THE AMERICAN MINERALOGIST, VOL. 55, SEPTEMBER-OCTOBER, 1970

STEREOCHEMISTRY AND ORDERING IN THE TETRAHEDRAL PORTION OF SILICATES

G. E. BROWN[1] AND G. V. GIBBS, *Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*

ABSTRACT

The dependence of Si–O(br) and Si–O(nbr) bond lengths on Si–O–Si angle and average electronegativity, $\bar{\chi}$, of non-tetrahedral cations has been examined for four $C2/m$ amphiboles and a number of other silicates with both bridging, O(br), and non-bridging, O(nbr), oxygens. When both $\bar{\chi}$ and Si–O–Si angle are large, the mean Si–O(nbr) bond lengths, <Si–O(nbr)>, are observed to be longer than the mean Si–O(br) bond lengths, <Si–O (br)>. However, when $\bar{\chi}$ is small, <Si–O(nbr)> are usually shorter than or equal to <Si–O(br)>, irrespective of angle. A correlation of <T–O> bond length (T≡Si,Al,P) with O··· O non-bonded distance in O–*T*–O linkages for compounds with SiO_4 as well as AlO_4 and PO_4 tetrahedra is consistent with Cruickshank's (1961) π–bonding hypothesis, with McDonald and Cruickshank's (1967) assumption that O(nbr) have larger negative charges than O(br) and with Gillespie's (1963) VSEPR Theory.

The distributions of tetrahedral Si and Al, B, Be or Mg in a number of framework silicates are examined in terms of Cruickshank's hypothesis and the difference in predicted Si–O, Al–O, B–O, Be–O and Mg–O bond orders for TO_4^{n-} tetrahedral ions and are found to be consistent with the proposal that Si should prefer those tetrahedra involved in the widest average *T*–O–*T* angles. Although the distribution of tetrahedral cations in the non-framework silicates cannot in general be explained in terms of this proposal, other factors involving *d*-*p* π-bonding in TO_4^{n-} ions are helpful in rationalizing the observed tetrahedral distribution of cations in the pyroxenes, hornblendes and micas. The role of OH and F in this ordering process is also briefly discussed.

INTRODUCTION

Since Pauling proposed his classic set of semi-empirical rules for predicting stable configurations of atoms in complex ionic crystals (Pauling, 1929), the crystal structures of a large number of silicates have been studied and found to agree with them remarkably well. The rules were developed to predict cation-anion distances and cation coordination polyhedra in addition to explaining the distortions and polymerization of these polyhedra based on the assumption that ions tend to adopt positions such that the potential energy of the resulting configuration is minimized. Although the radius sum of two bonded ions gives a reasonable estimate of mean cation-anion distance, it fails to predict variations in individual bond lengths other than those associated with shared polyhedral elements. In an attempt to circumvent this problem and to explain individual bond length variations in monoclinic metaboric acid,

---

[1] Present address: Department of Earth and Space Sciences, S.U.N.Y. at Stony Brook, Stony Brook, L.I., New York, 11790.

Zachariasen (1963) modified Pauling's second rule of local valence neutralization by quantitatively relating charge balance to interatomic distance such that bond strength is uniquely determined by interatomic distance.[1] The Pauling-Zachariasen method has since been applied with some success to datolite (Pant and Cruickshank, 1967), zoisite and clinozoisite (Dollase, 1968), α-$Na_2Si_2O_5$ (Pant and Cruickshank, 1968), β-$Na_2Si_2O_5$ (Pant, 1968), eight clinopyroxenes (Clark, Appleman and Papike, 1969) and asbecasite, taramellite, kauskopfite, meliphanite, leucophanite, aminoffite, macdonaldite, bavenite and neptunite (Coda, 1969). In the datolite study Pant and Cruickshank discussed the method and concluded that its success is independent of whether the nature of the bonding is ionic, covalent or a mixture. However, one possible mechanism for charge balance, in addition to ionic and σ-covalent bonding is discussed by Coulson and Dingle (1968) in a study of B–O bond lengths in a number of planar boron–oxygen compounds including monoclinic metaboric acid. They carried out standard Hückel-type molecular-orbital calculations on these compounds and found that a π-bonding model can account for the variation of B–O bond lengths, neglecting the perturbating effect of other cations (see also Svanson, 1969). Pant (1968) has indicated that π-bonding may also be part of the mechanism whereby local valence neutralization is achieved in the tetrahedral portion of a silicate structure. The importance of π-bonding in the silicates has been discussed in detail by Cruickshank (1961) who formalized a d-p π-bonding model for TO_4^{n-} ions ($T \equiv$ Si, P, S, Cl) of T_d or approximate T_d symmetry by showing that only two $d\pi$-orbitals (d_{z^2} and $d_{x^2-y^2}$) on T can form strong d-p π-bonds with the $p\pi$-oribtals on oxygen anions assuming that the tetrahedral σ-bonds are formed from sp^3 hybrid orbitals at T.[2,3] The predictions of bond length and bond angle variations for structures con-

---

[1] In a similar but qualitative fashion, Bauer (1962) has discussed a correlation between H–O bond lengths and the sum of the electrostatic bond strengths to oxygen in several hydrous sulfates.

[2] Although the point group symmetries of the majority of SiO_4 and AlO_4 tetrahedral groups in solids are lower than T_d symmetry, *e.g.*, C_s in the olivines and C_1 in the amphiboles and pyroxenes, the bonding assignments based on T_d symmetry are probably good approximations. This assumption can be made because the deviations from T_d symmetry are usually small ($\sim\pm 5°$ from the ideal tetrahedral angle and at most $\sim\pm 0.05$Å from the mean T–O bond length; see Fig. 7). Also, because sp^3 and sd^3 hybrids belong to the same representations of the T_d point group, the σ-orbitals on T very probably consist of a mixture of both of these hybrids (Cotton, 1963).

[3] Note added in proof. Recent *ab initio* molecular orbital calculations by D. W. J. Cruickshank (personal communication) for tetrahedral SiO_4^{4-} show that *all five* of the 3d orbitals on silicon are essential to describe the Si–O bonds in the ion. However, the three orbitals of the t_2 bases set have slightly larger overlap populations than the two of the e bases set. Nevertheless, this result does not alter the predictions enumerated by Brown,

taining TO_4 groups based on Cruickshank's proposal are discussed by Cruickshank (1961) and outlined by Brown, Gibbs and Ribbe (1969a).

Noll (1963) has extended Cruickshank's ideas to include the perturbating effect of non-tetrahedral cations on the Si–O bonds in silicates containing both bridging, O(br), and non-bridging oxygens O(nbr), and has cited data indicating that the differences in Si–O(br) and Si–O(nbr) bond lengths are dependent on the electronegativity of the non-tetrahedral cations bonded to O(nbr). Others have also discussed the effect of non-tetrahedral cations of varying electronegativity on Si–O(br) and Si–O(nbr) bond lengths in selected single-chain (McDonald and Cruickshank, 1967a) and double-chain silicates (Brown and Gibbs, 1969b; 1970).

