

## Stereochemistry and energies of single two-repeat silicate chains

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### Abstract

The wide variety of hypothetically possible two-repeat chains is discussed and results of CNDO/2 MO calculations on isolated  $H_8Si_3O_{10}$  clusters modeling these chains are presented. Calculations indicate that within the wide spectrum of possible chains a rather restricted range of conformations is energetically favored. Despite the neglect of M-cations between the chains, calculated conformations of minimum energy compare favorably with observed conformations. The chain of lowest calculated energy is similar to that found in  $Na_2SiO_3$ . Chains with conformations intermediate to  $Na_2SiO_3$  and a straight pyroxene chain are predicted to be favored over other conformations. This is in agreement with observed two-repeat chain structures.

### Introduction

The single-chain silicates comprise an important class of minerals because of their great abundance in crustal and upper mantle rocks. Members of this class possess continuous chains of silicate tetrahedra linked such that each tetrahedron possesses two bridging and two non-bridging oxygens, which results in a tetrahedral-cation: oxygen ratio of 1:3 and a sharing coefficient of 1.5 (Zoltai, 1960). The class is subdivided on the basis of the number of tetrahedra contained within a translational repeat along the chain and although "one-repeat silicate chains" have not been observed, those with repeats of 2, 3, 4, 5, 6, 7, 9, and 12 are known to exist (Liebau, 1972).

In the class of single chains, minerals with two-repeat chains are by far the most abundant, and within this subclass all members are described as having either the pyroxene type or the sodium metasilicate ( $Na_2SiO_3$ ) type chain. Minerals containing single chains of tetrahedral repeats three or greater are collectively referred to as pyroxenoids.

All single-chain silicates possess cations which occupy sites between the chains, thereby providing structural continuity. These M-cations are normally six to eight-coordinated by oxygen and range in size from 0.53 Å (Al) to 1.42 Å (Ba) with formal valences ranging from +1 to +3. Liebau (1980) has recently studied correlations between size and electronegativity of the M-cations and the repeat and exten-

sion of the chain in over fifty different structures. His study reveals that even-periodic chains become less stretched with higher mean electronegativity and higher mean valence of the M-cations. In odd-periodic chains the degree of chain shrinkage is strongly correlated with the mean electronegativity and less so with the mean radius of the M-cations. Such investigations are important for gaining a perspective about the relative importance of these variables in influencing the chain type, but at the present time reliable predictions about chain configurations based upon the chemistry of M-cations are not possible.

High-precision structure refinements of pyroxene and 3-repeat pyroxenoids of various compositions have prompted several crystal chemical investigations concerning the effect M-cations have on the detailed stereochemistry of a specific chain type (Clark *et al.*, 1969; Papike *et al.*, 1973; Ohashi *et al.* 1975; Ribbe and Prunier, 1977; Ohashi and Finger, 1978). For a given type of chain these investigations clearly relate the effect various M-cations have on small-scale interatomic-adjustments within the chain.

Since past investigations have explored the relationships between M-cations and the silicate chain configuration, attention in this paper will concentrate on the bonding and non-bonding interactions between the silicon and oxygen atoms in the chain independent of the effects of the M-cations. With such an approach perhaps some insight can be gained with regard to the relative influence that packing and

bonding requirements of M-cations have relative to the influence of Si–O, O–O and Si–Si interactions on the final conformation of the single chain.

For this reason, a series of molecular orbital calculations have been completed on isolated single-chain clusters which, in the current study, are limited to two-repeat chains. Within the realm of two-repeat chains there is an infinite variety of geometrically feasible chains to be considered. The energies of representatives of this continuum of possible two-repeat chains will be computed and their conformations compared to observed structures. In a subsequent paper, single chains with repeats greater than two will be examined.

### Computations

It is generally believed that the Si–O bond in silicate minerals is partly ionic and partly covalent in character (Pauling, 1939; Hübner, 1977). Accordingly, if one is to evaluate relative energies of silicate chains with different conformations, one must use a bonding model which includes both the ionic and covalent contributions to the energy. Therefore, one must consider the variation of electron distributions between atomic centers as a function of changing conformations.

A methodology commonly used to compute electron distributions between multiple atomic centers is the molecular orbital (MO) theory. Basically, one is seeking approximate wave functions for a molecular group by assigning each electron to a one-electron wave function which generally extends over the whole molecule. If these wave functions (molecular orbitals) are approximated as Linear Combinations of Atomic Orbitals (LCAO) the computational effort is considerably lessened. This linear combination is most easily expressed as:

$$\psi_i = \sum_j c_{ji} \phi_j \quad (1)$$

where  $\psi_i$  represents the molecular orbital,  $\phi_j$  the atomic orbital, and  $c_{ji}$  the numerical coefficients.

If we approximate the molecular orbitals as a linear combination of atomic orbitals we must find the set of coefficients,  $c_{ji}$ , for which the total electronic energy of our system is minimized. Roothaan (1951) formulated the mathematical treatment of this problem through use of the variational method. The Roothaan equations take the final form:

$$\sum_j (F_{kj} - E_i S_{kj}) c_{ji} = 0 \quad (2)$$

where  $F_{kj}$  is a matrix representation of the Hartree–Fock Hamiltonian operator,  $E_i$  is the energy of the  $i^{\text{th}}$  molecular orbital,  $S_{kj}$  is the matrix of atomic orbital overlap integrals, and  $c_{ji}$  is the set of numerical coefficients in the LCAO approximation of equation 1.

The elements of the matrix representation ( $F_{kj}$ ) to the Hartree–Fock Hamiltonian operator contain terms which relate to the kinetic and potential energies of the electrons in a molecule. If we are to solve for the linear coefficients,  $c_{ji}$ , and the corresponding MO energies,  $E_i$ , we must have previously determined the elements of matrix  $F_{kj}$ , which requires that we know the electron distribution in the molecule. This, of course, is what we are trying to determine. Therefore to solve the Roothaan equations the coefficients  $c_{ji}$  are initially estimated, a first approximation of  $F_{kj}$  is made, and a new set of  $c_{ji}$  values is then computed which, in turn, is used to construct a new  $F_{kj}$ . This procedure is continued until the change in coefficients between successive iterations is diminishingly small. The resulting molecular orbitals are self-consistent with the potential field they generate and this procedure is referred to as the Self Consistent Field (SCF) or LCAO SCF molecular orbital method.

