

Configuration Change in Silicates with Particular Reference to Network Structures

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Many phenomena depend upon internal configuration change. Silicate network structures have characteristic general features. The essential geometry of a variety of mechanisms, whereby changes of local anionic configuration can be brought about, is described and illustrated. They are classified under the headings of linkage mutation, network-former migration, aggregation and disaggregation, rotation. Such processes are reversible, an arbitrary direction being chosen for descriptive purposes. By their operation network breaks are created, destroyed or moved and the oxygen coordination of elements such as aluminum is varied. In some cases electrostatic defects are generated, while in others electrostatic neutrality is maintained. Migration of low valency cations is possible without mass transfer of oxygen. Certain mechanisms are limited to particular types of bulk composition.

Introduction

There are many phenomena depending upon internal configuration change. In the field of crystalline solids nucleation and crystal growth, polymorphic transition, simple grain growth in solid aggregates, recrystallization to a new phase assemblage, the generation of thermal defects, ordering and ex-solution, plastic deformation, metasomatic change and damage by irradiation are to be included. In melts and glasses viscous flow, delayed elasticity, annealing, hydration, loss of volatile components, attack by aqueous solutions, diffusion effects and pressure induced structural changes are encountered. It would seem reasonable to postulate that collectively a variety of mechanisms is involved, of which some may be common to a number of phenomena.

The present study would appear to be the first systematic survey of the possibilities and establishes the essential geometrical basis for the theoretical treatment of configuration change in structures where silicon, aluminum and boron, singly or together, serve as network-forming elements. A comprehensive set of hypothetical processes is described. They involve either the creation or the extinction of breaks in the three-dimensional linkage system or their transfer from one location to another, or the migration of network-forming ions or else involve changes in the oxygen coordination of aluminum and boron. It is believed that no significant process, compatible with established structural principles, has been overlooked.

Network silicates have variable oxygen densities, defined as the number of oxygen atoms in 10^{-20} cm³ (Lacy, 1955, 1963), *e.g.* 343 for sodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$), 476 for albite ($\text{NaAlSi}_3\text{O}_8$), 535 for quartz (SiO_2) and 407 for orthoclase glass (KAlSi_3O_8). Compared with the theoretical figure of 768 for oxygen ions in closest packing, these are mainly values denoting a relatively

open structure, such as would offer considerable freedom of movement and hence the most generalized opportunities for internal change.

By contrast a number of authors (Gay & LeMaitre, 1961; Glasser & Glasser, 1961; Ball & Taylor, 1963) have recently discussed reactions of a topotactic character in closely packed lattices. Silicates of this kind show a range of oxygen densities exemplified by 552 for forsterite (Mg_2SiO_4), 627 for almandine ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) and 690 for kyanite (Al_2SiO_5). It is evident that such packing must impose limitations, particularly upon mechanisms involving the movement of coherent groups of atoms. Lacy (1965) has shown that the degree of tightness of the oxygen packing in silicates is an important factor influencing the height of the energy barrier to be overcome during change.

In the more open of the network structures cations such as sodium may show relative ease of mobility as in the analcite (Barrer & Hinds, 1950) and albite (Šćavničar & Sabatier, 1957) structures and in vitreous alumino-silicates (Isard, 1959). Such motion is however, not the main concern of the present work which, rather, is with the anionic framework.

Some of the processes to be described are of a simple character and are completed in one movement. Others are composite and represent a sequence of events. The discussion does not exclude arrangements which only rarely are seen in minerals, *e.g.* the AlO_5 group, or which have not been reported in any analysed structure, *e.g.* an SiO_4 group sharing an edge with an AlO_4 group. Some configurations such as these may characterize melts under high pressure or solids undergoing penetrative shearing. Others, including free SiO_2 or other oxide groups, may appear as unstable transients in a dynamic setting such as the disturbance brought about by neutron impact.

In principle each process is regarded as reversible,

and hence each description represents an arbitrary choice of direction. Some mechanisms, proceeding from a state of local electrostatic balance to one of unbalance, represent means by which particular types of local defect may be generated as, for instance, during the attainment of thermal equilibrium. Others result in no electrostatic disturbance or are such that electrostatic compensation, either by moving or by static cations, can be maintained continuously. As a classification strictly according to function results in overlapping, they have been gathered into four simple groups. A nomenclature for the principal mechanisms and their variants is proposed.

The descriptions in the classified account below and the individual diagrams in Figs. 1-5 are numbered to correspond. They relate to areas of structure dissected from a main mass. The bonds with the latter are not shown, as normally these connections are not affected by the local happenings depicted. Minor variations of particular configurations are omitted and a few descriptions are not illustrated.

The nature of network structures

A variety of features distinguish silicates from the metals, in which configurational change is now well understood. These include the presence of oppositely charged atoms in the structure, the characteristic oxygen clusters coordinating small highly charged ions, the sharing of oxygen between coordination groups, and the possibility of the formation of relatively loosely packed networks. Furthermore, silicate melts and glasses have well developed structure, although of a non-periodic kind.

The simplest three-dimensional silicate networks have the SiO_4 tetrahedral group as the building unit, each oxygen atom being shared between two groups. In more complex structures elements such as aluminium, boron, beryllium, zinc, and magnesium may appear in four-coordination with oxygen. In the majority of these structures, individual oxygen atoms are shared between not more than two tetrahedra, but in the mineral euclase, and in phenacite, oxygen is found shared between an SiO_4 group and two BeO_4 groups. Other cases are known in which oxygen is held in common by various combinations of three polyhedra.