The present study is an extension of earlier work on the role of π-bonding in the framework and double-chain silicates and embodies the substance of a paper (Brown and Gibbs, 1970) presented at the Amphibole-Pyroxene Symposium held at the Virginia Polytechnic Institute at Blacksburg, Virginia in September 1969. The purpose of the study is to present further correlations between Si–O bond length and electronegativity of non-tetrahedral cations in the $C2/m$ amphiboles discussed earlier and between Si–O bond length and Si–O–Si and O–Si–O angles in structures containing both bridging and non-bridging oxygens. Similar correlations are given for the P–O bond in phosphates. A mechanism for the ordering of Si and Al, Be, B or Mg in the tetrahedral portions of framework silicates is proposed based on the relative bond orders[1] of the T–O bonds. The ordering of these cations is also examined in the non-framework silicates and the role of OH and F in the ordering process is discussed.

DEPENDENCE OF Si–O(br) AND Si–O(nbr) BOND LENGTHS ON Si–O–Si ANGLE AND ELECTRONEGATIVITY OF NON-TETRAHEDRAL CATIONS

The stereochemistry of polymerized SiO_4^{4-} tetrahedral ions in many silicates is consistent with Cruickshank's (1961) hypothesis of π-bonding: (1) the Si–O(nbr) bonds are usually shorter than Si–O(br) bonds (*c.f.* Coda, 1968), (2) the lengths of the Si–O(br) bonds are usually related to the Si–O–Si angle, the shortest bonds being associated with widest angles (Cannillo, Rossi, Ungaretti, 1968; Brown, Gibbs and Ribbe, 1969a) and

---

Gibbs and Ribbe (1969a) on page 1045 where it was assumed after Cruickshank (1961) that only the orbitals of the *e* basis set form strong d–p π-bonds with the p-orbitals on oxygen. Cruickshank's calculations also show that the residual charge on Si is not 4+ as predicted by the ionic model but is close to zero in agreement with Pauling's electroneutrality principle.

[1] Bond order can be defined as the average number of electron pairs per bond.

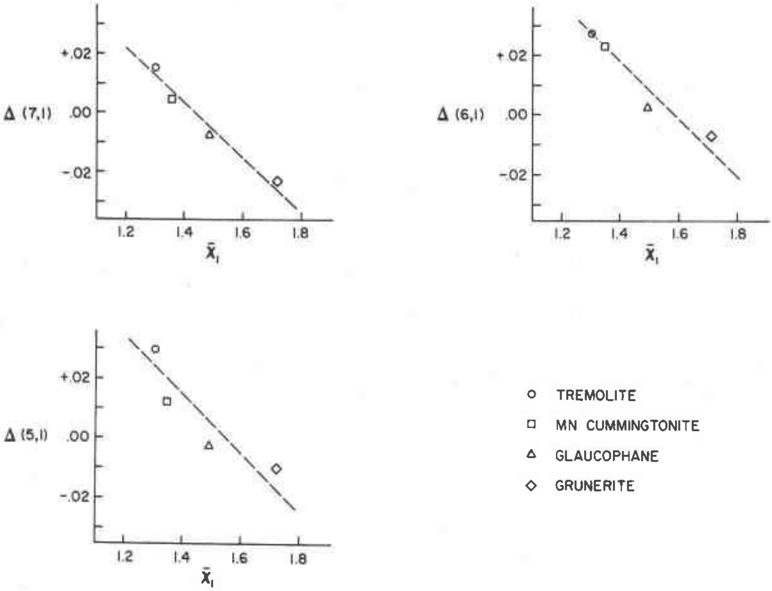

FIG. 1. Difference, Δ(i, 1), between average Si–O(br) and Si–O(nbr) bond lengths for the Si(1) tetrahedron plotted against the average electronegativity, $\bar{\chi}$, of non-tetrahedral cations bonded to O(nbr) for four *C2/m* amphiboles with vacant A-sites:

tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	Papike, Ross and Clark (1969)
Mn-cummingtonite	$Ca_{0.2}Mn_2Mg_{4.1}Fe_{0.5}Si_8O_{22}(OH)_2$	Papike, Ross and Clark (1969)
glaucophane	$Na_2Mg_{2.4}Al_{1.6}FeSi_8O_{22}(OH)_2$	Papike and Clark (1968)
grunerite	$Fe_2Fe_{4.2}Mg_{0.8}Si_8O_{22}(OH)_2$	Finger (1969)

$\Delta(7,1) \equiv [Si(1)\text{–}O(7)]\text{-}[Si(1)\text{–}O(1)]$
$\Delta(5,1) \equiv [Si(1)\text{–}O(5)]\text{-}[Si(1)\text{–}O(1)]$
$\Delta(6,1) \equiv [Si(1)\text{–}O(6)]\text{-}[Si(1)\text{–}O(1)]$

Allred and Rochow electronegativity values for elements in various oxidation states were taken from Table 2.9, Douglas and McDaniel (1965).

(3) the tetrahedral angles usually decrease in the order O(nbr)–Si–O(nbr) > O(nbr)–Si–O(br) > O(br)–Si–O(br) (McDonald and Cruickshank, 1967a; Gibbs, 1969). The fact that Si–O(nbr) bonds are usually shorter than Si–O(br) bonds has been convincing evidence in support of Cruickshank's hypothesis. However, McDonald and Cruickshank (1967a) recognized that as the non-tetrahedral cations become more electronegative in the series of compounds sodium metasilicate (Na_2SiO_3), wollastonite ($CaSiO_3$), bustamite ($CaMnSi_2O_6$), rhodonite ($Mn_{0.80}Ca_{0.16}X_{0.04}SiO_3$) and stokesite ($CaSnSi_3O_9 \cdot 2H_2O$), the differences between the Si–O(br) and Si–O(nbr) bond lengths decrease. Paralleling this decrease they also noted a concomitant widening of the mean Si–O–Si angle from about 134°

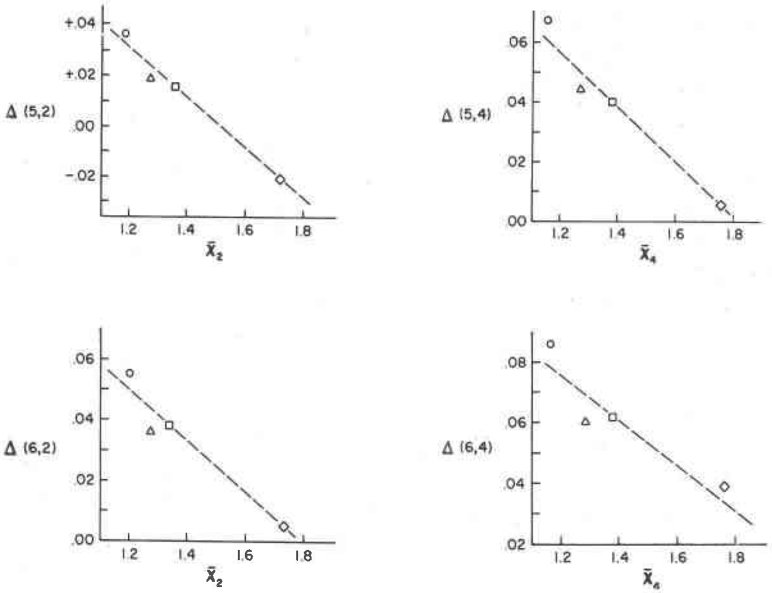

FIG. 2. Difference, Δ(i,2), between average Si–O(br) and (Si–O(nbr) bond lengths for the Si(2) tetrahedron plotted aginst the average electronegativity, $\bar{\chi}$, of non-tetrahedral cations bonded to O(nbr) for the four *C*2/*m* amphiboles described in the caption of Fig. 1.

