The role of the BeOSi bond in the structures of beryllosilicate minerals

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Abstract

Ab initio STO-3G molecular orbital methods have been used to calculate equilibrium geometries for the dimers, BeSi(OH)$_2$ and H$_2$BeSiO$_3$, to model the BeOSi bonds in beryllosilicate minerals. The optimized geometry and calculated potential energy surface for the dimer BeSi(OH)$_2$ are consistent with the Be-O and Si-O bridging bond length and BeOSi angle variations observed for these minerals. This indicates that the structures of beryllosilicates are determined in part by the same kind of short range forces that govern the geometry of the BeOSi bond in the dimer. Calculations for H$_2$BeSiO$_3$ indicate that the BeOSi angle is an intrinsic consequence of the electronic structure of the BeOSi bond and not merely a property of the coordination number of the bridging oxygen. The calculations also indicate that coupled substitutions of Be for either Si or Al will tend to occur in silicate structures that have TOT angles near the calculated equilibrium value (129°) for the BeOSi angle.

A refinement of the anisotropic temperature factors and Ap maps of asbecasite, Ca$_3$(Ti,Sn)As$_2$Si$_2$Be$_2$O$_{10}$, calculated with the published data of Cannillo et al. (1969) indicate that the BeOSi bond in the mineral may not be straight as reported. The potential energy surface for H$_2$BeSiO$_3$ appears to conform with the anisotropic charge density distribution observed for the BeOSi bond in asbecasite. When the short Be-O bond in the mineral is omitted from a regression analysis of experimental data, only two percent of the variation in d(Be-O) can be explained in terms of a linear dependence on the BeOSi angle.

Introduction

More than 40 beryllium minerals have been described in the literature of which more than half are silicates (Ross, 1964). In minerals, Be has thus far only been observed in tetrahedral coordination with O, OH, or F as ligands. Although triangular BeO$_3$ groups have been observed in the synthetic phases Ca$_{12}$Be$_{12}$O$_{39}$, Y$_2$BeO$_4$, SrBe$_2$O$_6$ (Harris and Yakel, 1966, 1967, 1969), and Rb$_2$Be$_2$Si$_2$O$_7$ (Howie and West, 1977), it has been argued that these phases may be metastable (Harris and Yakel, 1969). Beryllium plays a crystal chemical role in minerals similar to that of Si. Indeed, isomorphic substitution of as much as 0.1 weight percent Be for the tetrahedral cations in garnets, pyroxenes, amphiboles, micas, and feldspars is known. Silicates containing substantial amounts of Be, however, tend to adopt structures unique to beryllosilicates.

A prominent structural feature of beryllosilicates is the BeOSi bond. It is likely that the configuration of a beryllosilicate structure is governed in part by the inherent geometry of this bond as it often embodies the dominant bonding forces in the crystal. In this paper, the energetics of two beryllosilicate dimers, BeSi(OH)$_2$, and H$_2$BeSiO$_3$, are investigated with ab initio self-consistent field (SCF) molecular orbital (MO) calculations to determine the extent to which their minimum energy geometries mimic the observed bond lengths and angles of BeOSi bonds in beryllosilicate minerals (Downs, 1980).
gest that the Be–O bond is also substantially covalent (40–60%). Furthermore, experimental charge deformation maps through BeOSi units in euclase, Al–BeSiO₄(OH), show a significant accumulation of electron density in the bonds, indicating that both the Be–O and the Si–O bonds possess significant covalent character (Downs, 1980; Downs et al., 1981). Since these bonds are indicated to be substantially covalent, any formalism used to calculate the total energy of systems containing the bonds should include interactions of a covalent as well as ionic nature.

In a purely ionic model, only coulombic interactions between charged atomic centers are considered. Since covalency indicates sharing of electrons between bonded centers, a method that optimizes the electron distribution is required to model covalent effects. Clearly the calculation of the total wave function of the system is most desirable inasmuch as such a method would model ionic, as well as covalent interactions since both depend ultimately upon the electron distribution. Molecular orbital (MO) methods satisfy this criterion in that the total wave function $\Psi$ of the system is approximated by a product of one electron MO's expressed as

$$\Psi = \prod_{i=1}^{n} \phi_1 \phi_2 \cdots \phi_n$$  

where the $\phi_i$'s have been "antisymmetrized" with respect to the permutation of electrons to be consistent with the Pauli exclusion principle. These MO's are in turn approximated by a linear combination of atomic orbitals (LCAO) as in