Examples are:

sillimanite:	SiO_4 , AlO_4 , AlO_6 ;
euclase:	SiO_4 , BeO_4 , AlO_6 ;
andalusite:	SiO_4 , AlO_5 , AlO_6 ;
beryl:	SiO_4 , BeO_4 , AlO_6 ;
muscovite:	SiO_4 , AlO_6 , AlO_6 ;
topaz:	SiO_4 , AlO_6 , AlO_6 .

Similarly the present author (Lacy, 1963) has advanced evidence pointing to the occurrence, in certain alumino-silicate glasses, of SiO_4 , SiO_4 , AlO_4

'triclusters' in which the oxygen common to three groups is 'passive' relative to one of them.

The present study takes note of all these configurations but, for the sake of simplicity, four-coordinated atomic species other than silicon, aluminium and boron will not be further discussed. It will be convenient to consider the AlO_6 group and the BO_3 group as having parity of function with SiO_4 , AlO_4 and BO_4 groups in the building of network structures, whilst not making any assumptions about their quantitative importance.

Many minerals and glasses contain O_4 tetrahedra in which an oxygen atom is not shared with another coordination group. Such an atom is designated a non-bridging oxygen atom, and this term will be extended to cover a similarly disposed oxygen atom in O_3 and O_6 groups. The presence of non-bridging oxygen in a network necessitates that a stoichiometric proportion of oppositely charged atoms should be present in its interstices. With increase in the proportion of non-bridging oxygen the three-dimensional network character eventually will be lost.

Interstitial positive ions are also an essential feature of structures containing fully connected AlO_4 or AlO_6 groups, because such groups carry a net negative charge, even when all their oxygen is shared with neighbouring coordination polyhedra.

In the specialist literature upon glasses, elements such as silicon and aluminum are described as 'glass-formers'. The equivalent term 'network-former' is used here because of its more general applicability.

A CLASSIFIED ACCOUNT OF THE MECHANISMS BRINGING ABOUT CHANGES OF CONFIGURATION

1. Linkage mutation processes

Gliding

Gliding comprises a number of mechanisms differing in detail. The essential feature, shared by them all, is the existence of a non-bridging oxygen atom belonging to, or in the immediate vicinity of, a pair of coordination groups, normally tetrahedra, linked by a common oxygen atom. This link is broken, producing, for instance, an O_3 triangle (which may or may not have oxygen atoms in common with other coordination groups) and also a new non-bridging oxygen atom. Translation of the O_3 group in a direction within a plane in or near to its own brings it into contact with the original non-bridging oxygen, a new tetrahedral group being formed. This may be accompanied by movement of a low valency cation.

1-1. *Simple or base/edge glide.* The O_3 triangle shifts from contact with one oxygen atom to another of the same tetrahedral group, moving along an edge of the group as it does so.

1-2. *Cross or base/apex glide.* The O_3 triangle shifts

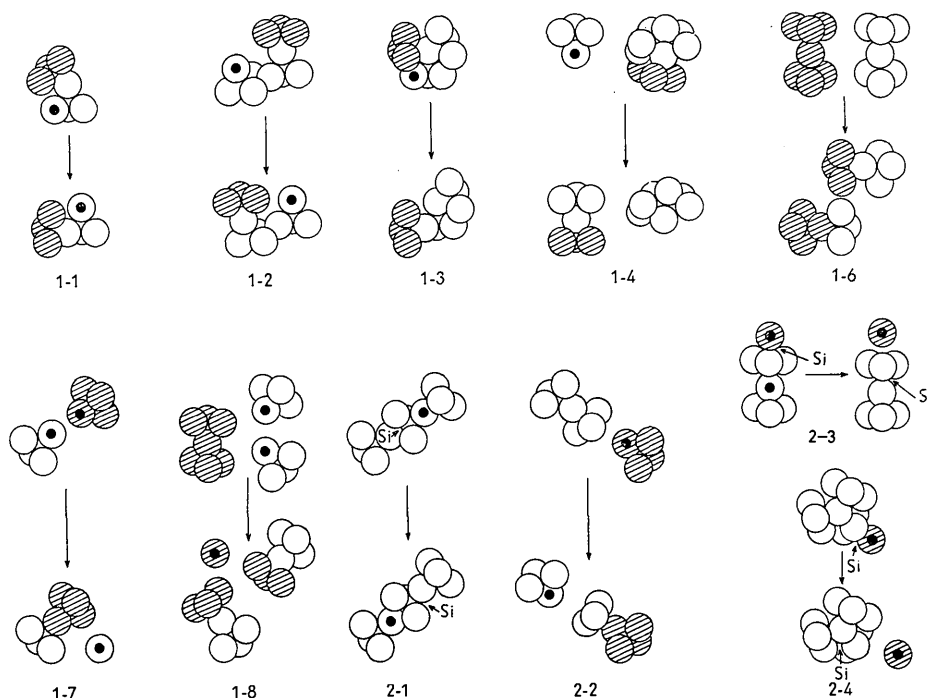


Fig. 1. Changes of local configuration: 1-1 to 2-4 (numbered as in the text). Unshared oxygen atoms dotted. Network-former atoms not drawn. Larger arrows indicate successive stages.

from contact with one oxygen atom to another not belonging to the same tetrahedral group.

1-3. *Simple redistributive glide*. This is similar to base/edge glide except that the O_3 triangle glides from an oxygen atom shared between three coordination clusters. An oxygen atom is converted from a non-bridging to a bridging function without a complementary conversion of another from a bridging to a non-bridging function.