Δ(5,2) = [Si(2)–O(5)]-[Si(2)–O(2)]
Δ(6,2) = [Si(2)–O(6)]-[Si(2)–O(2)]
Δ(5,4) = [Si(2)–O(5)]-[Si(2)–O(4)]
Δ(6,4) = [Si(2)–O(6)]-[Si(2)–O(4)]

for sodium metasilicate to 147° for stokesite. The correlation between Si–O bond lengths and electronegativity has also been discussed by Noll (1963) for a number of silicates containing both bridging and non-bridging oxygens and more recently by Gibbs (1969) for protoamphibole and cummingtonite and by Brown and Gibbs (1969b) for four C2/*m* amphiboles. Figures 1 and 2 show similar correlations between the difference in length, Δ(*i*, *j*), between the Si–O bond to the *i*th O(br) and *j*th O(nbr) and the average electronegativity of the non-tetrahedral cations, $\bar{\chi}$, for the Si(1) and Si(2) tetrahedra, respectively, in four *C*2/*m* amphiboles [tremolite and Mn-cummingtonite (Papike, Ross and Clark, 1969); glaucophane (Papike and Clark, 1968); grunerite (Finger, 1969)]· For the Si(1) tetrahedron (Fig. 1), Δ(i, 1) is between 0.01 to 0.03 Å for tremolite and Mn-cummingtonite, ∼0.0 Å for glaucophane and between −0.01 and −0.02 Å for grunerite reflecting the replacement of relatively electropositive Mg and Ca cations in tremolite and Mn-cummingtonite by the more electronegative Al and Fe cations in glaucophane and grunerite. Similar trends exist for the Si(2) tetrahedron (Fig. 2) except that $\Delta(5, 4)$ and $\Delta(6, 4)$ are positive in these four amphiboles reflecting the highly underbonded nature of O(4) and its high residual electron density, δ, (see Brown and Gibbs, 1969b). The O(2) oxygen is only slightly underbonded resulting in $\Delta(i, 2)$ values intermediate between those for O(1) and O(4).

The Si–O–Si angles in these four amphiboles are fairly constant ranging within about ±5° of the mean value of 141°. Therefore, the variation in $\Delta(i, j)$ should be virtually independent of Si–O–Si angle. However, the dependence of $\Delta \equiv [\langle \text{Si–O(br)} \rangle] - [\langle \text{Si–O(nbr)} \rangle]$ on Si–O–Si angle in a number of silicates containing both O(br) and O(nbr) is shown in Figure 3, indicating that angle also plays a significant role in determining Δ. The Δ value is negative for angles greater than ~170°; the two data points at 180°, which represent thortveitite ($Sc_2Si_2O_7$) (Cruickshank, *et al.*, 1962; Prewitt, personal communication) and haradaite ($SrVSi_2O_7$) (Takeuchi and Joswig, 1967), show that the ⟨Si–O(nbr)⟩ bonds in these structures are as long or longer than the ⟨Si–O(br)⟩ bonds, a result which is apparently at variance with the expected stereochemistry of the $Si_2O_7^{6-}$ ion (Cruickshank, 1961). The effect of Si–O–Si angle on Δ is evidently as important as the effect of the non-tetrahedral cations and explains, in part, the Si–O bond lengths in both thortveitite and haradaite. In fact, when both $\bar{\chi}$ and Si–O–Si angle are large, the ⟨Si–O(nbr)⟩ bonds should be longer than the ⟨Si–O(br)⟩ bonds; however, when $\bar{\chi}$ is small, (~1.0 or less) the ⟨Si–O(nbr)⟩ bonds should be shorter than or equal to the ⟨Si–O(br)⟩ bonds, irrespective of angle. The same result should be true when the Si–O–Si angle is narrow, irrespective of $\bar{\chi}$. The correlation coefficient for the data in Figure 3 (-0.67) indicates that only about 45 percent of the variation in Δ can be explained in terms of a linear dependence on Si–O–Si angle; the scatter of data above and below the regression line near 140° can be related, with a few exceptions, to the average electronegativity of the non-tetrahedral cations; those values plotting above the line are from structures containing relatively electropositive cations in comparison to those below. Certainly, other factors such as (1) the isovalent hybridization of the orbitals on oxygen, (2) the number of lone pair orbitals on oxygen[1] available for *d-p* π-bond formation, and (3) geometrical and electrostatic effects must play an equally important role in the variation of Si–O(br) and Si–O(nbr) bond lengths. In fact, the correlation between ⟨Si–O⟩ and the mean coordination number of the oxygens bonded to Si (Gibbs and Brown, 1968; Shannon

---

[1] ~0, ~1 and ~2 in silicates containing four-, three- and two-coordinated oxygens, respectively.

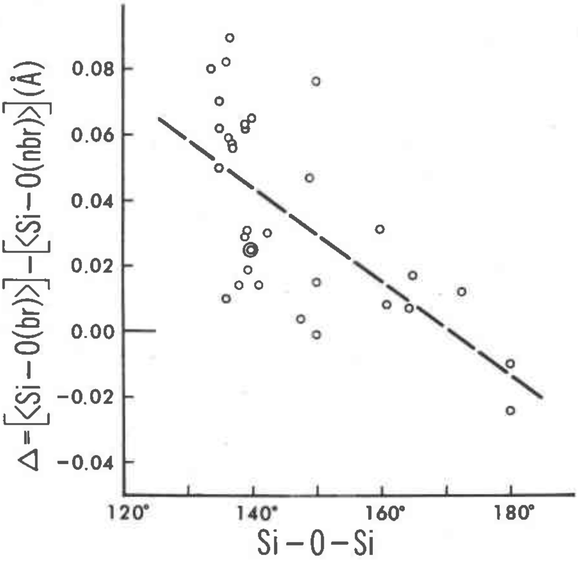

FIG. 3. Variation of $\Delta \equiv [<Si-O(br)>]-[<Si-O(nbr)>]$ with Si–O–Si angle for the following silicates: pectolite ($CaNaHSi_3O_9$) (Prewitt, 1967); wollastonite ($CaSiO_3$) (Prewitt and Buerger, 1963); bustamite ($CaMnSi_2O_6$) (Peacor and Buerger (1962a); narsarsukite ($Na_2TiOSi_4O_{10}$) (Peacor and Buerger (1962b); hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) (McDonald and Cruickshank, 1967b); epidote ($HCa_2(Al,Fe)Al_2Si_3O_{13}$) (Fang, personal cummunication); zoisite and clinozoisite ($Ca_2Al_3Si_3O_{12}OH$) (Dollase, 1968); tilleyite ($Ca_5Si_2O_7(CO_3)_2$) (Smith, 1953b) and personal communication); haradaite ($SrVSi_2O_7$) (Takeuchi and Joswig, 1967); thortveitite ($Sc_2Si_2O_7$) (Cruickshank *et al.*, 1962); spodumene ($LiAlSi_2O_6$) (Clark *et al.*, 1968); Fe-spodumene ($LiFeSi_2O_6$) (Clark, *et al.*, 1968); cosmochlore ($NaCrSi_2O_6$) (Clark *et al.*, 1968); acmite ($NaFeSi_2O_6$) (Clark *et al.*, 1968); diopside ($CaMgSi_2O_6$) (Clark *et al.*, 1968); johannesenite ($CaMnSi_2O_6$) (Freed and Peacor, 1967); jadeite ($NaAlSi_2O_6$) (Prewitt and Burnham, 1966); $NaInSi_2O_6$ (Christensen and Hazell, 1967); Na_2SiO_3 (McDonald and Cruickshank, 1967a); α-$Na_2Si_2O_5$ (Pant and Cruickshank, 1968); β-$Na_2Si_2O_5$ (Pant, 1968).

and Prewitt, 1969; Brown and Gibbs, 1969b) is probably due in part to the number of lone pair electrons on oxygen available for back-bonding with *d* orbitals on Si. Figure 4 was prepared for a number of phosphates containing both O(br) and O(nbr). However, unlike the data for silicates (Fig. 3), the Δ values for the phosphates remain positive throughout the range of P–O–P angles. This is probably due to the tendency of the PO_4^{3-} ion to lose less of its π-bonding potential in the formation of covalent bonds to non-tetrahedral cations (see McDonald and Cruickshank, 1967a).

