^\circ} \tfrac{1}{n}(\text{Ph}_2\text{SiO})_n + \text{H}_2\text{O} \quad n = 3(\text{cyclo}), 4(\text{cyclo}), \text{ or } \infty$$

$$\text{Me}_2\text{SiCl}_2 \xrightarrow{\text{NH}_3/-35^\circ} \underset{\text{not isolated}}{\{\text{Me}_2\text{Si(NH}_2)_2\}} \longrightarrow [\text{cyclo-}(\text{Me}_2\text{SiNH})_3] + [\text{cyclo-}(\text{Me}_2\text{SiNH})_4]$$

For both economic and technical reasons, commercial production of such polymers is almost entirely restricted to the methyl derivatives (and to a lesser extent the phenyl derivatives) and hydrolysis of the various methylchlorosilanes has, accordingly, been much studied. Hydrolysis of Me_3SiCl yields trimethylsilanol as a volatile liquid (bp 99°); it is noticeably more acidic than the corresponding Bu^tOH and can be converted to its Na salt by aqueous NaOH (12M). Condensation gives hexamethyldisiloxane which has a very similar bp (100.8°):

$$2\text{Me}_3\text{SiCl} \xrightarrow[(-2\text{HCl})]{+2\text{H}_2\text{O}} 2\text{Me}_3\text{SiOH} \xrightarrow{-\text{H}_2\text{O}} [\text{O}(\text{SiMe}_3)_2]$$

Hydrolysis of Me_2SiCl_2 usually gives high polymers, but under carefully controlled conditions leads to cyclic dimethylsiloxanes $[(\text{Me}_2\text{SiO})_n]$ ($n = 3, 4, 5, 6$). Linear siloxanes have also been made by hydrolysing Me_2SiCl_2 in the presence of varying amounts of Me_3SiCl as a "chain-stopping" group, i.e. $[\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_x\text{SiMe}_3]$ ($x = 0, 1, 2, 3, 4$), etc. Cross-linking is achieved by hydrolysis and condensation in the presence of MeSiCl_3 since this generates a third Si–O function in addition to the two required for polymerization:

$$\text{Me}_3\text{SiCl} \xrightarrow{\text{H}_2\text{O}} \text{Me}_3\text{Si–O–} \quad \text{terminal group}$$

$$\text{Me}_2\text{SiCl}_2 \xrightarrow{\text{H}_2\text{O}} \text{–O–SiMe}_2\text{–O–} \quad \text{chain-forming group}$$

$$\text{MeSiCl}_3 \xrightarrow{\text{H}_2\text{O}} \text{MeSi(–O–)}_3 \quad \text{branching and bridging group}$$

Comparison with the mineral silicates is instructive since there is a 1:1 correspondence between the two sets of compounds, the methyl groups in the silicones being replaced by the formally isoelectronic O^- in the silicates (see p. 366). This reminds us of the essentially covalent nature of the Si–O–Si linkage, but the analogy should not be taken to imply identity of structures in detail, particularly for the more highly condensed polymers. Some aspects of the technology of silicones are summarized in the concluding Panel.

While siloxanes and silicones are generally regarded as being unreactive, it is well to remember that they do indeed react with fluorinating agents and with concentrated hydroxide solutions. In certain cases they can even be employed as mild selective reagents for specific syntheses. For example, $(\text{Me}_3\text{Si})_2\text{O}$ is a useful reagent for the convenient high-yield

Silicone Polymers[1,2]

Silicones have good thermal and oxidative stability, valuable resistance to high and low temperatures, excellent water repellency, good dielectric properties, desirable antistick and antifoam properties, chemical inertness, prolonged resistance to ultraviolet irradiation and weathering, and complete physiological inertness. They can be made as fluids (oils), greases, emulsions, elastomers (rubbers) and resins.

Silicone oils are made by shaking suitable proportions of $[O(SiMe_3)_2]$ and $[cyclo\text{-}(Me_2SiO)_4]$ with a small quantity of 100% H_2SO_4; this randomizes the siloxane links by repeatedly cleaving the Si–O bonds to form HSO_4 esters and then reforming new Si–O bonds by hydrolysing the ester group:

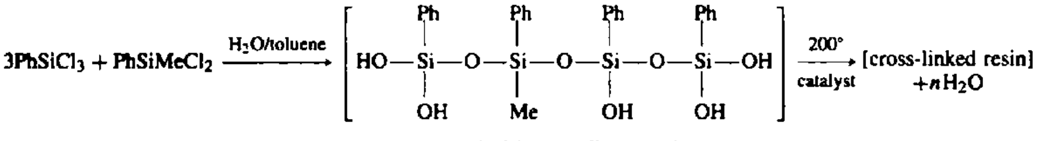
$$\equiv Si\text{-}O\text{-}Si\equiv + H_2SO_4 \longrightarrow \equiv Si\text{-}O\text{-}SO_3H + \equiv Si\text{-}OH$$

$$\equiv Si\text{-}OH + HO_3S\text{-}O\text{-}Si\equiv \longrightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2SO_4$$