1-4. *Redistributive cross glide* is a process similar to the last, except that the O_3 triangle shifts from contact with one oxygen atom to another not a member of the same tetrahedral group.

1-5. O_6 *gliding*. Gliding movements may take place in which one or more octahedral groups are directly involved, but, in view of the full details given above for 1-1 to 1-4, they will not be further described.

Linkage exchange

This type of change takes place between two juxtaposed pairs of coordination groups. Each pair has an oxygen atom common to its constituent groups but no oxygen is shared between the two pairs. The linkage between the members of each pair is broken. Recombination takes place between a mutilated group of one pair and an intact group of the other. The illustration (1-6) depicts one of the two alternative ways in which it may be effected at any particular site. The mechanism is not limited to tetrahedral clusters, nor to situations where all the groups contain the same number of oxygen atoms.

Condensation

By a type of reaction that may be described as condensation the number of oxygen atoms that are not shared between two coordination groups is reduced.

1-7. *Simple condensation*. Initially two adjacent coordination clusters have unshared oxygen atoms which are in close proximity. One divalent or two monovalent cations are associated with these breaks in the three-dimensional network. Condensation results in the formation of an oxygen bridge between the clusters and the liberation of an oxygen atom which forms an oxide group with the low valency cation or cations.

1-8. *Reconstructive condensation*. The original configuration features a pair of coordination clusters sharing an oxygen atom and two neighbouring groups, not necessarily in mutual contact, each one having an unshared oxygen atom. The oxygen linkage between the pair is severed. The broken ends establish new connections with the two other clusters *via* the hitherto unshared oxygen atoms. The final configuration thus has two complete oxygen bridges instead of one. One oxygen atom is liberated together with one or more cations carrying a total of two positive charges. Detailed variants of this process will depend on the subordinate features of the original arrangement, such as the presence or absence of broken linkages additional to the essential two.

2. Processes featuring network-former migration

2-1. *Simple network-former transfer.* Three tetrahedra are involved. A tetrahedral group having an unshared oxygen atom is in apposition to a pair of tetrahedra sharing an oxygen atom in such a way that its unshared oxygen touches three oxygen atoms of the pair. These three atoms do not include the one that is shared between the pair.

It will be seen that a centrally placed O_3 triangle may be traced in this grouping. The configurational change consists simply in migration of a network-forming atom from its station on one side of the O_3 triangle to the symmetrical position on the other. The oxygen atom previously unshared has now become the connecting oxygen shared by two tetrahedra. The oxygen atom previously shared is now unshared. Ideally the migration of a silicon atom will be accompanied by a counterwise movement of a balancing cation of low valency, but the migration of an aluminum atom calls for no such complementary movement. After the transfer of the network-former the tetrahedral group with the unshared oxygen will be free to separate from that part of the configuration to which it had previously been bonded.

2-2. *O_3 transfer.* The initial configuration closely resembles that of the preceding example, except that there is a gap between the unshared oxygen atom and those of the pair of tetrahedra. The O_3 triangle moves in a direction at right angles to its own plane

until contact is made with the unshared oxygen, when the silicon atom transfers from one side of the O_3 triangle to the other. One linkage has then been broken and a new one made.

2-3. *Transfer with oxygen loss.* Two tetrahedra each have one non-bridging oxygen atom and are in contact in such a way that three shared oxygen atoms of one touch the unshared oxygen of the other. Transfer of one network-forming ion converts an oxygen atom from a non-bridging to a bridging function and sets the other non-bridging atom free. Electrostatic balance is maintained by low-valency cation movements.

2-4. *Transfer with tricluster formation.* Two tetrahedra share an oxygen atom with which three oxygen atoms of a further tetrahedral group are also in contact. Transfer of the network-forming ion of this third group results in the formation of a tricluster. In order that the arrangement may be stable, excess negative charge on the 'abandoned' oxygen must be neutralized by positive charge on a low-valency cation or cations already associated with the configuration.

2-5. *Inversion.* A tetrahedral group shares three oxygen atoms with other tetrahedra. The remaining oxygen atom becomes dislodged and describes a path around the outside of the O_3 triangle so created. It reaches a position where it is again in contact with each of the three oxygen atoms, but on the other side of the group as compared with its original