Figure 5 is a scatter diagram of the average length of the Si–O(br) bond in tetrahedra with both bridging and non-bridging oxygens versus

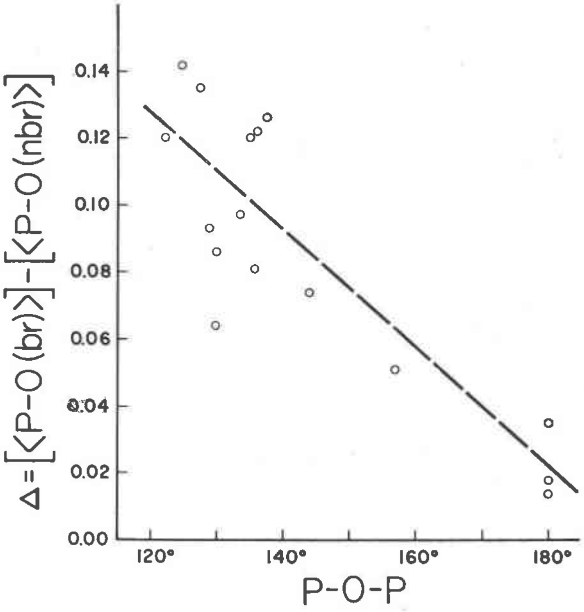

FIG. 4. Variation of Δ≡[<P–O(br)>]-[<P–O(nbr)>] with P–O–P angle for the following phosphates: β-$Mg_2P_2O_7$ (Calvo, 1965a); β-$Zn_2P_2O_7$ (Calvo, 1965b); α-$Mg_2P_2O_7$(Calvo, 1967); α-$Ca_2P_2O_7$ (Calvo, 1968); $Na_4P_2O_7 \cdot 10H_2O$ (Cruickshank, 1964a); $Na_5P_3O_{10}$ (Cruickshank, 1964b); $(RbPO_3)_\infty$ (Cruickshank, 1964e); $Na_2H_2P_4O_{12}$ (Jarchow, 1964); $(NaPO_3)_x$ (McAdam *et al.*, 1968); $Na_4P_4O_{12} \cdot 4H_2O$ (Ondik, 1964); α-$Cu_2P_2O_7$ (Robertson and Calvo, 1967); β-$Cu_2P_2O_7$ (Robertson and Calvo, 1968).

the Si–O–Si angle (Brown, Gibbs, Ribbe, 1969b). Cannillo, Rossi and Ungaretti (1968) have prepared a similar plot except theirs correlates the average Si–O(br) length to Si–O–Si angle for two types of tetrahedra: those with bridging oxygens only and those with both bridging and nonbridging oxygens. Figure 5 shows that in silicates containing both O(nbr) and O(br), ⟨Si–O(br)⟩ depends in part on the Si–O–Si angle, the shortest ones being associated with the widest angle. Such a correlation is expected if some degree of *d*-orbital participation (Cruickshank, 1961; Lazarev, 1964; Cotton and Wilkinson, 1966; Mitchell, 1969) is important in determining the variation of Si–O bond lengths and the steric details of the tetrahedral portion of a silicate. The increase in Si–O–Si angle with the shortening of Si–O bond length may be considered a means of (1) maximizing the π-orbital overlap, (2) minimizing the resulting repulsions between the increased electron density in the partial double bonds, (3) minimizing the repulsions between the positive charges on the Si ions (Mitchell, 1969) and (4) increasing the fraction of *s*-character in the

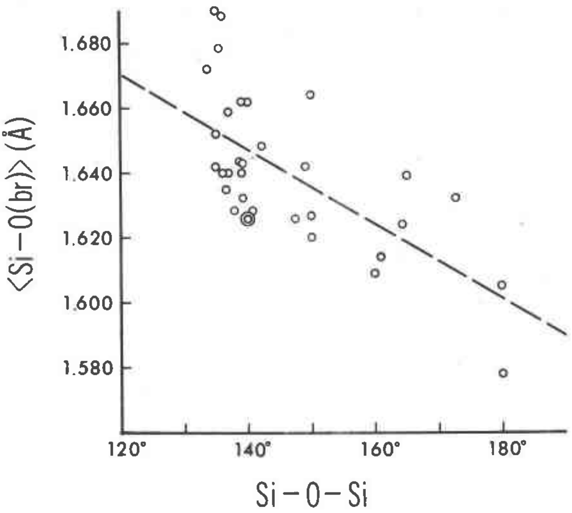

FIG. 5. Variation of mean Si–O(br) bond length with Si–O–Si angle for a number of silicates containing both bridging and non-bridging oxygens. Data from the structures listed in the caption of Fig. 3 were used.

Si–O bonds (Fyfe, 1954). Brown, Gibbs and Ribbe (1969a) have made similar correlations between the Si–O(br) bond lengths and Si–O–Si angles in the framework silicates which contain only bridging oxygens. The slope of the regression line in Figure 5 is statistically identical to that found for the same correlation with the data from the SiO_2 polymorphs; however, its intercept is ~0.035 Å greater than that for the SiO_2 polymorphs for a given Si–O–Si angle. This increase in average Si–O bond length can be attributed, in part, to the perturbating effect of the non-tetrahedral cations on the Si–O bond, to the absence of O(nbr) and to the constant coordination number of O(br) in the SiO_2 polymorphs.

The variation of ⟨P–O(br)⟩ bond length versus P–O–P angle from structures containing both O(br) and O(nbr) is shown in Figure 6 and is similar to the variation shown in Figure 5 for the silicates. The slopes of the regression lines in Figures 5 and 6 are identical $(-0.001, \hat{\sigma}=0.003)$ resulting in a constant difference of ~0.05 Å over the entire range of T–O–T angles. This difference is the same as that between the Si–O (1.76 Å) and the P–O (1.71 Å) single-bond values predicted using the Schomaker-Stevenson (1941) equation and implies similar degrees of d-orbital participation in the Si–O(br) and P–O(br) bonds. Gillespie and Robinson (1964); however, suggest that Si–O(br) bonds are generally of higher bond order than P–O(br) bonds.