Because of the enormous computational effort involved in evaluation of the Roothaan equations the applications have generally been limited to small molecular groups. Application of the Roothaan equations to large molecular groups has been achieved through various methods of approximation. One such method is the approximate self-consistent field molecular orbital theory known as CNDO/2 (Pople *et al.*, 1965). In this approximate method all two-element repulsion integrals which depend on the overlapping of charge densities of different atomic orbitals are neglected, hence the term Complete Neglect of Differential Overlap. Although the more important electron repulsion integrals are approximated, the neglect of differential overlap significantly reduces computation time. This is especially evident when one considers that the number of electron repulsion integrals increases as the fourth power of the number of atomic orbitals used in the LCAO technique. In the CNDO/2 method only the valence electrons are considered explicitly, since all inner electrons are taken as part of an unpolarizable core. The method is semi-empirical in that some of the terms included in the  $F_{kj}$  matrix are approximated with atomic data such as electronegativities or by fitting to accurate non-empirical SCF LCAO calculations on diatomic molecules (Pople and Segal, 1965).

As in the original Roothaan method, the CNDO/2 calculation is iterative in that successive approximations of the molecular orbitals are made through adjustment of coefficients in the linear combination of atomic orbitals until convergence of the electronic energy is achieved (*i.e.*, a minimized energy is obtained). The total energy of the system is given relative to isolated atom cores and valence electrons.

The computer program CNINDO (Dobash, 1974) was used for all CNDO/2 calculations with bonding parameters for H and O and for Si taken from Pople and Segal (1965) and from Santry and Segal (1967), respectively. The atomic basis set was limited to *s* and *p* orbitals for Si and O. All calculations were made on an Amdahl 470/V6 computer at the University of British Columbia.

A cluster of  $H_8Si_3O_{10}$  composition consisting of three silicate tetrahedra linked through corners was used in this study to model two-repeat chains. All tetrahedra possess  $T_d$  point symmetry with OSiO angles equal to  $109.47^\circ$  and all Si–O distances,  $d(\text{Si–O})$ , are set equal to the sum of the Shannon and Prewitt (1969) ionic radii of  $1.61\text{\AA}$ . The cluster is neutral in charge as a result of the addition of hydrogen atoms  $1.0\text{\AA}$  from each non-bridging oxygen with an SiOH angle of  $180^\circ$ .

### Discussion

From a purely geometrical point of view it is possible to construct an infinite number of unique two-repeat chains. Because the chains in this study are constructed of ideal tetrahedra, they can be described by three angular values. The first of these angles,  $\phi$ , is defined to be the angle between the  $\text{Si}_1\text{–O}_1$  and  $\text{Si}_2\text{–O}_2$  vectors projected on the plane containing  $\text{Si}_1$  and the two non-bridging oxygens (Fig. 1). The remaining angles are  $\angle(\text{SiOSi})$  (the valence angle  $\text{Si}_1\text{–O}_1\text{–Si}_2$  in Fig. 1) and  $\angle(\text{OOO})_{br}$  (the angle  $\text{O}_2\text{–O}_1\text{–O}'_2$  between bridging oxygens). Figure 1 illustrates the linkage between adjacent tetrahedra for chains with  $\phi = 0^\circ, 149^\circ, \text{ and } 180^\circ$ . For two-repeat chains the  $\text{Si}_1$  tetrahedron will be related by translational periodicity to a third tetrahedron (not shown) which is linked to the  $\text{Si}_2$  tetrahedron through oxygen  $\text{O}_2$ . The chain in Figure 1a has a special angular relationship [ $\angle(\text{SiOSi}) = 109.47^\circ$  and  $\angle(\text{OOO})_{br} = 180^\circ$ ], which results in a one-repeat chain; however, it will be included in the discussion of two-repeat chains.

Geometric relations between the chains can be compared graphically by plotting  $\phi$  and  $\angle(\text{OOO})_{br}$  as polar coordinates (Fig. 2). Because these two angles do not uniquely define a two-repeat chain, the

$\angle(\text{SiOSi})$  angles must also be given for each plot. In the general case two symmetry non-equivalent  $\angle(\text{SiOSi})$  angles are possible although the overwhelming majority of observed two-repeat chains have equal  $\angle(\text{SiOSi})$  values. The notable exception is omphacite with non-equivalent  $\angle(\text{SiOSi})$  angles of  $140.0^\circ$  and  $135.4^\circ$  (Matsumoto *et al.*, 1975). The continuum of all possible  $\phi$  and  $\angle(\text{OOO})_{br}$  values is plotted in Figure 2 for chains with both  $\angle(\text{SiOSi})$  angles equal to  $135^\circ$  (solid line) and  $140^\circ$  (dashed line). Only half the polar coordinates are plotted, since chains with  $\phi$  and  $360^\circ - \phi$  are equivalent. Similarly, chains along the line from A to E are equivalent by reflection symmetry to those along the line A to J. To illustrate how the chains plotted in Figure 2 differ, a series of these chains is shown in Figures 3 and 4. The chain in Figure 3A corresponds to the plot of point A in Figure 2 with  $\angle(\text{OOO})_{br} = 180^\circ$ ,  $\phi = 97^\circ$ , and  $\angle\text{SiOSi} = 135^\circ$ ; Figure 3B is the chain related to point B, *etc.*

Figure 3 illustrates that chains which plot in the general region between points A and D resemble pyroxenes whereas the chains plotting about point E in Figure 2 resemble the  $\text{Na}_2\text{SiO}_3$  chain (McDonald and Cruickshank, 1967). The chains in Figure 4 (E through J) refer to points E through J in Figure 2. Chains 4E and 4J are the  $\text{Na}_2\text{SiO}_3$  type chain while the intermediate chains G and H have not as yet been observed in natural or synthetic compounds. Note that chain E in Figure 4 is viewed from a different direction from that in Figure 3, but is otherwise identical.

In the preceding discussion an  $\angle(\text{SiOSi})$  of  $135^\circ$  was chosen because it is close to those values observed in two-repeat single-chain compounds. For comparison, the dashed line in Figure 2 illustrates all possible  $\phi$  and  $\angle(\text{OOO})_{br}$  values for chains with both  $\angle(\text{SiOSi})$  equal  $140^\circ$ . In the course of this investigation, however, energies of over 200 different chains within the allowable range of angular values have been computed by the CNDO/2 method.