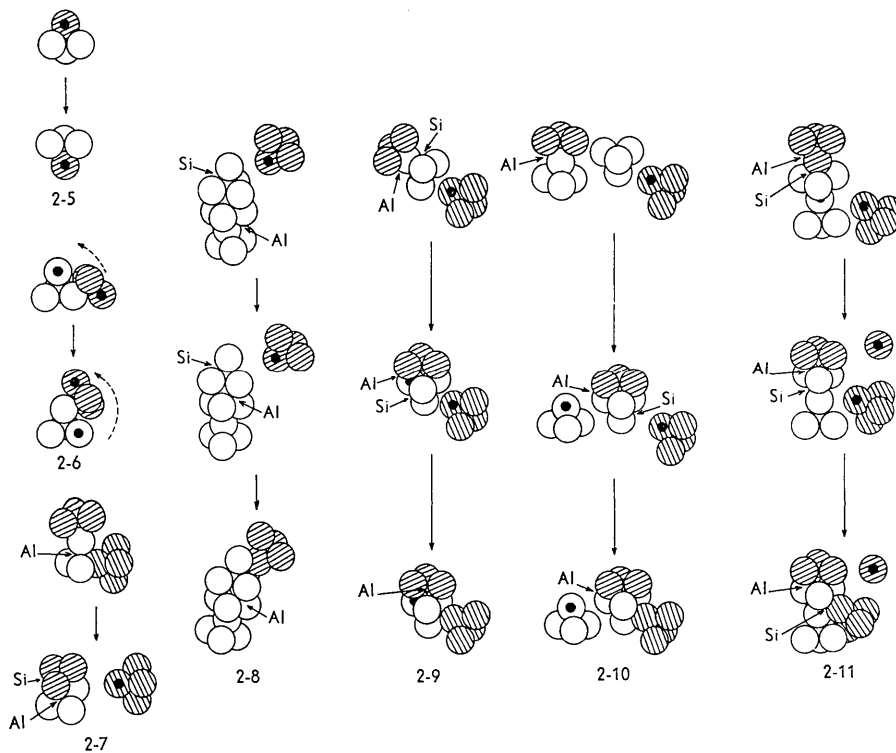


Fig. 2. Changes of local configuration: 2-7 to 2-11 (numbered as in the text). Unshared oxygen atoms dotted. Network-former atoms not drawn. Unbroken arrows indicate successive stages and hidden atoms.

situation. The network-forming atom passes through the centre of the O_3 triangle to the other side. Ideally the movement of the oxygen ion will be accompanied by positional adjustment of a low valency cation.

2-6. *Overturn.* Two tetrahedral coordination groups share an oxygen atom and each has an unshared oxygen atom. One tetrahedron is temporarily disrupted as its unshared oxygen atom swings through an arc which brings it into contact with the unshared oxygen atom of the other group. The silicon atom is thus transported between three oxygen atoms to a new location where tetrahedral coordination is once more established. By this means a break in the network is transferred from one oxygen atom to another. Two of the oxygen atoms concerned may require to move very little.

2-7. *Roll and transfer.* The initial configuration consists of an AlO_4 tetrahedron sharing two oxygen atoms with other groups, one being tetrahedral. One group withdraws from the AlO_4 tetrahedron which loses one oxygen atom. The other tetrahedron rolls about the oxygen atom shared with the damaged AlO_4 group, until one of its oxygen atoms comes into contact with the three of the latter on the side opposite to that from which an oxygen was withdrawn. The aluminum ion then transfers to the centre of the O_4 group so formed. The final configuration thus features two tetrahedral groups sharing two oxygen atoms. During these changes complementary movements of the balancing low-valency cations may be expected. The extent of the rolling movement required depends on the initial disposition of the groups. It need not be large. A number of minor variants of the overall arrangement are possible, depending upon the extent to which the remaining oxygen atoms are shared. If the oxygen which converts the O_3 remnant into an AlO_4 group was originally shared between two groups the end arrangement will include an oxygen atom common to three groups and passive relative to one of them.

2-8. *Complex or double network-former transfer.* The initial configuration includes two tetrahedra sharing an oxygen atom. One of these coordinates an aluminum ion. In contact with three oxygen atoms of the AlO_4 group are three belonging to a third tetrahedron. Thus there exists a sixfold oxygen cluster which contains no network-forming ion. The aluminum ion passes through the O_3 triangle, which lies between its original site and the centre of the octahedral cluster. The latter now coordinates a network-former but shares three of its oxygen atoms with the third original tetrahedron, an unstable arrangement. A satisfactory readjustment is possible if an unshared oxygen atom of a further coordination group is in the vicinity of three oxygen atoms of the third tetrahedron. This unshared oxygen atom closes up into contact with the other three oxygen atoms, thus forming a tetrahedral cluster. The network-former, originally coordinated by the third tetrahedral group, passes between the

three oxygen atoms into the vacant site in the newly constituted tetrahedron.

The final configuration is seen to be somewhat complicated. An octahedral group encloses an aluminum ion. This group has the unshared oxygen atom of a tetrahedron in contact with it. The octahedron shares two oxygen atoms with another tetrahedron. These will have become passive oxygen atoms if originally shared between two groups. The tetrahedron, in turn, shares one oxygen atom with a further coordination group. Other linkages of the groups concerned are incidental and need not be detailed. During the course of the changes adjustments of the positions of low valency cations may occur.

2-9. *Glide and transfer.* This mechanism has several features in common with that preceding. Two tetrahedra share oxygen atoms. The presence of an aluminum atom in one tetrahedron is essential as is also an unshared oxygen atom, belonging to an external group, in the vicinity of the other tetrahedron. The terminal O_3 triangle of the AlO_4 group glides into full contact with three oxygen atoms of the second tetrahedron.

The configuration is now an O_6 octahedron having three oxygen atoms in common with a tetrahedron. The arrangement, at this stage, is unstable because two network-formers have been brought into very close proximity. One network-forming atom therefore transfers to the other side of three oxygen atoms of its tetrahedron so as to face the unshared oxygen atom of the external group. This closes up into contact and a new tetrahedron is formed, sharing two oxygen atoms with the sixfold group. These movements are accompanied by corresponding adjustments of the positions of balancing cations. Depending on the original external linkages of the reacting groups the final configuration may contain up to two oxygen atoms shared between three coordination groups.

2-10. *Cross glide and transfer.* This process is almost identical with that just detailed. The initial configuration features two tetrahedra sharing an oxygen atom. The AlO_6 octahedron is formed by the detachment and glide of an AlO_3 triangle from an external group. The remaining movements are similar. The incidental connections possible for certain of the oxygen atoms need not be described.