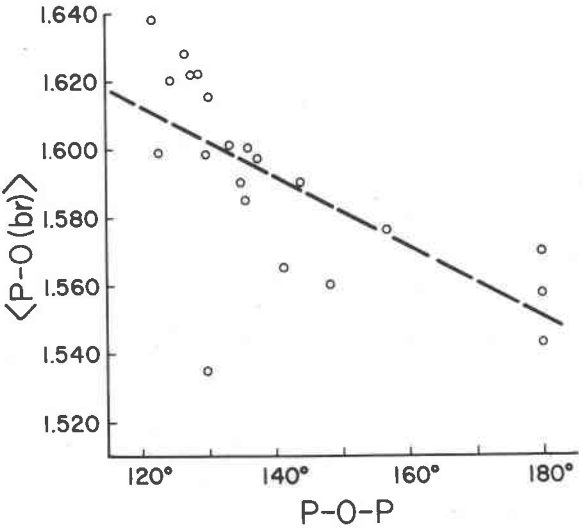

FIG. 6. Variation of mean P–O(br) bond length with P–O–P angle for a number of phosphates containing bath bridging and non-bridging oxygens. Data from the structures listed in the caption of Fig. 4 were used. Additional data points are from: $(NH_4)_4$ P_4O_{12} (Cruickshank, 1964c); P_2O_5 (Cruickshank, 1964d); P_4O_9 (Beagley *et al.*, 1967)

VARIATION OF *T*–O(br) AND *T*–O(nbr) BOND LENGTHS WITH O–*T*–O ANGLE

In a comparative study of the tetrahedral distortions in chlorates, sulfates, phosphates and silicates, McDonald and Cruickshank (1967a) have correlated ⟨*T*–O⟩ bond length with non-bonded O · · · O distance in O–*T*–O linkages and have concluded from the negative slopes of the silicate and phosphate lines that O(nbr) have larger negative electronic charges than O(br). Figure 7 is a revision and modification of their Figure 4 including new data for O–Si–O and O–P–O tetrahedral angles and the addition of a few data for O–Al–O angles taken from structure analyses of sapphirine (Moore, 1969a) and sillimanite (Burnham, 1963). Gibbs (1969) found that the majority of the tetrahedral angles in protoamphibole decrease in the order O(nbr)–Si–O(nbr) > O(nbr)–Si–O(br) > O(br)–Si–O(br) and argued that this order can be consistently interpreted in terms of Cruickshank's (1961) *d-p* π-bonding hypothesis and Gillespie's (1963) Valence Shell Electron-Pair Repulsion Theory. The new data for silicates with both O(br) and O(nbr) corroborate this interpretation as well as that proposed by McDonald and Cruickshank (1967a). However, these two interpretations are not mutually exclusive because *d-p* π-bond formation gives a polarity to the Si–O bond similar

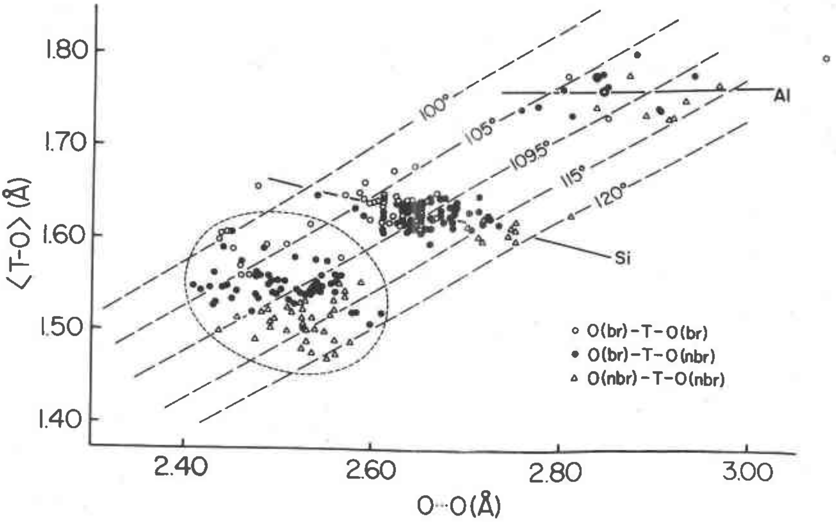

FIG. 7. Variation of mean *T*–O bond length with O · · · O nonbonded distance in O–*T*–O linkages (*T*≡P,Si,Al). Data for the Si line were taken from the following structures: protoamphibole ($Li_{1.2}Mg_{6.4}Si_8O_{22}(F)_2$) (Gibbs, 1969); glaucophane ($Na_2Mg_{2.4}Al_{1.6}FeSi_8O_{22}(OH)_2$) (Papike and Clark, 1968); rhodonite ($Mn_{0.80}Ca_{0.16}X_{0.04}SiO_3$) (Peacor and Niizeki, 1963); narsarsukite ($Na_2TiOSi_4O_{10}$) (Peacor and Buerger, 1962b); pectolite ($CaNaHSi_3O_9$) (Prewitt, 1967); Na_2SiO_3 (McDonald and Cruickshank, 1967a); α-$Na_2Si_2O_5$ (Pant and Cruickshank, 1968); β-$Na_2Si_2O_5$ (Pant, 1968). Data for the Al line were taken from: sapphirine ($Mg_{3.5}Al_{9.0}Si_{1.5}O_{20}$) (Moore, 1969a); sillimanite ($Al_2Si_2O_5$) (Burnham, 1963). Data for O–P–O linkages are the same as those listed in the captions of Fig. 4 and Fig. 6 and are encircled with a dash line.

to that predicted from electrostatic considerations with the negative charge concentrated in the vicinity of the oxygen atom (Bissey, 1967; Mitchell, 1969). The data for phosphates follow a similar but much less well-defined trend (correlation coefficient = −0.31), somewhat at variance with that reported by McDonald and Cruickshank (1967a).

Cotton and Wilkinson (1966) have suggested that *d-p* π-bond formation between Al, Si and O may account for the nearly coplanar arrangement of one Si- and two Al-cations about each oxygen in tetramethyl-OO′-bistrimethylsilyl-cyclodialumoxane. More recently, estimates of the *d-p* π-overlap integral (0.18) for the AlO_4^{5-} tetrahedral ion together with correlations of Al–O bond lengths with Al–O–Si angles and data from X-ray emission studies have led Brown, Gibbs and Ribbe (1969a) to suggest that *d-p* π-bonding also plays an important role in the variation of the Al–O bond lengths in the framework silicates. If these arguments can be extended to all structures containing tetrahedral Al, Al–O(br) bonds should be longer, in general, than Al–O(nbr) bonds providing the effects of $\bar{\chi}$ and T–O–T angle on Al–O bond lengths are not significant. The curve constructed for the small number of data in Figure 7 for AlO_4 tetrahedra with both O(br) and O(nbr) is roughly horizontal. This indicates that the Al–O(nbr) bonds in sapphirine and sillimanite are not shorter or of higher bond order, on the average, than the Al–O(br) bonds. If the effects of the Al–O–Si angle and $\bar{\chi}$ are ignored, the Si–O bond lengths in sillimanite (Burnham, 1963) also appear to be at variance with double bonding; the Si–O(nbr) bond (1.629 Å) is longer than the ⟨Si–O(br)⟩ bond (1.610 Å). However, when Al–O–Si angle and $\bar{\chi}$ are examined, the Si–O and Al–O bonds involved in the Al–O–Si linkages in sillimanite agree with the predictions of double bonding: short T–O(br) bonds (Si–O_c = 1.564; Al–O_c = 1.721 Å) are involved in the wide angle (Al–O_c–Si = 171.6°)[1] and long T–O(br) bonds (Si–O_d = 1.633, Al–O_d = 1.800 Å) with the narrow angle (Al–O_d–Si = 114.4°). Considering these results as well as the relatively large $\bar{\chi}$ of the non-tetrahedral cations (Al) in sillimanite, the fact that Si–O(nbr) = 1.629 Å and Al–O(nbr) = 1.758 Å are intermediate in length between Si–O_c and Si–O_d and Al–O_c and Al–O_d, respectively, is predictable and not at variance with the hypothesis of double bonding. In other words, when $\bar{\chi}$ and T–O–T angle are both large (T = Al, Si), the ⟨T–O(nbr)⟩ bonds are expected to be longer than ⟨T–O(br)⟩ bonds; but when $\bar{\chi}$ is large and the angle is narrow, the ⟨T–O(nbr)⟩ bonds are expected to be shorter than or equal to the ⟨T–O(br)⟩⟩ bonds.