$$\phi_i = \sum_{k} c_{ik} \chi_k$$  

where the MO coefficients $c_{ik}$ are obtained by the iterative self-consistent solution of the Roothaan equations. In ab initio MO theory all resulting matrix elements are accurately evaluated. In these calculations the atomic orbital (AO) basis functions $\chi_k$ are represented by Slater Type Orbitals (STO's) which are approximated by a linear combination of Gaussian functions denoted STO-NG, where $N$ is the number of Gaussians used in the expansion. In this study each STO was represented by a linear combination of three Gaussian functions (Hehre et al., 1969, 1970) which has been found useful in providing insight into the nature of the bonding forces in minerals (Sauer and Zurawski, 1979; Newton and Gibbs, 1979, 1980; Meier and Ha, 1980; Swanson, 1980; Chakoumakos, 1981; Gupta et al, 1981; Gibbs et al., 1981).

In this study, our main purpose is to calculate the total energy $E$ for the molecule in question. Recalling the Schrödinger equation,

$$H \Psi = E \Psi$$  

where $H$ is the Hamiltonian operator, multiplying both sides by the complex conjugate of the wave function $\Psi^\ast$, and integrating over all spatial coordinates yields

$$E = \frac{\int \Psi^\ast H \Psi \, d\tau}{\int \Psi^\ast \Psi \, d\tau}$$

such that the total energy $E$ is the expectation value of the Schrödinger Hamiltonian. The correct wave function for a molecule of fixed geometry is obtained using the variation theorem of quantum mechanics which states that the energy calculated using the equations of quantum mechanics with the use of the correct wave function $\Psi_{\text{ref}}$ for the ground state of the system is less than that calculated with any other wave function $\Psi$ that might be proposed. Using this technique then to calculate the total energy for a given geometry, we may then vary the geometry (usually within certain symmetry constraints) and thus find the lowest possible energy, as well as the "optimized" geometry for the molecule. The calculations reported in this paper were completed using the Pople et al. (1973) GAUSSIAN 70 computer program (QCPE, 11, 236).

Theoretical and experimental chemistry of the BeOSi bond

The equilibrium geometry of the BeOSi bond

The BeOSi bonds of the dimers BeSi(OH)$_2$ and H$_2$BeSiO$_4$, were chosen as models for the corresponding bonds in the beryllosilicates. In the study, the bond lengths and bridging angle for each dimer were optimized within the constraint of $C_2$ symmetry with the terminal OH bonds fixed at 0.96 Å, and the OTO and TOH angles fixed at 109.47°. The resulting geometries are shown in Figure 1.

The bridging oxygen of BeSi(OH)$_2$, is clearly overbonded with $p_o = 2.5$ (where $p_o$ is the Pauling bond strength sum to oxygen) whereas that of H$_2$BeSiO$_4$ is underbonded with $p_o = 1.5$. As expected the bridging bonds are longer in the overbonded case relative to the underbonded case. The mean bridging bond lengths calculated for the two dimers (tantamount to
when plotted as a function of bridging Be–O bond length and angle results in the potential energy surfaces shown in Figure 2a and 2b, respectively. Examination of the surface for BeSi(OH)$_7$ indicates that the total energy varies rapidly with angle but slowly with bond length. Hence, we may expect to observe a fairly wide range of Be–O bridging bond lengths and a relatively narrow range of BeOSi angles in beryllosilicates. This is in contrast to the behavior of the Si–O–Si bond.

Fig. 1. Optimized geometries for (a) BeSi(OH)$_7$ and (b) H$_2$BeSiO$_7$, calculated using ab initio theory with a minimal STO-3G basis. Large spheres represent oxygen, small spheres represent hydrogen; no significance is attached to the relative sizes of these spheres. Angles O–Be–O = O–Si–O = 109.47°, d(O–H) = 0.096 Å. During optimization, four sets of bond lengths were independently varied, namely non-bridging Be–O and Si–O, and bridging Be–O and Si–O. Both molecules are in doubly eclipsed conformation with C$_2$ symmetry.

interpolating to $r_0 = 2.0$ are $\langle d(\text{Be–O}) \rangle = 1.63$ Å and $\langle d(\text{Si–O}) \rangle = 1.62$ Å, in exact agreement with bond distances calculated using the Shannon and Prewitt radii (1969). Since the Shannon–Prewitt radii give good estimates of observed bond lengths, our results indicate that the BeOSi bond in beryllosilicates may be adequately modeled with small BeOSi containing diners when using ab initio methods.