2-11. *Complex condensation or condensation with network-former transfer.* In this case two tetrahedra, one being an AlO_4 group, share an oxygen atom. The remaining connections of the AlO_4 oxygen atoms are immaterial. The corresponding three oxygen atoms of the other group are in contact with an unshared oxygen atom belonging to a third group. The process of change entails the loss of the shared oxygen, followed by a closing together of the six oxygen atoms with which it was in contact. The six coordinate the aluminum ion. The second network-former transfers to the space enclosed by three of the sixfold oxygen atoms and the unshared oxygen of the third-men-

tioned group. This arrangement is unstable. If an unshared oxygen atom of a further group is in close proximity to the middle of an exposed side of the newly formed tetrahedron a second transfer of the network-former will place it once more in a tetrahedral environment. This time only two oxygen atoms are shared with the AlO_6 octahedron. These changes will be accompanied by adjustment of the positions of low-valency cations. The process is closely analogous to that described above as complex network-former transfer, the difference lying in the freeing of an oxygen atom and its attendant cations.

3. Aggregation and disaggregation

A number of processes lead to variation of the size of the groups coordinating network-formers, or to a tighter or looser association of such groups.

Dissociation involves reduction in the number of oxygen atoms coordinating a network-forming ion. Most of the examples relate to the removal of a single oxygen.

3-1. *Dissociation of a BO_4 group.* A stable BO_3 triangle is formed irrespective of whether the group originally was four-connected or not or whether, in the latter case, the loss was of a bridging or of a non-bridging oxygen atom.

3-2. *Dissociation of an AlO_4 group* will similarly give rise to an electrostatically balanced AlO_3 configuration, but this will have no long term stability

as the aluminum ion is left inadequately screened.

3-3. *Replication* is an interesting special case where initially an SiO_4 tetrahedron shares three oxygen atoms with other tetrahedra. Break-up occurs because of the movement away from it of one of these tetrahedra. The modifying cation associated with the original unshared oxygen follows the intact tetrahedral group which now, instead of being four-connected, has one unshared and three shared oxygen atoms. The initial arrangement has thus been reproduced, but an SiO_3 configuration also has been generated. Although electrostatic balance is preserved, the latter will be transient in character because of the unsatisfactory screening of the silicon ion.

3-4. *Dissociation of a fully connected SiO_4 group.* Oxygen is lost exactly as in the previous example but there is no replication. The resultant SiO_3 group is unstable, not merely because of the poor screening of the silicon ion, but because electrostatic balance is completely disturbed.

3-5. *Loss of unshared oxygen* from an AlO_6 group yields an AlO_5 or AlO_4 cluster. An AlO_6 group carries excess negative charge normally compensated by low valency cations and these, as necessary, will accompany the migrating oxygen upon dissociation of the group.

3-6. *Loss of shared oxygen*, from any type of structural position, may occur provided the requisite energy is available. The structure will be left in a state of strong local electrostatic unbalance.

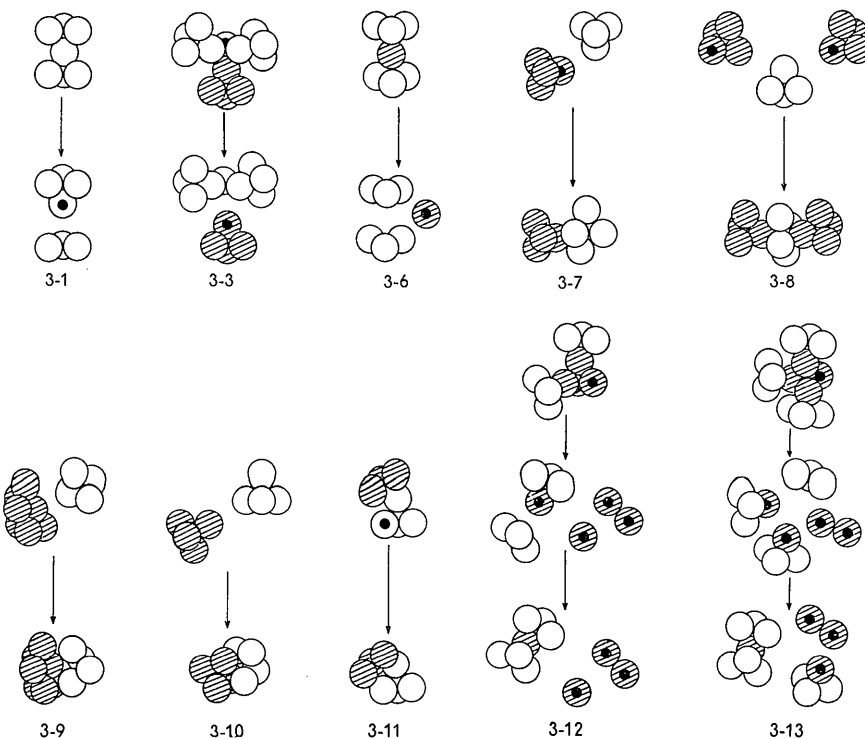


Fig. 3. Changes of local configuration: 3-1 to 3-13 (numbered as in the text). Unshared oxygen atoms dotted. Network-former atoms not drawn. Arrows indicate successive stages.

Simple penetrative interaction of two coordination groups is illustrated by the five following examples:

3-7. A fivefold group may arise from the admission to an AlO_4 group of a non-bridging oxygen atom forming part of another. If it is intruded symmetrically into the middle of the tetrahedron base an ideal pentamerous cluster is formed, with only slight displacement of the oxygen atoms from their original positions. If the penetrating oxygen atom initially touches only two members of the tetrahedral group there is less likelihood of the attainment of a symmetrical configuration.