The molecular weight of the resulting polymer depends only on the initial proportion of the chain-ending groups (Me_3SiO– and Me_3Si–) and the chain-building groups (–Me_2SiO–) from the two components. Viscosity at room temperature is typically in the range 50–300 000 times that of water and it changes only slowly with temperature. These liquids are used as dielectric insulating media, hydraulic oils and compressible fluids for liquid springs. Pure methylsilicone oils are good lubricants at light loads but cannot be used for heavy-duty steel gears and shafts since they contain no polar film-forming groups and so are too readily exuded under high pressure. The introduction of some phenyl groups improves performance, and satisfactory greases can be made by thickening methyl phenyl silicone oil with Li soaps. Other uses are as heat transfer media in heating baths and as components in car polish, sun-tan lotion, lipstick and other cosmetic formulations. Their low surface tension leads to their extensive use as antifoams in textile dyeing, fermentation processes and sewage disposal: about 10^{-2} to 10^{-4}% is sufficient for these applications. Likewise their complete non-toxicity allows them to be used to prevent frothing in cooking oils, the processing of fruit juices and the production of potato crisps.

Silicone elastomers (rubbers) are reinforced linear dimethylpolysiloxanes of exceedingly high molecular weight ($5 \times 10^5 - 10^7$). The reinforcing agent, without which the viscous gum is useless, is usually fumed silica (p. 345). Polymerization can be acid-catalysed but KOH produces a rubber with superior physical properties; in either case scrupulous care must be taken to avoid the presence of precursors of chain-blocking groups [Me_3Si–O–] or cross-linking groups [$MeSi(\text{–}O\text{–})_3$]. The reinforced silicone rubber composition can be "vulcanized" by oxidative cross-linking using 1–3% of benzoyl peroxide or similar reagents; the mixture is heated to 150° for 10 min at the time of pressing or moulding and then cured for 1–10 h at 250°. Alternatively, and more elegantly, the process can be achieved at room temperature or slightly above by incorporating a small controlled concentration of Si–H groups which can be catalytically added across pre-introduced $Si\text{–}CH{=}CH_2$ groups in adjacent chains. Again, the cross-linking of 1-component silicone rubbers containing acetoxy groups can be readily effected at room temperature by exposure to moisture: Such rubbers generally have 1 cross-link for every 100–1000 Si atoms and are unmatched by any other synthetic or natural rubbers in retaining their inertness, flexibility, elasticity and strength up to 250° and down to –100°. They find use in cable-insulation sleeving, static and rotary seals, gaskets, belting, rollers, diaphragms, industrial sealants and adhesives, electrical tape insulation, plug-and-socket connectors, oxygen masks, medical tubing, space suits, fabrication of heart-valve implants, etc. They are also much used for making accurate moulds and to give rapid, accurate and flexible impressions for dentures and inlays.