In most beryllosilicates, the bridging oxygen of the BeOSi bond is either bonded to another fairly electronegative atom (e.g., Al, Be) or it is bonded to one or more electropositive atoms (e.g., Ca, Na). A two-coordinated bridging oxygen involved in a BeOSi bond is extremely rare (e.g., asbecasite, Cannillo et al., 1969). Thus, the dimer BeSi(OH)$_2$, whose bridging oxygen is bonded to Be, Si, and H is possibly the simplest model for the BeOSi bonds observed in most beryllosilicates.

The total energy for BeSi(OH)$_7$ and H$_2$BeSiO$_7$, Fig. 2. Potential energy as a function of Be–O bridging bond length, d(\text{Be–Obr}), and bridging angle BeOSi for (a) BeSi(OH)$_7$ and (b) H$_2$BeSiO$_7$ calculated with all non-bridging bonds and the Si–O bridging bond fixed at the optimized values. One contour = 0.001 atomic units = 0.63 kcal = 2.63 kJ. The Be–O bridging bond length and angle data from 28 beryllosilicate structure refinements are shown as dots in (a). The mean values for these data are $\langle d(\text{Be–Obr}) \rangle = 1.64$ Å and $\langle \text{BeOSi} \rangle = 126°$. 

The total energy for BeSi(OH)$_7$ and H$_2$BeSiO$_7$,
A comparison of experimental and theoretical SiOBe geometries

It has been proposed by Ganguli (1979) that a correlation obtains between Be–O bridging bond length and BeOSi angle with wider angles involving shorter bonds. The fact that the minimum energy portion of the potential energy surface for BeSi(OH)₃ forms a narrow valley symmetric about BeOSi angle = 130° indicates that no such correlation should exist. It is noteworthy that a similar potential energy surface calculated for the dimer H₂Si₂O₅ (Meagher et al., 1980; Gibbs et al., 1981) shows that the energy varies rapidly with Si–O bond length but slowly with SiOSi angle, just opposite to that calculated here for BeSi(OH)₃. The H₂Si₂O₅ potential energy surface has been shown to be consistent with the observed Si–O bridging bond length and angle variations in the silica polyhydrates and siloxanes (Newton and Gibbs, 1980; Meagher et al., 1980; Gibbs et al., 1981). When the bridging Be–O bond lengths and angles from observed structures are plotted on the potential energy surface for BeSi(OH)₃, a wide scatter of values obtained with the bond lengths varying between 1.56 Å and 1.72 Å and most of the angles varying between 115° and 140°. The mean values for these data are \( \langle d(\text{Be–O}) \rangle = 1.64 \) Å and \( \langle \text{BeOSi} \rangle = 126^\circ \) which agree with the values \((1.66 \) Å, \(129^\circ\)) optimized for BeSi(OH)₃. This result is consistent with an observation made previously by Brown and Gibbs (1970) that Be tends to be involved in narrow TOT angles. The agreement between calculated and observed values indicates that the observed geometries of BeOSi bonds are governed mainly by the local bonding forces within these units themselves rather than by the long range forces of the crystal field.

Figure 2a includes data from three-membered tetrahedral rings (e.g., euclase and phenacite) which tend to cluster in the narrow angle range (Downs, 1980). It is noteworthy that three-membered tetrahedral rings are relatively common in beryllosilicates. In contrast, they are relatively uncommon in silicates because of the inherent instability of the narrow SiOSi angles (approximately \(126^\circ\)) required to form such a ring (Chakoumakos and Gibbs, 1980; Chakoumakos, 1981; Chakoumakos et al., 1981). The inherent tendency of the BeOSi bond to adopt an angle of \(129^\circ\) indicates that three-membered beryllosilicate rings are unstrained. On the other hand, when the ring consists of three silicate tetrahedra, it represents a strained configuration because of the inherent tendency of the disiloxyl unit to adopt an angle of \(145^\circ\) (Newton and Gibbs, 1980; Chakoumakos and Gibbs, 1980; Chakoumakos, 1981; Chakoumakos et al., 1981). Cases where a bridging oxygen is bonded to two edge-sharing Be tetrahedra and one Si tetrahedron, as in epididymite, require narrow BeOBe angles with a concomitant widening of the BeOSi angles. Data from such topologies tend to cluster near the wide angle range of the stable region. Thus it appears that whatever topology is adopted by the tetrahedral frame of a beryllosilicate that the resulting BeOSi angles should correspond to the minimum energy region of the potential energy surface for BeSi(OH)₃.