3-8. An AlO_4 group is converted into an octahedral group by the intrusion of two non-bridging oxygen atoms which are already members of other clusters. Electrostatic balance is preserved by the proximity of low-valency cations.

3-9. *Passive oxygen.* The coordination state of a network-forming atom may be raised by the admission to its oxygen group of an oxygen atom already shared between two coordination groups. The Si-O-Si bond angle of the penetrating oxygen atom must be considerably less than 180° . Although, for convenience, the added oxygen may be described as passive in its relationship to the group it disturbs, there must be, in actuality, an appreciable redistribution of charge. The formation of a fivefold group is illustrated.

3-10. Two tetrahedra may be brought into contact in such a way that an edge of one meets the mid point of an edge of the other squarely and symmetrically. If the tetrahedra are then forced together and the oxygen atoms of one edge are wedged apart the resulting configuration will consist of an octahedral sixfold group sharing an edge with a tetrahedron.

3-11. A fivefold group may result from two tetrahedra that share an oxygen atom if an O_3 triangle, belonging to one, is dislodged from the common oxygen and moves so that its plane of symmetry remains parallel to an edge of the intact tetrahedron. If the translation is of the correct amount a minor penetration of the O_3 triangle by the tetrahedron edge will result in the formation of a regular fivefold coordination cluster. The change will be less liable to be subject to steric hindrance if the oxygen of the tetrahedron edge is unshared.

Cluster fragmentation may be described as a group of processes leading to the formation of products which, at least initially, are unstable and include units larger than single atoms. Several of the descriptions feature SiO_4 groups, but the break up of AlO_4 tetrahedra would follow courses differing only in detail.

3-12. A fourfold group having two non-bridging oxygen atoms breaks up with the production of a free SiO_2 group and a free oxygen atom. Partial reconstruction leads to the formation of a pair of SiO_4 groups sharing a common oxygen atom, together with a free SiO_2 group and a free metallic oxide group incorporating the modifying cation, *e.g.* Na_2O .

Association of the SiO_2 and Na_2O may occur, giving an Na_2SiO_3 group as a further transient entity.

3-13. A tetrahedron, with one unshared oxygen atom, fragments. One fourfold group and one SiO_3 group with complementary excess charge are produced and combine. A free SiO_2 group also results, together with a SiO_4 tetrahedron having one unshared oxygen atom.

3-14. An SiO_4 tetrahedron with two unshared oxygen atoms disrupts. A continuous linkage is broken, two different tetrahedra are left with an unshared oxygen atom each and an SiO_2 group is set free.

3-15. A further case is the one where the disintegrating SiO_4 group has three unshared oxygen atoms. The break-up yields a tetrahedron with one unshared oxygen atom, an independent SiO_2 group and a metallic oxide group such as Na_2O . Alternatively the break-up may yield a Na_2SiO_3 group as a transient product.

3-16. The edgewise interaction of two tetrahedra (one being an AlO_4 group) was described in a previous section, the result being an AlO_6 octahedron sharing two oxygen atoms with a tetrahedral group. Taking this as a starting configuration it is easy to envisage the loss of two oxygen atoms and a silicon ion, a simple octahedral group being left.

3-17. *Substitutional shearing.* By this mechanism an oxygen atom shared between two coordination groups is sheared from its connection with one of them by an oxygen atom, common to two further groups, which takes its place. This kind of change is more easily accomplished at a site where a balancing cation is associated with an unshared oxygen atom or with an oxygen group coordinating aluminum. The low-valency cation is then available to neutralize the excess negative charge that is developed on the displaced portion of the configuration.

3-18. A four-connected fourfold group is concerned. The break-up of the tetrahedron leaves two complete fourfold groups each with one excess negative charge and two SiO_3 triangles, each with an excess of positive charge, and sets free an SiO_2 group. Joining of each fourfold group with a threefold one restores electrostatic balance. Two pairs of SiO_4 groups, each pair having an oxygen atom common to its constituent clusters, result.

3-19. A fully connected tetrahedral group breaks up, giving an SiO_3 triangle with one unshared oxygen atom, an SiO_4 group with one unshared oxygen atom and an SiO_3 triangle sharing all three oxygen atoms. Union of the two latter will give a stable linkage. The remaining SiO_3 group, though electrostatically neutral, will be expected to be short lived only.

3-20. A sixfold cluster shares all its oxygen with other coordination groups, of which two only are depicted in the figure. The oxygen bond with one of these is broken. The oxygen ion escapes completely, accompanied by two univalent ions, or one divalent cation. An irregular five-connected fivefold