#### *Energies of straight chains with $\angle(\text{OOO})_{br} = 180^\circ$*

The first in a series of calculations is concerned with straight chains of  $\angle(\text{OOO})_{br} = 180^\circ$  but with variable  $\phi$  and  $\angle(\text{SiOSi})$  angles. Figure 5 illustrates six of a continuum of possible straight chains which vary from the one-repeat chain (chain K) to a chain with  $\angle(\text{SiOSi}) = 180^\circ$  (chain P). The total energies of these chains reveal a minimum at an  $\angle(\text{SiOSi})$  of approximately  $140^\circ$ , corresponding to chain M, which has the conformation of a straight pyroxene chain.

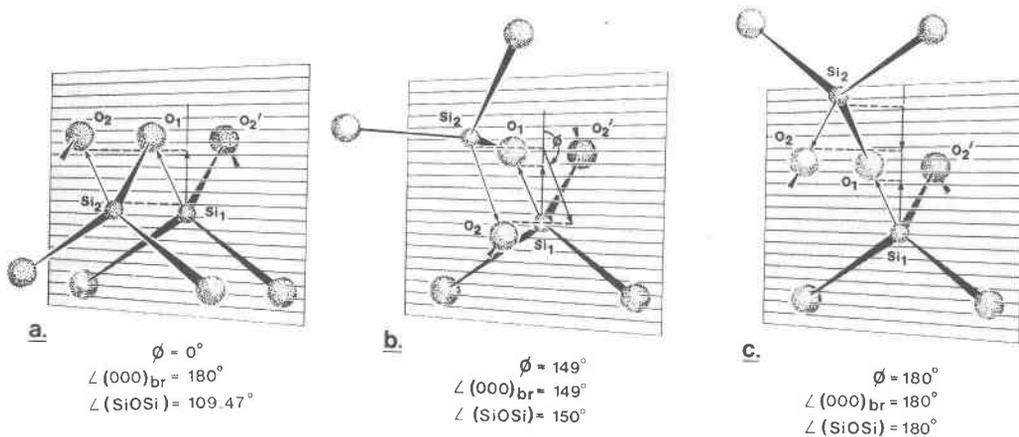


Fig. 1. Segments of single chains illustrating the angular values of  $\phi$ ,  $\angle(\text{OOO})_{\text{br}}$  (angle  $\text{O}_2\text{-O}_1\text{-O}_2'$ ), and  $\angle(\text{SiOSi})$  (angle  $\text{Si}_1\text{-O}_1\text{-Si}_2$ ) which can be used to describe chain conformations.

Figure 5 also reveals that CNDO/2 predicts the one-repeat chain (K) to be the least stable of all the straight chains. To date no such silicate chain is known to occur in crystalline materials.

In the initial stages of this investigation it was decided to test whether a larger cluster would yield significantly different results; therefore, the above calculations were repeated with a two-repeat chain, five tetrahedra in length. Alternate tetrahedra were rotated, once again maintaining a straight chain, and the resulting energy minimum was observed within  $1^\circ$  of the value for the  $\text{H}_8\text{Si}_3\text{O}_{10}$  cluster. Although a cluster with more than three tetrahedra adds considerably to the expense of the calculation it does not appear to significantly change the results.

#### Energies of chains with $\phi = 180^\circ$

A second series of calculations were completed on chains along the line  $\phi = 180^\circ$  for  $\angle(\text{OOO})_{\text{br}}$  values between  $120^\circ$  and  $180^\circ$  (Fig. 2). The results illustrated in Figure 6 show a total energy minimum at approximately  $135^\circ$ . This chain (equivalent to both E and J of Fig. 4) with  $\angle(\text{OOO})_{\text{br}} = (\text{SiOSi}) = 135^\circ$ , is very similar in conformation to that of the  $\text{Na}_2\text{SiO}_3$  chain with  $\angle(\text{OOO})_{\text{br}} = 134.0^\circ$  and  $\angle(\text{SiOSi}) = 133.7^\circ$  (McDonald and Cruickshank, 1967). This conformation has also been reported in  $\text{Li}_2\text{SiO}_3$  (Hesse, 1977), high-temperature  $\text{BaSiO}_3$  (Grosse and Tillmanns, 1974) and  $\text{Na}_2\text{BaSi}_2\text{O}_6$  (Gunawardane *et al.*, 1973).

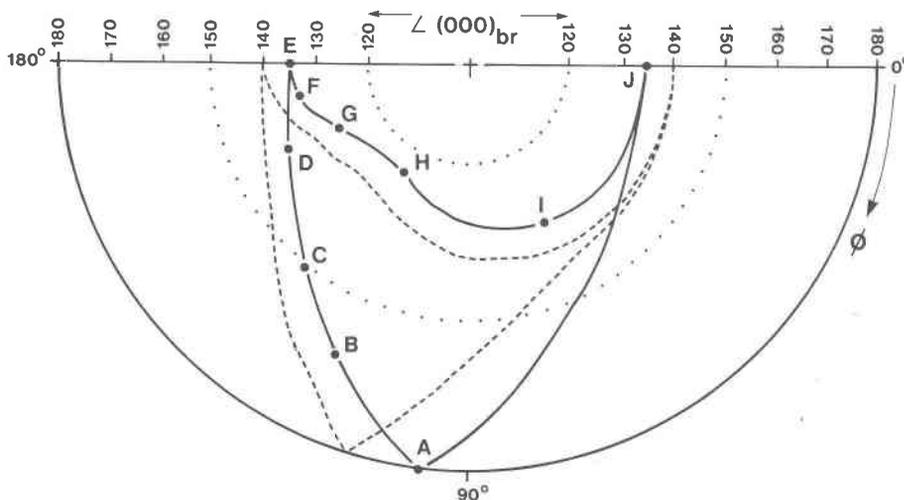


Fig. 2. A polar coordinate plot of  $\theta$  and  $\angle(\text{OOO})_{\text{br}}$  for all possible chains with both  $\angle(\text{SiOSi}) = 135^\circ$  (solid line) and for those chains with both  $\angle(\text{SiOSi}) = 140^\circ$  (dashed line). Points labeled A-J represent the polar coordinates for chains illustrated in Figs. 3 and 4.