A linear regression analysis calculated for the data in Figure 2a yields an \( r^2 \) value of only 0.02, suggesting that only two percent of the variation in \(d(\text{Be–O})\) can be explained in terms of a linear dependence on the BeOSi angle. This result is contrary to that obtained by Ganguli (1979) who calculated an \( r^2 \) value of 0.35 for this correlation. Our data are somewhat more extensive than those used by Ganguli and we have excluded a questionable point for asbecasite at \(d(\text{Be–O}) = 1.53 \) Å and BeOSi angle = \(180^\circ\) on which his proposed correlation is highly dependent. If the correlation is real, we might expect that it would persist with the omission of this one point. Inasmuch as our data (Fig. 2a) show a relatively wide scatter, we suggest that the evidence for such a correlation is lacking.

The BeOSi angle dependence on the coordination number of the bridging oxygen

We will now examine the extent to which the equilibrium BeOSi angle may depend on the fact that the bridging oxygen of BeSi(OH)₃ is three-coordinated. To investigate this dependence we examined the optimized geometry and potential energy surface for H₄BeSiO₄ (which is essentially BeSi(OH)₃ with the hydrogen removed from the bridging oxygen). The fact that the optimized BeOSi angle of \(131^\circ\) is practically the same as that calculated for BeSi(OH)₃ indicates that the preference for the BeOSi angles in beryllosilicates to be bent is not merely a proclivity of the bridging oxygen to form more bonds in order to satisfy its valence. The potential energy surface for H₄BeSiO₄ is quite similar to that for BeSi(OH)₃ at narrow angles; however, at wide angles, the H₄BeSiO₄ surface is less steep. This result indicates that although the equilibrium BeOSi angle with a two-coordinated bridging oxygen is \(131^\circ\), the energy barrier to widening the angle is less than for a three-coordinated oxygen. In other words, if a BeOSi angle
wider than 131° were required in order to satisfy
steric constraints this could be accommodated with
minimal destabilization of the structure. The shape
of the H₂BeSiO₄ surface also hints at the existence of
a possible weak correlation between d(Be–O₁) and
angle BeOSi when the oxygen is two-coordinated.
However, the paucity of two-coordinated oxygens
bridging Be and Si tetrahedra makes it impossible at
this time to investigate this suggestion.

BeSi(OH)₃ and H₂BeSiO₄ are similar to the dimers
Si₂H₂O₂BeH₂ and SiH₂OBeH₂ studied by Tossell and
Gibbs (1978) using the CNDO/2 MO method. In
their calculations none of the bond lengths were opti-
mized because of the limitations of the method. The
minimum energy BeOSi angles reported are 124°
and 114° for the three-coordinated and two-coordi-
nated oxygen, respectively. Tossell and Gibbs (1978)
ascribe the calculated angles to the underbonded (or
overbonded) nature of the bridging oxygen and in-
dicate that the two dimers may be poor models for
beryllosilicate systems. The optimized angles of 124°
and 114° calculated for the two dimers were consid-
ered to be fortuitous and unrealistic. It appears that
the use of TH₂O tetrahedra together with the limita-
tions of the CNDO/2 method may have an even
greater effect upon the optimized angle than the
overbonded or underbonded nature of the bridging
oxygen.