CONFIGURATION CHANGE IN SILICATES

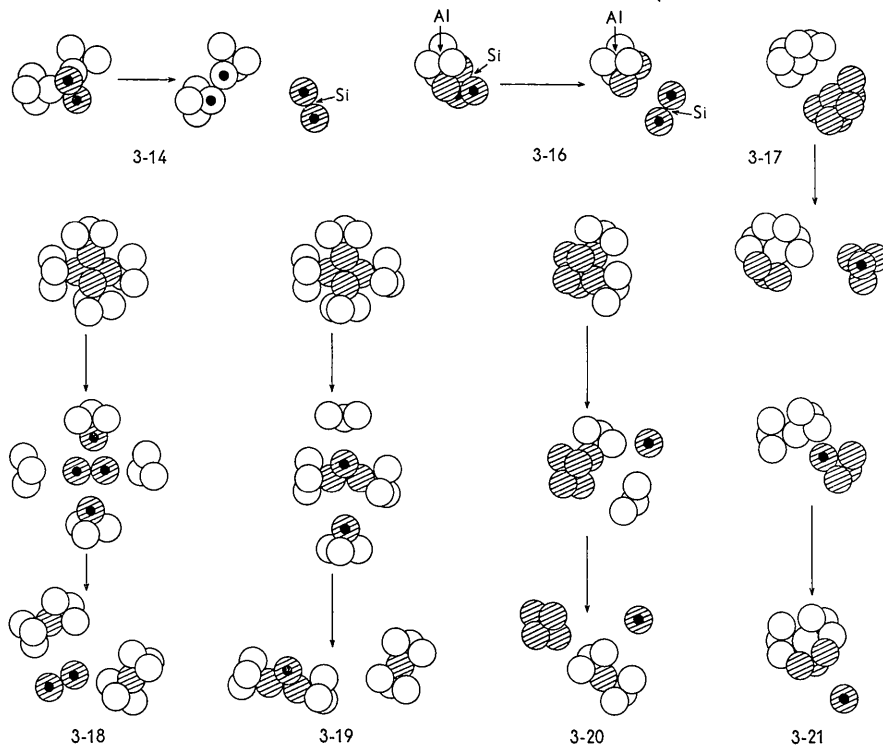


Fig. 4. Changes of local configuration: 3-14 to 3-21 (numbered as in the text). Unshared oxygen atoms dotted. Network-former atoms not drawn. Larger arrows indicate successive stages.

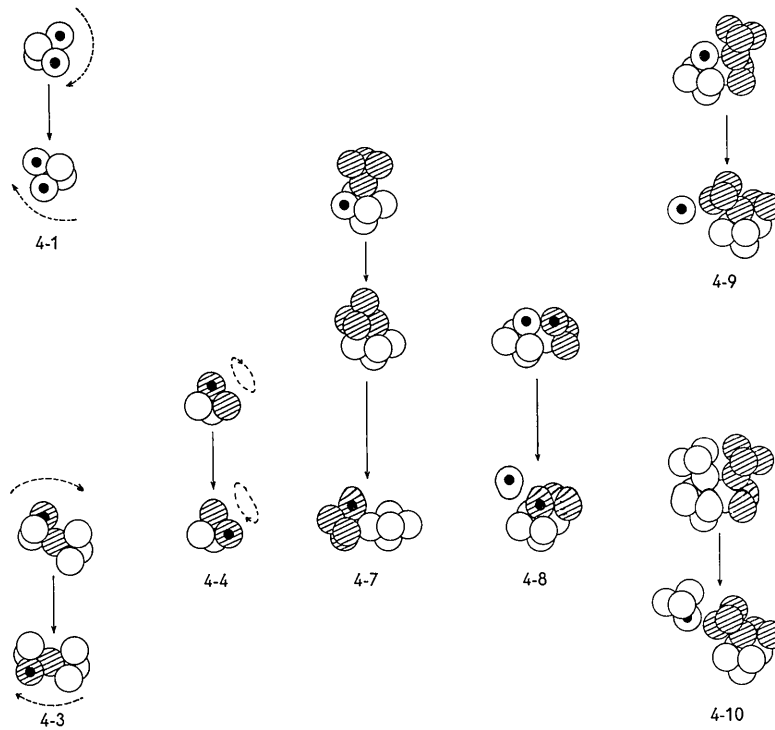


Fig. 5. Changes of local configuration: 4-1 to 4-10 (numbered as in the text). Unshared oxygen atoms dotted. Network-former atoms not drawn. Unbroken arrows indicate successive stages.

group and an incomplete neighbouring group remain. The latter is repaired by union with an oxygen atom originally shared between the sixfold cluster and another network group, the oxygen leaving the erstwhile octahedral group to form the new linkage. Of the original sixfold cluster only four oxygen atoms now remain. These retain their linkages with other groups and, after small adjustments of position, they constitute a normal fully connected tetrahedral group.

3-21. *Substitutional condensation.* This kind of change may be visualized in terms of a simple shearing movement. For example, two tetrahedra share an oxygen atom, the Si-O-Si bond angle being considerably less than 180° . Adjacent to the shared oxygen is another cluster, coordinating an aluminum atom. This group has an unshared oxygen atom. A shearing movement occurs during which the shared oxygen forces the unshared oxygen from its cluster and takes its place. The resultant configuration is, of course, one in which an oxygen atom is common to three coordination groups. If the displaced oxygen atom migrates from the site, it will be accompanied by a divalent cation or by two monovalent cations. An SiO_4 group may suffer this process provided that initially it has two unshared oxygen atoms.

4. Rotational Movements

As the rotation of a group of non-bridging oxygen atoms about an axis of symmetry does not lead to an altered configuration, such possibilities will not be detailed.

Simple rotation

A coordination group has, as axis of rotation, two oxygen atoms shared with other groups. No other oxygen is shared. The two cases of practical importance are those where (4-1) an O_4 group or (4-2) an O_3 group is concerned.

4-3. *Linkage switching.* A tetrahedral group has three oxygen atoms shared with other groups and rotates about the line joining two of these oxygen atoms. By this rotation the third shared oxygen atom is displaced from the external group and the hitherto unshared atom takes its place.

Twisting

Here are classified local torsional movements involving rotation of a portion of a coordination group relative to the other.

4-4. Two atoms of a tetrahedron are restrained by their linkages or by steric hindrance. Of the other two, one only is shared with another coordination group. Rotation of this second pair through 180° , breaking and reforming the tetrahedron, need entail only limited movement of the external group linked to it.