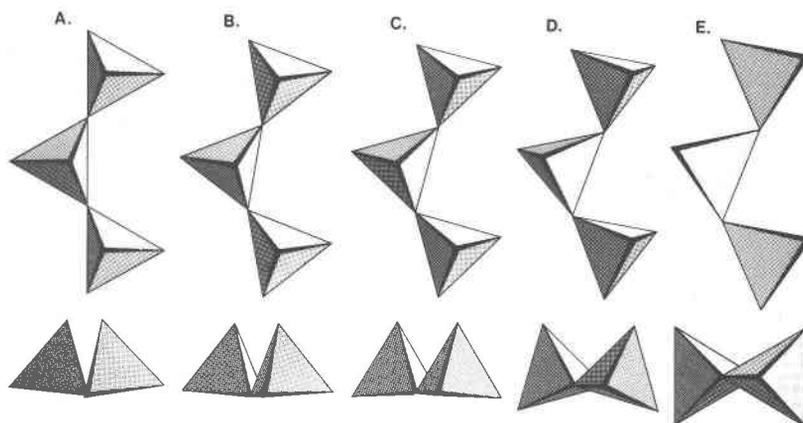


Fig. 3. Chains with both  $\angle(\text{SiOSi})$  angles equal  $135^\circ$  which correspond to the  $\theta$  and  $\angle(\text{OOO})_{\text{br}}$  values of points A-E of Fig. 2. Note the similarity of chain C with a pyroxene chain and chain E with the chain in  $\text{Na}_2\text{SiO}_3$ .

*Energies of chains with variable  $\phi$ ,  $\angle(\text{OOO})_{\text{br}}$ , and  $\angle(\text{SiOSi})$*

To this point the discussion has been restricted to chains with special types of conformations. In the general case all possible combinations of  $\phi$ ,  $\angle(\text{OOO})_{\text{br}}$ , and  $\angle(\text{SiOSi})$  must be considered, which results in a formidable task. This becomes apparent when one considers that a continuum of chains with varying  $\phi$  and  $\angle(\text{OOO})_{\text{br}}$  values exists for every pair of non-equivalent  $\angle(\text{SiOSi})$  angles chosen. The effort is simplified somewhat if we consider only those chains for which  $\angle(\text{SiOSi})$  angles are equivalent, as occurs in practically all the chains observed to date. In doing so, however, it is important to understand how chains with non-equivalent  $\angle(\text{SiOSi})$  values relate, energetically, to chains with equivalent  $\angle(\text{SiOSi})$  angles.

It will be shown in a subsequent section that chain

E (Figs. 2 and 3) is the lowest-energy chain of all possible chains with equivalent  $\angle(\text{SiOSi})$  angles. If we change one of the two  $\angle(\text{SiOSi})$  angles from  $135^\circ$  to a non-equivalent value, say  $130^\circ$ , the total energy of the chain increases. This is illustrated (Fig. 7) by a series of calculations where one angle is locked at  $135^\circ$  while the remaining  $\angle(\text{SiOSi})$  angle is varied. Each point plotted in Figure 7 represents the conformation of minimum energy of all the chains which can possess that given pair of  $\angle(\text{SiOSi})$  values. An increase in energy will also result if we change both  $\angle(\text{SiOSi})$  values so that an average  $\angle(\text{SiOSi})$  angle of  $135^\circ$  is maintained.

This does not necessarily mean that a chain with non-equivalent  $\angle(\text{SiOSi})$  angle is always higher in energy. For example, the minimum-energy chain with both  $\angle(\text{SiOSi})$  angles equal to  $150^\circ$  will have a higher energy than one with  $\angle(\text{SiOSi})$  angles of  $150^\circ$  and

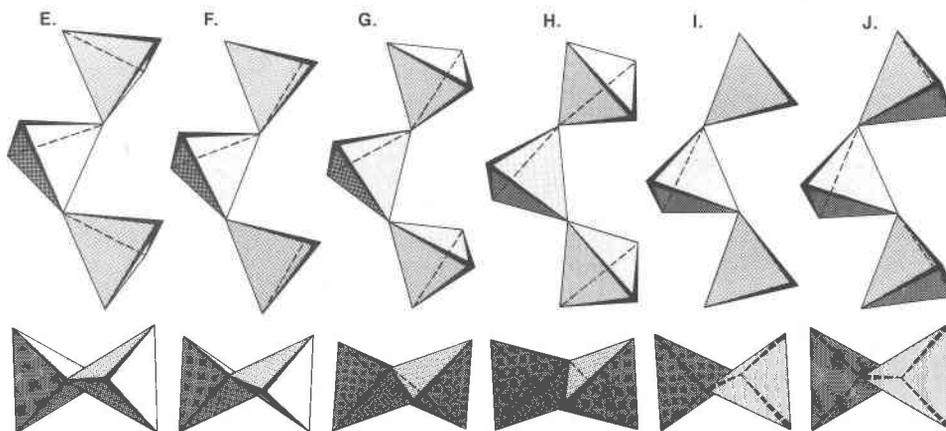


Fig. 4. Chains with both  $\angle(\text{SiOSi})$  angles equal  $135^\circ$  which correspond to the  $\theta$  and  $\angle(\text{OOO})_{\text{br}}$  values of points E-J of Fig. 2. Chains E and J are  $\text{Na}_2\text{SiO}_3$  chains rotated  $180^\circ$  relative to each other.

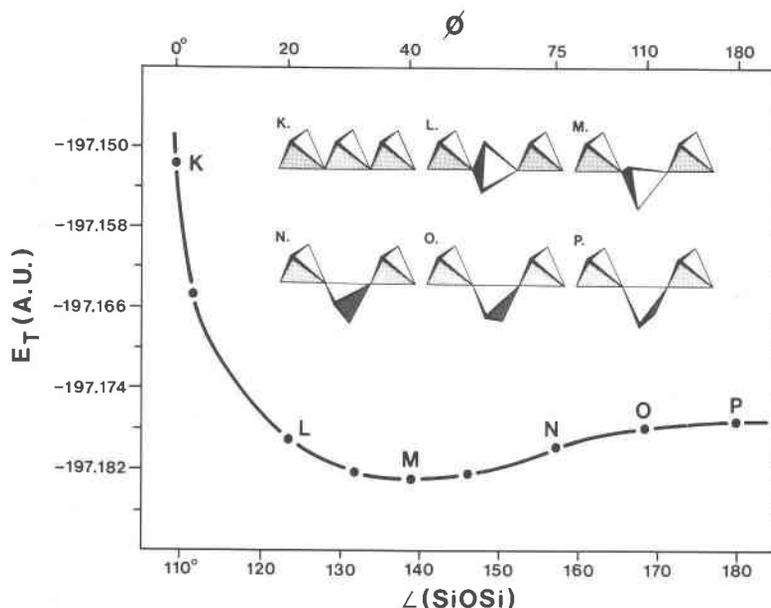


Fig. 5. Total energy vs.  $\angle(\text{SiOSi})$  for straight chains with  $\angle(\text{OOO})_{\text{br}} = 180^\circ$ . The chains K–P correspond to points plotted in the energy curve, with chain M representing a minimum energy conformation at an  $\angle(\text{SiOSi})$  of approximately  $139^\circ$ . Chain M has a conformation nearly identical to that found in the pyroxene  $\text{LiFeSi}_2\text{O}_6$ . (1 A.U. = 627.51 kcal/mole.)