Tetrahedral Ordering in Silicates

The well-known Al-avoidance rule (Loewenstein, 1954), which Goldsmith and Laves (1955) explained in terms of Pauling's rule of local valence neutralization, is usually invoked to explain the observed distributions of tetrahedral Al and Si and the almost total absence of tetrahedral Al–O(br)–Al linkages in silicates. As discussed above, valence neutralization is believed to be achieved by some means of charge transfer from anion to cation, whether it is by ionic or covalent bonding, or more probably, by a mixture of the two, including a degree of electron delocalization associated with double bonding. If double bonding is significant in the tetrahedral portion of a silicate, valence neutralization involving Si–O, Al–O, Mg–O, B–O or Be–O bonds, as well as the distribution of these cations, should depend, in part, on their bond orders. Because a difference exists between the predicted π-bond orders for the

---

[1] In cases of significant local charge imbalance at oxygen in structures containing O(br), *e.g.*, the highly underbonded nature of O_c in sillimanite, T–O bonds shorten and T–O–T angles widen to contribute to valence neutralization. On the other hand, for highly overbonded oxygens, *e.g.*, O_d in sillimanite, T–O bonds lengthen and T–O–T angles close.

Si–O (0.32), Al–O (0.18), Mg–O (0.08), B–O (0.0) and Be–O (0.0) bonds in tetrahedral ions, a mechanism for tetrahedral ordering based on the relative bond orders of the T–O bonds is proposed.

Recalling that T–O(br) bonds in T–O–T linkages with wide angles are usually of higher bond order than those involved in narrow angles and that Al, B, Be and Mg have lower "π-bonding potentials" in tetrahedral coordination than Si, the following proposal concerning tetrahedral site preference in framework silicates can be made:

> Si should prefer those tetrahedral sites involved in the widest average T–O–T angles and Al, B, Be or Mg those involved in the narrowest average T–O–T angles.

This proposal is examined below for a number of silicates and appears to apply to the framework but not to the non-framework silicates in general.

The ordering of Al and Si in the framework silicate low albite (Ribbe, Megaw and Taylor, 1969) has been discussed (Brown, Gibbs and Ribbe, 1969b; Stewart and Ribbe, 1969) in terms of the proposal, and it was pointed out that Al, with lower predicted "π-bonding potential" than Si, prefers the $T_1(0)$ site, in part, because the average $T_1(0)$–O–T angle is 3 to 10° smaller than the average T–O–T angles to the T_1(m). $T_2(0)$ and $T_2(m)$ tetrahedral sites. In disordered high albite (Ribbe *et al.*, 1969) the average T–O–T angles to the $T_1(m)$, $T_2(0)$ and $T_2(m)$ tetrahedra are all slightly smaller than those in ordered low albite, whereas the average $T_1(0)$–O–T angle is larger. Therefore, it appears that upon ordering the structure adopts a configuration which tends to optimize the overlap of $d\pi$- and $p\pi$-orbitals on T and O, respectively, with wider T–O–T angles being formed at the Si-rich sites. Ideally, we would also expect the angle at the Al-rich site to widen with ordering. However, this does not take place, possibly because the change of angle for the Al-rich site will have less effect in altering the potential energy of the structure than corresponding changes in angle at the Si-rich sites.

Because of the preceding observations, Table 1 was prepared including data from eight additional, precisely determined framework structures containing Si and Al, B, Mg or Be in tetrahedral coordination. In each case the average T–O–T angles to the Si-rich tetrahedra are widest with the possible exception of maximum microcline where the average T–O–T angles to the Si-rich sites is only 0.3° wider than that to the Al-rich site. However, tetrahedral Al in low albite, osumilite, low-cordierite, laumontite and natrolite, tetrahedral B in reedmergnerite, tetrahedral Be in beryl and tetrahedral Mg and Al in Mg-rich cordierite all prefer those sites involved in the narrowest average T–O–T angles, agreeing with the smaller predicted degree of dπ-orbital participation of Al and Mg relative to Si

TABLE I: AVERAGE T–O–T ANGLES FOR SI-RICH AND AL-, B-, MG- OR BE-RICH TETRAHEDRA IN NINE FRAMEWORK SILICATES.

Mineral	$<T\text{–O–}T>$ (Si-rich tetrahedra)	$<T\text{–O–}T>$ (Al-, B-, Mg- or Be-tetrahedra)	Reference
Low albite	141.7°	136.0°	Ribbe, *et al.* (1969)
Reedmergnerite	140.2°	136.0°[a]	Appleman and Clark (1965)
Maximum microcline	141.9°	141.6°	Finney and Bailey (1964)
Osumilite	150.1°	125.0°	Brown and Gibbs (1969a)
Beryl	168.3°	127.0°[b]	Gibbs, Breck and Meagher (1968)
Low-cordierite	145.3°	139.7°	Gibbs (1966)
Mg-rich cordierite	151.6°	129.0°[c]	Meagher and Gibbs (1967)
Natrolite	145.2°	142.2°	Meier (1960)
Laumontite	140.3°	136.4°	Schramm and Fischer (1970)

[a] B-rich tetrahedra
[b] Be-rich tetrahedra
[c] Mg, Al-rich tetrahedra

and the negligible degrees of dπ-orbital participation expected for the B and Be atoms. The proposal cannot be verified for those framework silicates like anorthite which consist of a perfect alternation of Al-rich and Si-rich tetrahedra (Megaw, Kempster and Radoslovich, 1962) because the T–O–T angles at the Al-rich sites must perforce equal those at the Si-rich sites on the average.

The proposal is also consistent with the distribution of Al and Si in the rare, non-framework silicate zunyite (Pauling, 1933; Kamb, 1960) where Si is ordered into a T_5O_{16} group consisting of four peripheral tetrahedra with three O(nbr) and one O(br) and a central tetrahedron with four O(br) and where Al is ordered into an isolated tetrahedron with four O(nbr). The T_d point symmetry of the T_5O_{16} group requires that the T–O–T angle equals 180° permitting maximum d-p π-overlap. This example suggests that T–O–T angle may play a role in tetrahedral ordering in silicates containing both O(br) and O(nbr). However, Zagal'skaya and Belov (1962) question the Pauling-Kamb distribution and suggest that Al occupies the central tetrahedron in the T_5O_{16} group with Si occupying the isolated tetrahedron. The Zagal'skaya-Belov distribution results in severe charge imbalances and violates the proposal on tetrahedral ordering. Nevertheless, because the estimated bond length and angle errors are relatively large (Kamb, 1960) and because the Si–O(br) bonds are somewhat longer than expected for a straight Si–O–Si angle and a relatively large $\bar{\chi}$, a study of F- and OH-containing zunyites is currently underway at VPI to clarify the Al/Si distribution as well as to establish the steric effects induced by replacing OH by F.