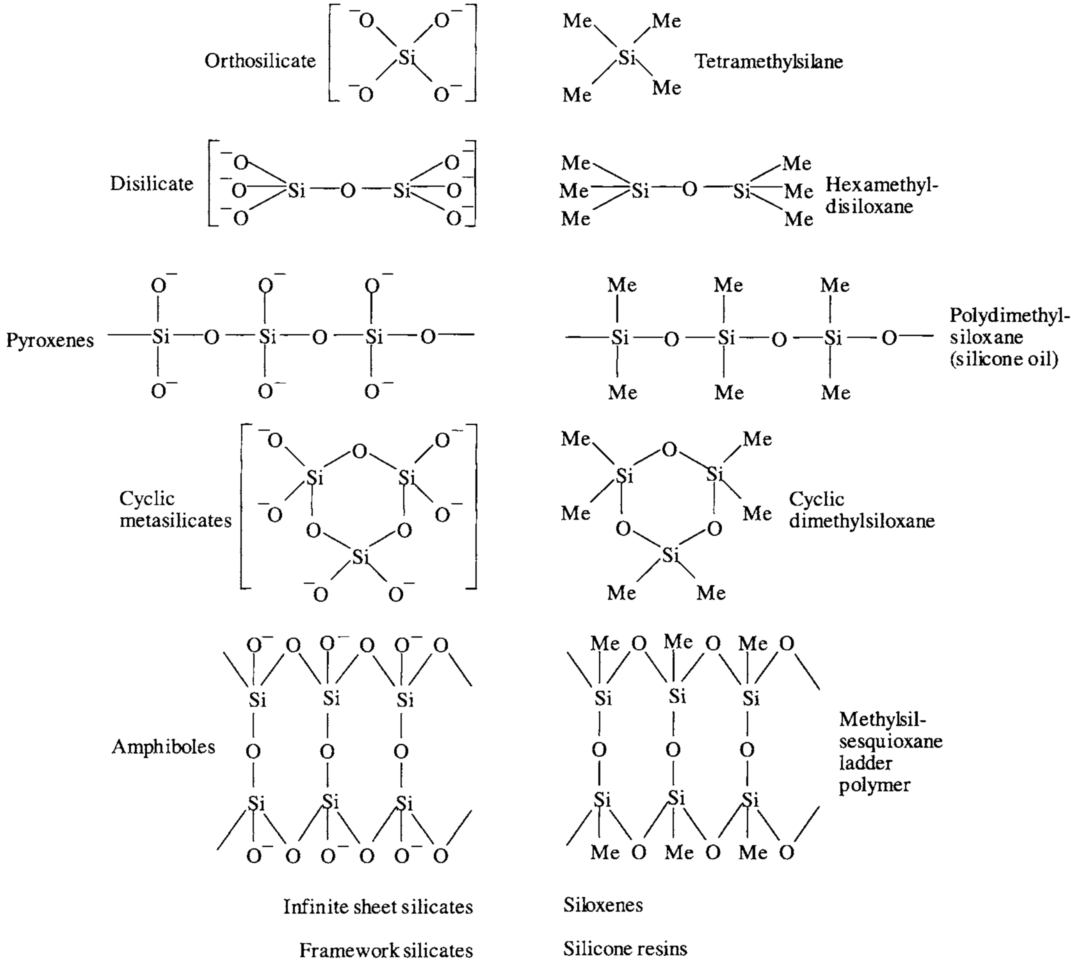
Silicone resins are prepared by hydrolysing phenyl substituted dichloro- and trichloro-silanes in toluene. The Ph groups increase the heat stability, flexibility, and processability of the resins. The hydrolysed mixture is washed with water to remove HCl and then partly polymerized or "bodied" to a carefully controlled stage at which the resin is still soluble. It is in this form that the resins are normally applied, after which the final cross-linking to a 3D siloxane network is effected by heating to 200° in the presence of a heavy metal or quaternary ammonium catalyst to condense the silanol groups, e.g.:



$$3PhSiCl_3 + PhSiMeCl_2 \xrightarrow{H_2O/\text{toluene}} \left[HO\text{—}\overset{Ph}{\underset{OH}{Si}}\text{—}O\text{—}\overset{Ph}{\underset{Me}{Si}}\text{—}O\text{—}\overset{Ph}{\underset{OH}{Si}}\text{—}O\text{—}\overset{Ph}{\underset{OH}{Si}}\text{—}OH \right] \xrightarrow[\text{catalyst}]{200^\circ} [\text{cross-linked resin}] + nH_2O$$

a typical intermediate species

Silicone resins are used in the insulation of electrical equipment and machinery, and in electronics as laminates for printed circuit boards; they are also used for the encapsulation of components such as resistors and integrated circuits by means of transfer moulding. Non-electrical uses include high-temperature paints and the resinous release coatings familiar on domestic cooking ware and industrial tyre moulds. When one recalls the very small quantities of silicones needed in many of these individual applications, the global production figures are particularly impressive: they have grown from a few tonnes in the mid-1940s to over 100 000 tonnes in 1969 and an estimated production of 350 000 tonnes in 1982. About half of this is in the USA, distributed so that some 65–70% is as fluid silicones, 25–30% as elastomers, and 5–10% as resins. Over 1000 different silicone products are commercially available.



preparation of oxyhalide derivatives of Mo and W.(89) Thus, in CH_2Cl_2 solution, $(Me_3Si)_2O$ converts a suspension of WCl_6 quantitatively to red crystals of $W(O)Cl_4$ in less than 1 h at room temperature, and $W(O)Cl_4$ can then itself be converted to yellow $W(O)_2Cl_2$ in 95% yield (light petroleum, 100°, overnight). Likewise, $Mo(O)Cl_4$ when treated with $(Me_3Si)_2O$ in CH_2Cl_2 gives $Mo(O)_2Cl_2$ in 97% yield at r.t. Even silicone high-vacuum grease has been found unexpectedly to react with the potassium salt of an organoindium hydride to give crystals of the pseudo-crown ether complex $[cyclo\text{-}(Me_2SiO)_7K^+](K^+)_3[HIn(CH_2CMe_3)_3^-]_4$.(90)

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(89) V. C. GIBSON, T. P. KEE and A. SHAW, *Polyhedron* **7**, 579–80 (1988).

(90) M. R. CHURCHILL, C. H. LAKE, S.-H. L. CHAO and O. T. BEACHLEY, *J. Chem. Soc., Chem. Commun.*, 1577–8 (1993).