Calculations were also completed for both
BeSi(OH)₃ and H₂BeSiO₄ where all bond lengths
were fixed at the optimized values and the BeOSi
angle was varied from 100° to 180° resulting in the
energies listed in Table 1. The shapes of the resulting
potential energy curves for the two dimers are com-
pared by subtracting each energy from that calcu-
lated at angle BeOSi = 180° for each dimer in turn and
plotting the values vs. angle BeOSi as shown in
Figure 3. Using data at, and adjacent to, the energy
minimum, the calculated quadratic bending force
constant (given as the second derivative of the total
energy function scaled by the inverse product of the
two bond lengths forming the angle) for the BeOSi
angle is 14 Nm⁻¹ for both BeSi(OH)₃ and H₂BeSiO₄.
The reason for this equality is evident from Figure 3
which shows the curves to be nearly identical in
shape near the minimum energy. At angles wider
than 130°, however, the similarity disappears in that
the energy changes much more rapidly for
BeSi(OH)₃ than for H₂BeSiO₄. The resulting differ-
ence in depth of these potential energy wells is mani-
fest in the calculated barrier to linearity of 32 kT at
room temperature for BeSi(OH)₃, compared to that of
8 kT calculated for H₂BeSiO₄. This difference simply
reflects the improbability of a BeOSi unit adopting a

Table 1. The total energy, Eᵣ (atomic units), calculated as a
function of angle BeOSi for BeSi(OH)₃ and H₂BeSiO₄. Bond
lengths were fixed at the optimized values shown in Figure 1 for
these calculations. One atomic unit = 627.5 kcal = 2625.46 kJ.

<table>
<thead>
<tr>
<th>BeSi(OH)₃</th>
<th>ΔEᵣ (a.u.)</th>
<th>LBeOSi</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-821.01221</td>
<td>140</td>
</tr>
<tr>
<td>120</td>
<td>-821.03684</td>
<td>160</td>
</tr>
<tr>
<td>130</td>
<td>-821.03809</td>
<td>180</td>
</tr>
<tr>
<td>( \measuredangle \text{BeOSi} ) = 129°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂BeSiO₄</td>
<td>ΔEᵣ (a.u.)</td>
<td>LBeOSi</td>
</tr>
<tr>
<td>100</td>
<td>-820.14048</td>
<td>150</td>
</tr>
<tr>
<td>110</td>
<td>-820.16581</td>
<td>160</td>
</tr>
<tr>
<td>120</td>
<td>-820.17303</td>
<td>170</td>
</tr>
<tr>
<td>130</td>
<td>-820.17457</td>
<td>180</td>
</tr>
<tr>
<td>( \measuredangle \text{BeOSi} ) = 131°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Potential energy curves, \( \Delta Eᵣ = E(180°) - E(\measuredangle \text{BeOSi}) \)
atomic units), as a function of BeOSi angle in BeSi(OH)₃
(triangles) and H₂BeSiO₄ (diads) with bond lengths fixed at
the optimized values. The calculated quadratic bending force
constant for both molecules is 14 Nm⁻¹. The barrier to linearity
is 32 kT for BeSi(OH)₃ and 8 kT for H₂BeSiO₄ at 300 K.
straight BeO Si angle when the bridging oxygen is three-coordinated.

The curve for H₆BeSiO₄ is similar to that calculated by Newton and Gibbs (1980) for H₆Si₂O₇. Using the energies from the curve for BeSi(OH)₄, a Boltzmann distribution curve was calculated. This is shown together with a frequency plot (using the data in Fig. 2a) of the observed BeO Si angles in Figure 4. The frequency distribution is similar to that reported by Tossell and Gibbs (1978). The Boltzmann distribution curve is a plot of the function exp[-ΔE(∠BeO Si)/kT] where T = 300 K.

**Examination of the linear BeO Si bond in asbecasite**

The structure of asbecasite, Ca₃(Ti,Sn)As₆Si₂ Be₂O₁₀, solved from 3-dimensional film data, was refined by least-squares methods to R = 0.066 for all data using isotropic temperature factors on each atom and a correction for isotropic extinction (Can- nillo et al., 1969). Our attention is drawn to this structure because of the short Be–O (1.53 Å) and Si–O (1.58 Å) bonds, the wide BeO Si angle of 180°, and the fact that the bridging oxygen is two-coordinate. Our calculations on H₆BeSiO₄ indicate that a bent bond configuration is considerably more stable than a straight one. An investigation of the isotropic temperature factor for the BeO Si bridging O(4) oxygen of asbecasite shows it to be nearly twice the mean value of the other oxygen thermal parameters. This suggests that the short bond lengths and wide angle may be due in part to averaged positional disorder at the bridging oxygen atom. The structure was refined by Cannillo et al. (1969) in space group P₃c1 with Be, O(4), and Si located on a three-fold symmetry axis requiring the BeO Si angle to be straight.