$135^\circ$ . It appears, therefore, that for the particular model used here there is a preference for both  $\angle(\text{SiOSi})$  angles to be equal at values of approximately  $135^\circ$  or, less preferably, to have one  $\angle(\text{SiOSi})$  angle approaching  $135^\circ$ .

To compare chains with equivalent  $\angle(\text{SiOSi})$  angles the energies of such chains for various  $\phi$  and  $\angle(\text{OOO})_{\text{br}}$  values have been computed and contoured (Fig. 8). Chains within the hachured area of this fig-

ure will either possess non-equivalent  $\angle(\text{SiOSi})$ , or the  $\angle(\text{SiOSi})$  and  $\angle(\text{OOO})_{\text{br}}$  values will be geometrically impossible combinations for two-repeat chains composed of tetrahedra with point symmetry  $T_d$ . For example, a two-repeat chain with  $\angle(\text{SiOSi}) = 180^\circ$  cannot possess an  $\angle(\text{OOO})_{\text{br}}$  of  $110^\circ$ .

In the construction of Figure 8, 66 data points were used as input to a computer routine for contouring. The map is contoured with an interval of

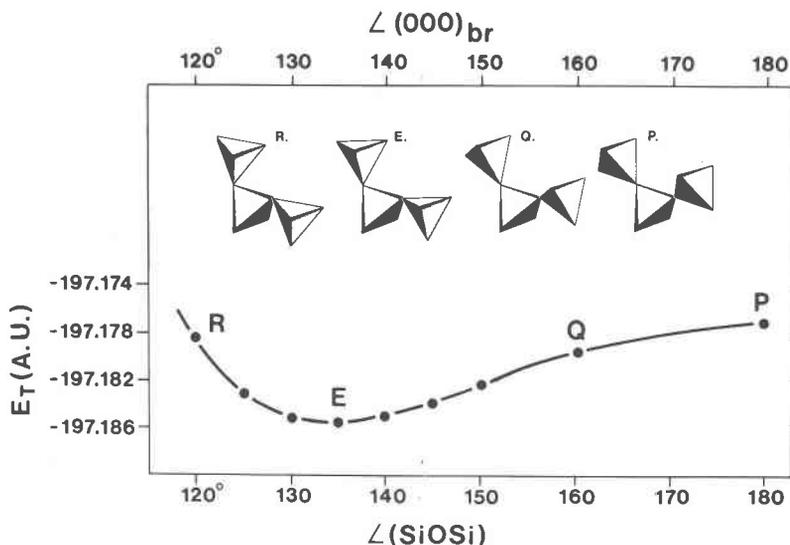


Fig. 6. Total energy vs.  $\angle(\text{SiOSi})$  for chains with  $\phi = 180^\circ$ . Chain E possesses the conformation of minimum energy for this series at approximately  $\angle(\text{SiOSi}) = 135^\circ$ , which is nearly identical to that of the  $\text{Na}_2\text{SiO}_3$  chain.

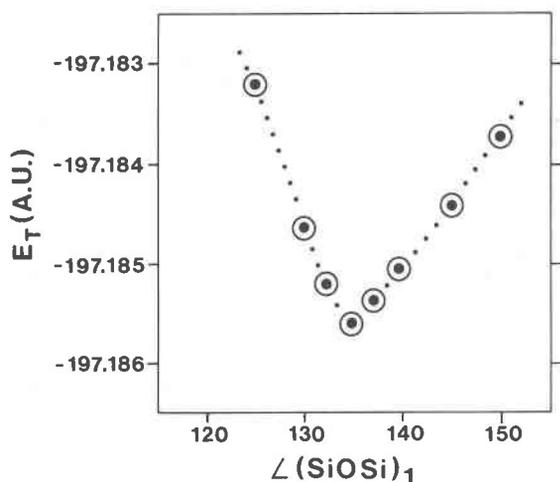


Fig. 7. Minimum total energies for chains with non-equivalent  $\angle(\text{SiOSi})$  angles. Energies are for minimum energy conformation of each series of chains with  $\angle(\text{SiOSi})_1$  set at the indicated value while  $\angle(\text{SiOSi})_2$  is locked at  $135^\circ$ .

100 energy units in the low-energy region, 200 units in the intermediate region, and 400 units in the high-energy region, to highlight the general features of the plot. The figure is only intended to give general trends of energies as a function of  $\angle(\text{SiOSi})$  and  $\angle(\text{OOO})_{\text{br}}$  angles and is not considered to be particularly accurate in detail, considering the small number of data points used in its construction. Nevertheless, the plot is informative in that it illustrates the regions where preferred conformations are predicted by CNDO/2 MO calculations. The lowest energies occur in the area  $\angle(\text{SiOSi}) = \angle(\text{OOO})_{\text{br}} = 135^\circ$ , from which a low-energy region extends to  $\angle(\text{SiOSi}) = 140^\circ$  and  $\angle(\text{OOO})_{\text{br}} = 180^\circ$ .

The crosses labeled with bold letters refer to those chains previously discussed and illustrated in Figures 3, 4, 5, and 6. In addition, the positions of observed pyroxene chains are plotted as squares, and those chains from compounds reported to be isostructural with  $\text{Na}_2\text{SiO}_3$  are plotted as circles. As indicated by this plot, there appears to be a good correlation between the predicted low-energy conformations of two-repeat silicate chains and those observed in natural and synthetic compounds. Nevertheless, if one recalls the simplifications built into the model, it would seem that only the general trends indicated in Figure 8 are meaningful and the exact angles of minimum energy are less significant. For example, the model includes ideal tetrahedra with all  $d(\text{Si-O})$  values equal to  $1.61\text{\AA}$ , which is the sum of the ionic radii for Si and O. In observed single-chain silicates Si-O bond lengths to non-bridging oxygens are usually