Papike, Ross and Clark (1969) have refined the structure of the Kakanui hornblende and have reported the following Al/Si occupancies estimated from a Smith-Bailey type plot (Smith and Bailey, 1963) for the $T(1)$ and $T(2)$ sites in the double chain: $T(1)$ (0.34 Al, 0.66 Si), $T(2)$ (0.16 Al, 0.84 Si). In this laboratory K. Robinson (pers. commun.) has since undertaken a site refinement for the Kakanui hornblende as well as for pargasite and kaersutite and has found that the $T(2)$ site in each contains only Si whereas the $T(1)$ site contains equal amounts of both Al and Si. However, these distributions are not consistent with the proposal on tetrahedral ordering because the average T–O–T angle to the Al-rich site is 0.2 to 1.0° larger than that to the Si-rich site. In view of this observation, additional factors such as local charge balance and the number of available lone pairs on oxygen must be operative in controlling the preference of Al for the $T(1)$ site. Gibbs (1969) has explained the distribution of Al and Si in these minerals in terms of the underbonded nature of O(4) and the suggestion that a relatively strong π-bond forms between Si(2) and O(4). Further examination shows that because all other oxygens are effectively four-coordinated and probably lack lone pairs, O(4) is the only oxygen in these hornblendes which may have a lone pair orbital available for strong π-bond formation. Accordingly, because Si has a higher "π-bonding potential" than Al, Si probably prefers the $T(2)$ site in order to take advantage of this lone pair in spite of the slightly wider average T–O–T angle to the $T(2)$ site. The ordering of Be and Si in the Be-containing amphibole, joesmithite, (Moore, 1969) can be rationalized in a similar fashion as pointed out in part by Moore.

The general lack of Al/Si ordering in the layer silicates has been discussed by Bailey (1967) who concludes that tetrahedral ordering is more difficult for a layer silicate than for a coexisting phase such as microcline or low albite. However, one exception is $3T$ muscovite (Güven and Burnham, 1967) where partial ordering of Al and Si is indicated by the mean T–O bond lengths. In the majority of sheet silicates all tetrahedra are of one basic type: the corresponding bridging and non-bridging oxygens for each tetrahedron have nearly identical coordination numbers and in any one sheet structure the average T–O–T angle for each tetrahedral site is constant. This results in tetrahedral sites of similar "π-bonding potential" and may explain the absence of ordering in most of these structures. A similar lack of tetrahedral Al/Si ordering is characteristic of the $C2/c$ pyroxenes (Peacor, 1967) because there is only one unique T–O–T angle and, as in the sheet silicates, only one unique type of tetrahedron.

The proposal on tetrahedral ordering was not tested for the melilites (Smith, 1953a; Louisnathan, 1969). $Y_2SiBe_2O_7$ (Bartram, 1969) or sapphirine (Moore, 1969a) because all of the *T*–O–*T* angles are not reported. Examination of local charge balance and coordination of oxygen in these structures, however, offers no explanation for the observed tetrahedral distributions. The most serious violations of the proposal made for the framework silicates are found in the non-framework silicates delhayelite (Cannillo, Rossi and Ungaretti, 1969), zussmanite (Lopes-Vieira and Zussman, 1969) and bavenite (Cannillo, Coda and Fagnani, 1966) where Si is found in tetrahedra with the smaller average *T*–O–*T* angles. These violations indicate that the proposal cannot be extended to include non-framework silicates in general and that the effect of *T*–O–*T* angle is not the factor controlling tetrahedral ordering in these structures.

The Be/Si distribution in leucophanite (Cannillo, Guiseppetti and Tazzoli, 1967) and meliphanite (Negro, Rossi and Ungaretti, 1967) can be related to the presence of TO_3F tetrahedral ions. Because the *p*-orbitals on fluorine will be smaller than those on oxygen, the Si(3*d*)-F(2*p*) overlap will be less than the Si(3*d*)-O(2*p*) overlap, leading to the ordering of Be into the TO_3F tetrahedra and of Si into the TO_4 tetrahedra. $TO_3(OH)$ and $TO_2(OH)_2$ tetrahedra also show a stronger affinity for cations other than Si or Al (for example, Zn in hemimorphite [McDonald and Cruickshank, 1967b], Be in aminoffite [Coda, Rossi and Ungaretti, 1967]; epididymite [Ito, 1947], euclase [Mrose and Appleman, 1962] and bertrandite [Solovieva and Belov, 1961] and B in datolite [Pant and Cruickshank, 1967]), suggesting that the *p*-orbitals on the hydroxyl oxygen are reduced in size, leading to smaller *d*-*p* π-overlap and a loss of double-bond character in the *T*–O(··· H) bonds (Cruickshank, 1961; Cruickshank and Robinson, 1966). The segregation of Be into $TO_3(OH)$ tetrahedra in bavenite is consistent with this reasoning.

In conclusion, the basic stereochemistry of the tetrahedral portion of a silicate is dictated primarily by the constraints imposed by ionic and σ-covalent bonding requirements. Cruickshank's π-bonding hypothesis represents a refinement of the theory and provides a more flexible framework within which the finer structural details can be rationalized. His hypothesis also permits an interpretation of the SiK_β X-ray emission (Dodd and Glen, 1969) and $L_{2,3}M$ X-ray fluorescence spectra of Si (Urch, 1969) for silicate minerals and glasses in terms of qualitative correlation diagrams deduced from (1) symmetry properties of the molecular orbitals for a SiO_4^{4-} ion with T_d symmetry and (2) estimates of relative binding energies of electrons in the atomic orbitals on oxygen and silicon. On the other hand, Mitchell (1969) has stated that "one cannot . . . expect experiments to establish whether *d*-orbitals are 'really' used, anymore than experiments can show *s* and *p* orbitals definitely occur in the bonding of first-row elements."

ACKNOWLEDGMENTS

The authors would like to thank Professor D. W. J. Cruickshank of the Chemistry Department at the University of Manchester Institute of Science and Technology, Manchester, England, M. W. Phillips and Professors F. D. Bloss and P. H. Ribbe of the Department of Geological Sciences and Professor J. C. Schug of the Chemistry Department, the Virginia Polytechnic Institute at Blacksburg, Virginia, Dr. J. W. McCauley at the Army Materials and Mechanics Research Center, Watertown, Massachusetts and Professor C. T. Prewitt of the Department of Earth and Space Sciences, SUNY at Stony Brook, New York for critically reviewing the manuscript and making helpful suggestions. The National Science Foundation is gratefully acknowledged for supporting Grants GA-1133 and GA-12702.

REFERENCES

APPLEMAN, D. E., AND J. R. CLARK (1965) Crystal structure of reedmergnerite, a boron albite and its relation to feldspar crystal chemistry. *Amer. Mineral.* **50,** 1827–1850.

BAILEY, S. W. (1967) *Layer Silicates.* Amer. Geol. Inst., Washington, D. C., p. SB-9C.

BARTRAM, S. F. (1969) Crystal structure of $Y_2SiBe_2O_7$. *Acta Crystallogr.*, **B25,** 791–795.