4-5. An O_3 triangle possesses one non-bridging oxygen atom and one of the bridging oxygen atoms is prevented from moving. The other two oxygen atoms may twist about the latter from one position to another through any angle permitted by local steric conditions.

4-6. The twisting, through 120° , of one set of three oxygen atoms of an O_6 group over the other three would appear to be possible even when all the oxygen atoms are fully connected, no great disturbance of the adjacent structure of necessity being involved.

4-7. *Rolling.* A tetrahedron shares an oxygen atom with an octahedral cluster, the remaining oxygen atoms of the fourfold group being designated, for convenience, as an O_3 triangle. By rolling about the shared oxygen atom the O_3 triangle reaches a position in which two of its oxygen atoms come into contact with one of four possible oxygen atoms of the sixfold group. At this stage three oxygen atoms of the tetrahedral group are in contact with this particular octahedral oxygen atom. The tetrahedral group as a whole now continues the rolling movement about the designated oxygen atom of the sixfold cluster. The original link between the two clusters is thus severed, the arrangement becoming such that only minor adjustments of position suffice to result in the formation of two fivefold groups which have one oxygen in common. The amount of movement required depends on the original disposition of the groups but need not be large.

Flexural shearing

This type of interaction may arise as a consequence of local flexural or torsional movements.

4-8. As an example we may consider an octahedral group with one unshared oxygen atom. This atom will be in contact with four others of the group. Any of the four neighbouring coordination clusters sharing these oxygen atoms may partake without hindrance in movements which flex the linkage between it and the octahedral group, provided that the linkage initially embraces an angle not less than about 140° . If the angle is smaller than this, flexure of the linkage, or rotation about it, may entail interference between an oxygen atom of one of the neighbouring clusters (depicted as unshared in the illustration) and the unshared oxygen atom of the octahedral group. If the interference is sufficiently severe one of the oxygen atoms may become detached from its group. Afterwards the arrangement will still feature a sixfold group, but two of its oxygen atoms will be shared with another coordination cluster. The oxygen atom set free will tend to draw after it one or more low-valency cations previously associated with the configuration.

4-9. A simple variant of this mechanism arises when one of the two interacting oxygen atoms is shared

between two clusters and one is unshared. The final configuration will include a sixfold group sharing two oxygen atoms with another coordination cluster. One of these two atoms will be shared between a total of three coordination groups.

4-10. In a further variant neither of the interacting oxygen atoms is unshared. The final arrangement is identical with that last described except that, instead of a free oxygen atom being discharged, the displaced oxygen atom is left as a non-bridging oxygen atom forming part of a coordination group, which now has no linkage with the modified sixfold group.

Two tetrahedra, or two octahedra, may interact in analogous fashion.

Discussion

Such are the moves of 'Silicate Chess'.

It might appear to be almost impossible to decide which mechanisms were responsible for any given phenomenon, because of the relatively large number of alternatives from which the choice must be made. In a given instance the problem may be eased because of inherent compositional, structural or spatial limitations. For instance, coordination-change processes may be ruled out if the system is non-aluminous and boron-free, and are likely to be of little significance in any case where the initial and final products are known to have four-coordinated structures. Similarly break-transfer processes and ones involving AlO_6 groups would not be expected to be important in systems where the ratio (R) of oxygen atoms relative to network-formers was low. For any form of SiO_2 the choice is most narrowly restricted and for many silica/metallic-oxide binary systems it is rather limited.

Further aid must be sought in kinetic analysis. Determination of the constants of the Arrhenius rate equation, and of the order of a reaction, together with the collection of thermal data, have for long been standard procedures. The dependence of the rate of a process upon composition, however, may yield just as much information about the kind of mechanism involved as study of its temperature dependence.

For instance, in disordered systems with four-connected network formers the chance of a randomly selected oxygen atom being non-bridging is $(2-4/R)$. It follows that the velocity of a change which depends upon the availability of n network breaks at each movement site will be related to changes of bulk composition by a $(2-4/R)^n$ law.

Detailed studies by the present author in which these principles are exploited will be reported elsewhere.

The presence of non-bridging oxygen is seen to confer important special properties upon any silicate system having a network character. If a break in the network exists at a given site it may be transferred to an adjacent one by the agency of a small local oxygen movement. Repeated migration of the break may follow, but no individual oxygen atom need move more than a trivial distance. A number of mechanisms may play a part in this, including: simple gliding (1-1), inversion (2-5), and simple rotation (4-1). Electrostatic neutrality is maintained by the handing on of a low valency cation from one site to another successively. An analogy may be drawn between such processes and the movement of dislocations within a metal. They constitute a means whereby metallic ions may diffuse within a silicate without the simultaneous mass transfer of oxygen.

Seen from this viewpoint some cases of crystallization essentially consist in the migration of cations and of network breaks into, or from, an expanding region of ordered arrangement.

Network-forming ions, in some circumstances, are able to move from one coordination group to another with virtually no disturbance of the structure. A distinctive set of mechanisms is involved. The more simple of them may be expected to be of greater importance in close-packed structures, with a relatively high proportion of oxygen relative to the high valency cations, rather than in open networks.

Similarly, little disturbance is occasioned by simple processes such as linkage switching (4-3), oxygen loss (3-6), simple rotation (4-1), and inversion (2-5). Their importance is, therefore, likely to extend to the densely packed silicates. The presence of lattice vacancies may enable them to come into play without high energy barriers having to be surmounted.

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