shorter than to bridging oxygens, and in most pyroxenes the average  $d(\text{Si-O})$  values are closer to  $1.63\text{\AA}$ . A series of CNDO/2 calculations on straight chains [ $\angle(\text{OOO})_{\text{br}} = 180^\circ$ ] with tetrahedra of  $T_d$  symmetry but with  $d(\text{Si-O})$  values equal to  $1.63\text{\AA}$  yielded a minimum energy  $\angle(\text{SiOSi})$  angle of about  $132^\circ$ , as compared to the value of  $138^\circ$  for chain M (Fig. 8). In a second series of calculations on straight chains with non-bridging Si-O bonds equal to  $1.62\text{\AA}$  and bridging Si-O bonds equal to  $1.64\text{\AA}$  (average  $1.63\text{\AA}$ ) an energy minimum occurred at approximately  $130^\circ$ , which is a shift of  $8^\circ$  from the ideal chain with  $d(\text{Si-O}) = 1.61\text{\AA}$ . It appears that the basic trend in energies of conformation shown in Figure 8 will not change with these types of adjustments. Nevertheless, future calculations, of a more rigorous nature, should include the Si-O bond length as an additional variable.

In addition to the correlation between the predicted minimum energy trough and the observed trend in angular values for the various two-repeat chains, Figure 8 reveals there is no clear break in observed  $\angle(\text{OOO})_{\text{br}}$  and  $\angle(\text{SiOSi})$  angles upon progressing from the nearly ideal straight pyroxene chain of  $\text{LiFeSi}_2\text{O}_6$  to  $\text{Na}_2\text{SiO}_3$  (Fig. 8). To further illustrate this point, the chains of  $\text{LiFeSi}_2\text{O}_6$ ,  $\text{Mg}_2\text{Si}_2\text{O}_6$ , and  $\text{Na}_2\text{SiO}_3$  are compared (Fig. 9). The fact that a continuous gradation appears to exist between the classic pyroxene type chain and the  $\text{Na}_2\text{SiO}_3$  chain is consistent with CNDO/2 calculations.

#### *Tetrahedral linkage and M-cation packing*

In the silicate minerals  $\text{SiO}_4$  tetrahedra are polymerized into a wide variety of linkages such as dimers, trimers, rings, chains, sheets, and frameworks. Although individual  $\angle(\text{SiOSi})$  values range from approximately  $125^\circ$  to  $180^\circ$ , it has been realized for some time that an overall average  $\angle(\text{SiOSi})$  value is close to  $140^\circ$  (Liebau, 1961). Tossell and Gibbs (1978), in a compilation of data for silicates whose structures were published prior to 1976, found the most frequently encountered  $\angle(\text{SiOSi})$  value to be in the  $140\text{--}142^\circ$  range, and the average value for their total data set to be  $144.3^\circ$ .

This observed preference in silicates for a bent  $\angle(\text{SiOSi})$  angle appears to reflect local bonding and nonbonding interactions among the silicon and oxygen atoms in the polymerized silicate group, independent of the influence of non-tetrahedral cations. In the silica polymorphs, where non-tetrahedral cation packing is not a factor, the preference for a bent  $\angle(\text{SiOSi})$  is evident. In quartz, tridymite, cristobalite,