Using the reported structure factors, we attempted a further refinement of the structure of asbecasite by expanding the calculation to include a refinement of the anisotropic temperature factors for each atom. After a full matrix refinement using isotropic temperature factors converged to R = 0.06 for all data, a difference Fourier (Δρ) map calculated through the Be–O(4)–Si linkage showed conspicuous anisotropy of charge density at the site of O(4) normal to the three-fold axis. In addition, anisotropy in the charge density parallel to the symmetry axis is exhibited by Be and Si. The introduction of anisotropic thermal parameters for O(4) alone yielded U₁₁ = U₂₂ = 0.0120 and U₃₃ = 0.0089. The introduction of anisotropic temperature factors for Si gave U₁₁ = U₂₂ = 0.0028 and U₃₃ = 0.0047. Attempts at full matrix refinement failed because the anisotropic temperature factors on several atoms (notably Be) were calculated as non-positive definite. Since we were using a data set averaged for P₃c1 symmetry, it was impossible to complete a refinement for the structure with the three-fold axis removed. An analysis of the atom shifts due to positional disorder from the Δρ map indicates that the Be–O(4)–Si angle may be close to 150°–160° rather than 180° as reported. Although this angle is still at the wide angle limit of observed BeO Si angles, the potential energy curve for H₆BeSiO₄ suggests that when the bridging oxygen is two-coordinated that wide angles are nearly as stable as that of equilibrium angle of 131°. The gentle slope of the H₆BeSiO₄ potential energy curve at wide angles indicates that a two-coordinated oxygen involved in a wide BeO Si angle may tend to exhibit increased anisotropic motion and positional disorder relative to a similar oxygen involved in a narrow
BeOSi angle (i.e., the quadratic bending force constant for the BeOSi angle is not constant but decreases in a regular way with widening angle when the bridging oxygen is two-coordinated).

**Conclusions**

*Ab initio* generated equilibrium geometries and potential energy surfaces calculated for BeSi(OH), and H₄BeSiO₇ are consistent with observed variations in Be–O and Si–O bridging bond lengths and angles BeOSi in beryllosilicates. These results suggest that the configuration of the tetrahedral frame of a beryllosilicate may depend in large measure upon the tendency for individual BeOSi bonds to adopt equilibrium geometries. The narrow nature of the resulting equilibrium BeOSi angles may permit structural units unstable in pure silicate systems (e.g., three-membered rings) to be stabilized in beryllosilicates. We may further expect beryllium not to participate extensively in coupled substitutions for Si or Al in structures that require large BeOSi angles (e.g., alkali feldspars). Rather we may expect such substitution to occur in structures where TOT angles near the equilibrium value for BeOSi predominate (e.g., cordierite, willemite).

**Acknowledgments**

It is a pleasure to thank the National Science Foundation for supporting this investigation with grant EAR-7723114 to G.V. Gibbs and P.H. Ribbe to study bonding in minerals. We are also pleased to acknowledge VPI & SU for promoting the development of an excellent University Computing Center and for contributing large sums of money to help defray the computing costs incurred in the molecular orbital calculations. We thank Ramonda Haycocks for typing the manuscript and Sharon Chiang for her deftness in drafting the figures for this paper.

**References**


Downs, J. W., Hill, R. J., Newton, M. D., Tossell, J. A. and Gibbs, G. V. (1980) Ab initio calculated geometries and potential energy surfaces calculated for BeSi(OH), and H₄BeSiO₇ are consistent with observed variations in Be–O and Si–O bridging bond lengths and angles BeOSi in beryllosilicates. These results suggest that the configuration of the tetrahedral frame of a beryllosilicate may depend in large measure upon the tendency for individual BeOSi bonds to adopt equilibrium geometries. The narrow nature of the resulting equilibrium BeOSi angles may permit structural units unstable in pure silicate systems (e.g., three-membered rings) to be stabilized in beryllosilicates. We may further expect beryllium not to participate extensively in coupled substitutions for Si or Al in structures that require large BeOSi angles (e.g., alkali feldspars). Rather we may expect such substitution to occur in structures where TOT angles near the equilibrium value for BeOSi predominate (e.g., cordierite, willemite).

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**References**


ometries and charge distributions for H₄SiO₄ and H₆Si₂O₇ compared with experimental values for silicates and siloxanes. Physics in Chemistry of Minerals, 6, 221-246.


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