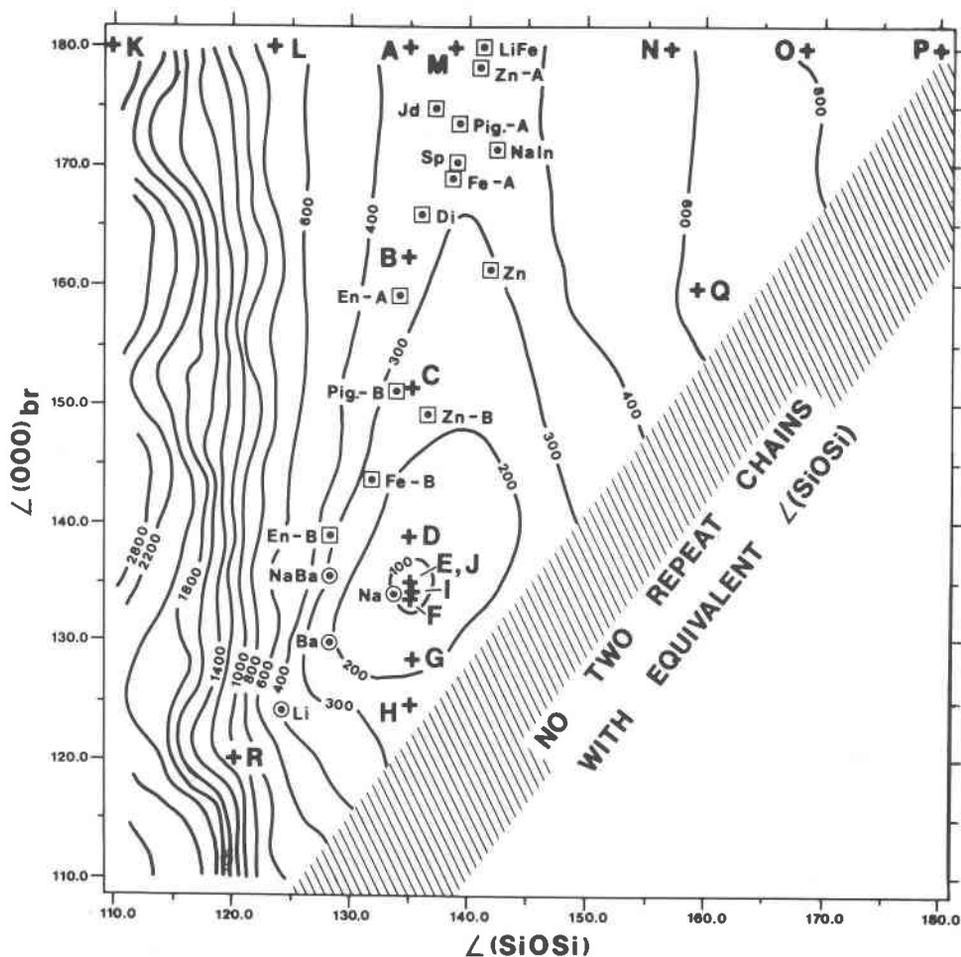


Fig. 8. A contoured total-energy map for two-repeat chains over a range of  $\angle(\text{SiOSi})$  and  $\angle(\text{OOO})_{\text{br}}$  values. Labeled crosses are for chains depicted in Figs. 2–6, squares are observed angular values for representatives of the pyroxene group, and circles are for materials associated with the  $\text{Na}_2\text{SiO}_3$  structure. Contours represent energy differences based on the lowest-energy chain (E and J) being arbitrarily assigned a value of 40 energy units. 100 energy units is approximately equal 0.001 A.U. The observed structures are: LiFe,  $\text{LiFeSi}_2\text{O}_6$ ; Zn-A,  $\text{ZnSiO}_3$  chain A; Jd, Jadeite; Pig-A, Pigeonite chain A; NaIn,  $\text{NaInSi}_2\text{O}_6$ ; Sp, spodumene; Fe-A, orthoferrosilite chain A; Di, diopside; Zn, clino  $\text{ZnSiO}_3$ ; En-A, orthoenstatite chain A; Pig-B, pigeonite chain B; Zn-B,  $\text{ZnSiO}_3$  chain B; Fe-B, orthoferrosilite chain B; En-B, orthoenstatite chain B; NaBa,  $\text{Na}_2\text{BaSi}_2\text{O}_6$ ; Na,  $\text{Na}_2\text{SiO}_3$ ; Ba, high-temperature  $\text{BaSiO}_3$ ; Li,  $\text{Li}_2\text{SiO}_3$ .

and coesite the range of mean  $\angle(\text{SiOSi})$  angles is from  $143.7^\circ$  to  $150.7^\circ$  with an overall mean  $\angle(\text{SiOSi})$  angle of  $147.6^\circ$  for all four structures (Meagher *et al.*, 1979). This intrinsic preference for a bent  $\angle(\text{SiOSi})$  angle approaching  $140^\circ$  has been reproduced in CNDO/2 calculations on  $\text{H}_{12}\text{Si}_5\text{O}_{16}$  framework clusters (Meagher *et al.*, 1979) and *ab initio* SCF calculations on  $\text{H}_6\text{Si}_2\text{O}$  and  $\text{H}_6\text{Si}_2\text{O}_7$  groups by Newton and Gibbs (1980).

In compounds with polymerized silicate groups such as single chains, the M-cations are an integral part of the structure and the final atomic arrangement will be one in which coordination of these cations is achieved through adjustment of bond lengths

and angles within and between the  $\text{SiO}_4$  tetrahedra. If there is an intrinsic preference with regard to the angular relationship between adjacent  $\text{SiO}_4$  tetrahedra, it would seem that in the attempt to accommodate M-cations certain adjustments within a chain will be energetically favorable while others will be improbable. The energy map (Fig. 8) indicates qualitatively that angular distortions in the chains are more restricted in the range of  $\angle(\text{SiOSi})$  values than  $\angle(\text{OOO})_{\text{br}}$  values, which is consistent with observed two-repeat silicate chain structures.

An alternate reason for the limited range in  $\angle(\text{SiOSi})$  values observed in chain structures may be that the high-energy chains in Figure 8 simply do not

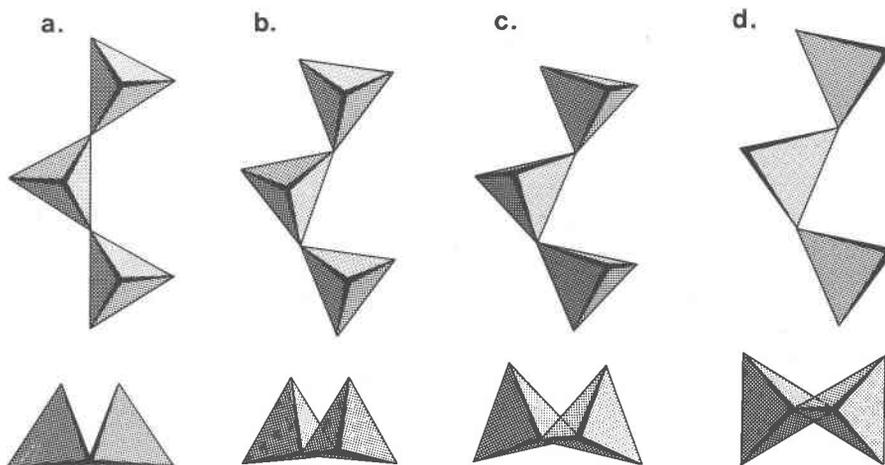


Fig. 9. Projections along and normal to the chains of (a)  $\text{LiFeSi}_2\text{O}_6$  (Clark *et al.*, 1969); (b) orthoenstatite chain B (Hawthorne and Ito, 1977); (c)  $\text{Na}_2\text{BaSi}_2\text{O}_6$  (Gunawardane *et al.*, 1973); (d)  $\text{Na}_2\text{SiO}_3$  (McDonald and Cruickshank, 1966).

pack together in a way that M-cations can be properly coordinated or that a crystal-chemically feasible structure will result. This does not negate the above premise regarding the high energy of these chains; however, it does point out the importance of the requirements of M-cations in forming a stable structure. The packing argument does not hold, however, for chains with a conformation similar to chain K in Figure 8. Although no such chain is observed in silicates, the chain does pack together so that M-cations can be accommodated as is demonstrated in the compound  $\text{CuGeO}_3$  (Völlenkler *et al.*, 1967). The Ge–O–Ge angle is  $113^\circ$  in this material, in keeping with the general preference for Ge compounds to possess narrow T–O–T angles (Völlenkler *et al.*, 1968).

#### Single chains with repeats greater than two

In an investigation of the influence of cation properties on the shape of silicate chains, Liebau (1980) found no correlation between the periodicity of chains and the radius, electronegativity, or valence of the M-cations. Nevertheless, bonding requirements of the M-cations will influence the periodicity of a chain and one can consider the periodicity, structurally, as an additional degree of freedom in establishing a configuration of minimum energy. In addition, if short-range Si–O, Si–Si, and O–O bonding and non-bonding interactions are important in the two-repeat chains they must also play an important role in chains with greater periodicities. The restricted range in average  $\angle(\text{SiOSi})$  values in chain silicates such as wollastonite (3-repeat:  $143^\circ$ ),  $\text{Cu}_3\text{Na}_2\text{Si}_4\text{O}_{12}$  (4-repeat:  $136^\circ$ ), rhodonite (5-repeat:  $137^\circ$ ), pyroxferroite (7-repeat:  $136^\circ$ ), and alamosite

(12-repeat:  $146^\circ$ ) is consistent with this observation. A general computational approach of the type used in this investigation becomes increasingly difficult to follow as the number of tetrahedra in the repeat distance increases; nevertheless, molecular orbital calculations on specific chain types are currently under way.

#### Conclusions

CNDO/2 MO calculations on isolated atomic clusters modeling portions of a complex three-dimensional solid, offer a semi-empirical means of evaluating short-range bonding and non-bonding interactions and their effect on structural conformation. Calculations on over 200 different conformations of an  $\text{H}_3\text{Si}_3\text{O}_{10}$  cluster modeling two-repeat chains indicate that chains with  $\angle(\text{SiOSi})$  ranging from approximately  $125^\circ$  to  $150^\circ$  and  $\angle(\text{OOO})_{\text{br}}$  from  $125^\circ$  to  $180^\circ$  are energetically favored over other possible conformations. This restricted range in predicted angular values is observed in natural and synthetic chain silicates, suggesting that Si–O, Si–Si, and O–O bonding and non-bonding interactions play an important role in determining chain conformations. The investigation is of a preliminary nature, and more rigorous MO calculations, which can evaluate equilibrium interatomic distances as well as angular relations, will be required to more accurately evaluate the relationships between M-cations and chain conformations in single-chain silicates.

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### References

- Clark, J. R., D. E. Appleman and J. J. Papike (1969) Crystal-chemical characterization of clinopyroxenes based on eight new structure refinements. *Mineral. Soc. Am. Spec. Pap.*, 2, 31–50.
- Dobash, P. A. (1974) *Quantum Chemistry Program Exchange No. 141* [available from QCPE, Indiana University, Bloomington, Indiana 47401].
- Grosse, H. and E. Tillmanns (1974) Bariummetasilicate, BaSiO<sub>3</sub>(h). *Cryst. Struct. Comm.*, 3, 603–605.
- Gunawardane, R. P., M. E. Cradwick and L. S. Dent (1973) Crystal structure of Na<sub>2</sub>BaSi<sub>2</sub>O<sub>6</sub>. *J. Chem. Soc. Dalton Trans.*, 2397–2400.
- Hawthorne, F. C. and J. Ito (1977) Synthesis and crystal-structure refinement of transition-metal orthopyroxenes. I: orthoenstatite and (Mg,Mn,Co) orthopyroxene. *Can. Mineral.*, 15, 321–338.
- Hesse, K. F. (1977) Refinement of the crystal structure of lithium polysilicate. *Acta Crystallogr.*, B33, 901–902.
- Hübner, K. (1977) Chemical bond and related properties of SiO<sub>2</sub>. I. Character of the chemical bond. *Phys. Status Solidi*, (A)40, 133–140.
- Liebau, F. (1961) Untersuchungen über die Grosse des Si–O–Si Valenzwinkels. *Acta Crystallogr.*, 14, 1103–1109.
- Liebau, F. (1972) Crystal chemistry of silicon. In K. H. Wedepohl, Ed., *Handbook of Geochemistry*, Vol. II/3, p. 14–32. Springer-Verlag, New York.
- (1980) The influence of cation properties on the shape of silicate chains. *Z. Kristallogr.*, in press.
- McDonald, W. S. and D. W. J. Cruickshank (1967) A reinvestigation of the structure of sodium metasilicate, Na<sub>2</sub>SiO<sub>3</sub>. *Acta Crystallogr.*, 22, 37–42.
- Matsumoto, T., M. Tokonami and N. Moromoto (1975) The crystal structure of omphacite. *Am. Mineral.*, 60, 634–641.
- Meagher, E. P., J. A. Tossell and G. V. Gibbs (1979) A CNDO/2 molecular orbital study of the silica polymorphs quartz, cristobalite and coesite. *Phys. Chem. Minerals*, 4, 11–21.
- Newton, M. D. and G. V. Gibbs (1980) *Ab initio* calculated geometries, charges and charge distributions for H<sub>4</sub>SiO<sub>4</sub> and H<sub>6</sub>Si<sub>2</sub>O<sub>7</sub> compared to experimental values for silicates and siloxanes. *Phys. Chem. Minerals*, in press.
- Ohashi, Y. and L. W. Finger (1978) The role of octahedral cations in pyroxenoid crystal chemistry. I. Bustamite, wollastonite, and the pectolite–schizolite–serandite series. *Am. Mineral.*, 63, 274–288.
- , C. W. Burnham and L. W. Finger (1975) The effect of Ca–Fe substitution on the clinopyroxene crystal structure. *Am. Mineral.*, 60, 423–434.
- Papike, J. J., C. T. Prewitt, S. Sueno and M. Cameron (1973) Pyroxenes: comparisons of real and ideal structural topologies. *Z. Kristallogr.*, 138, 254–273.
- Pauling, L. (1939) *The Nature of the Chemical Bond*. Cornell University Press, Ithaca, New York.
- Pople, J. A. and G. A. Segal (1965) Approximate self-consistent molecular orbital theory. II. Calculations with complete neglect of differential overlap. *J. Chem. Phys.*, 43, S136–S151.
- , D. P. Santry and G. A. Segal (1965) Approximate self-consistent molecular orbital theory. I. Invariant procedures. *J. Chem. Phys.*, 43, S129–S135.
- Ribbe, P. H. and A. R. Prunier, Jr. (1977) Stereochemical systematics of ordered C2/c silicate pyroxenes. *Am. Mineral.*, 62, 710–720.
- Roothaan, C. C. J. (1951) New developments in molecular orbital theory. *Rev. Mod. Physics*, 23, 69–89.
- Santry, D. P. and G. A. Segal (1967) Approximate self-consistent molecular orbital theory. IV. Calculations on molecules including the elements sodium through chlorine. *J. Chem. Phys.*, 47, 158–174.
- Shannon, R. D. and C. T. Prewitt (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.*, B25, 925–946.
- Tossell, J. A. and G. V. Gibbs (1978) The use of molecular orbital calculations on model systems for the prediction of bridging bond angle variations in siloxanes, silicates, silicon nitrides and silicon sulfides. *Acta Crystallogr.*, A34, 463–472.
- Völlenkne, H., A. Wittmann and H. Nowotny (1967) Zur Kristallstruktur von CuGeO<sub>3</sub>. *Monatsh. Chem.*, 98, 1352–1357.
- , ——— and ——— (1968) Die Kristallstruktur von Li<sub>2</sub>(Si<sub>0.25</sub>Ge<sub>0.75</sub>)<sub>2</sub>O<sub>5</sub>. *Z. Kristallogr.*, 126, 37–45.
- Zoltai, T. (1960) Classification of silicates and other minerals with tetrahedral structures. *Am. Mineral.*, 45, 960–973.

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