BAUER, W. H. (1962) Zur Kristallchemie der Salzhydrate. Die Kristallstrukturen von $MgSO_4 \cdot 4H_2O$ (Leonhardtit) und $FeSO_4 \cdot 4H_2O$ (Rezenit). *Acta Crystallogr.* **15,** 815–826.

BEAGLEY, B., D. W. J. CRUICKSHANK AND T. G. HEWITT AND (in part) A. HALLAND (1967) Molecular structures of P_4O_{10} and P_4O_9. *Trans. Faraday Soc.* **63,** 836–845.

BISSEY, J. E. (1967) Some aspects of d-orbital participation in phosphorous and silicon chemistry. *J. Chem. Educ.* **44,** 95–100.

BROWN, G. E., AND G. V. GIBBS (1969a) Refinement of the crystal structure of osumilite. *Amer. Mineral.* **54,** 101–116.

———, AND ——— (1969b) Oxygen coordination and the Si–O bond. *Amer. Mineral.* **54,** 1528–1539.

———, AND ——— (1970) The variation of the Si–O bond lengths, Si–O–Si and O–Si–O angles in the chain and sorosilicates. [Abstr.] *Amer. Mineral.* **55,** 298.

———, ———, AND P. H. RIBBE (1969a) The nature and variation in length of the Si–O and Al–O bonds in framework silicates. *Amer. Mineral.* **54,** 1044–1061.

———, ———, AND ——— (1969b) The role of d-p π–bonding in minerals containing SiO_4^{4-}, AlO_4^{5-} and MgO_{6-} tetrahedral ions. [Abstr.] *Geol. Soc. Amer. Abstr. Programs 1969, pt. 4,* p. 11.

BURNHAM, C. W. (1963) Refinement of the crystal structure of sillimanite. *Z. Kristallogr.* **118,** 127–148.

CALVO, CRISPIN (1965a) Refinement of the crystal structure of β-Mg P_2O_7. *Can. J. Chem.* **43,** 1139–1146.

——— (1965b) The crystal structure and phase transitions of β-$Zn_2P_2O_7$. *Can. J. Chem.* **43,** 1147–1153.

——— (1967) The crystal structure of α-$Mg_2P_2O_7$. *Acta Crystallogr.* **23,** 289–295.

——— (1968) The crystal structure of α-$Ca_2P_2O_7$. *Inorg. Chem.* **7,** 1345–1351.

CANNILLO, E., G. ROSSI, AND L. UNGARETTI (1968) The crystal structure of macdonaldite. *Accad. Naz. Dei Lincei,* **45,** 399–414.

———, AND ——— (1969) The crystal structure of delhayelite. *Rend. Soc. Ital. Mineral. Petrologia*, **26,** 3–15.

———, A. CODA, AND G. FAGNANI (1966) The crystal structure of bavenite. *Acta Crystallogr.* **20,** 301–309.

———, G. GUISEPPETTI AND V. TAZZOLI (1967) The crystal structure of leocophanite. *Acta Crystallogr.* **23,** 255–259.

CHRISTENSEN, A. N., AND R. G. HAZELL (1967) The crystal structure of $NaIn(SiO_3)_2$. *Acta Chem. Scand.* **21,** 1425–1429.

CLARK, J. R., D. E. APPLEMAN, AND J. J. PAPIKE (1968) Bonding in eight ordered clinopyroxenes isostructural with diopside. *Contrib. Mineral. Petrology*, **20,** 81–85.

CODA, A. (1968) A review of the structures of some silicates recently studied. *Izvj. Jugoslav. Centr. Krist. (Zagreb)*, **3,** 5–20.

——— (1969) Le distanze silicio-ossigeno in alcuni silicati recentemente studiati. *Atti. Soc. Ital. Sci. Natur. Museo Civico Storia Natur. Milano*, **109,** 491–510.

COTTON, F. A. (1963) *Chemical Applications of Group Theory,* Interscience Publishers, New York, New York, p. 94–95.

———, AND G. WILKINSON (1966) *Advanced Inorganic Chemistry, 2nd Ed.*, Interscience Publishers, New York, New York, p. 363.

COULSON, C. A., AND T. W. DINGLE (1968) the B–O bond lengths in boron-oxygen compounds. *Acta Crystallogr.* **B24,** 153–155.

CRUICKSHANK, D. W. J. (1961) The role of 3d-orbitals in π-bonds between (a) silicon, phosphorus, sulfur, or chlorine and (b) oxygen or nitrogen. *J. Chem. Soc.* **1961,** 5486–5504.

——— (1964a) Refinements of structures containing bonds between Si, P, S or Cl and O or N. II. $Na_4P_2O_7 \cdot 10H_2O$. *Acta Crystallogr.* **17,** 672–673.

——— (1964b) Refinements of structures containing bonds between Si, P, S or Cl and O or N. III. $Na_5P_3O_{10}$; Phase II. *Acta Crystallogr.* **17,** 674–675.

——— (1964c) Refinements of structures containing bonds between Si, P, S or Cl and O or N. IV. $(NH_4)_4P_4O_{12}$. *Acta Crystallogr.* **17,** 675–676.

——— (1964d) Refinements of structures containing bonds between Si, P, S or Cl and O or N. VI. P_2O_5, Form III. *Acta Crystallogr.* **17,** 679–680.

——— (1964e) Refinements of structures containing bonds between Si, P, S or Cl and O or N. VII. $(RbPO_3)_\infty$. *Acta Crystallogr.* **17,** 681–682.

———, H. LYNTON, AND (in part) G. A. BARCLAY (1962) A reinvestigation of the crystal structure of thortveitite $Sc_2Si_2O_7$. *Acta Crystallogr.* **15,** 491–498.

———, AND E. A. ROBINSON (1966) Bonding in orthophosphates and orthosulphates. *Spectrochim. Acta*, **22,** 555–563.

DOLLASE, W. A. (1968) Refinement and comparison of the structures of zoisite and clinozoisite. *Amer. Mineral.* **53,** 1882–1898.

DODD, C. G., AND G. L. GLEN (1969) A survey of chemical bonding in silicate minerals by x-ray emission spectroscopy. *Amer. Mineral.* **54,** 1299–1311.

DOUGLAS, B. E., AND D. H. MCDANIEL (1965) *Concepts and Models of Inorganic Chemistry,* Blaisdell Publishing Company, New York, New York.

FINGER, L. W. (1969) The crystal structure and cation distribution of a grunerite. *Mineral. Soc. Amer. Spec. Pap.* **2,** 95–100.

FINNEY, J. J., AND S. W. BAILEY (1964) Crystal structure of authigenic maximum microcline. *Z. Kristallogr.* **119,** 413–436.

FREED, R. L., AND D. R. PEACOR (1967) Refinement of the crystal structure of johannsenite *Amer. Mineral.* **52**. 709–720.

FYFE, W. S. (1954) The problem of bond type. *Amer. Mineral.* **39,** 991–1004.

GIBBS, G. V. (1966) The polymorphism of cordierite I: The crystal structure of low cordierite. *Amer. Mineral.* **51,** 1068–1087.

——— (1969) The crystal structure of protoamphibole. *Mineral. Soc. Amer. Spec. Pap.* **2,** 101–109.

———, D. W. BRECK AND E. P. MEAGHER (1968) Structural refinement of hydrous and anhydrous synthetic beryl, $Al_2(Be_3Si_6)O_{18}$ and emerald, $Al_{1.9}Cr_{0.1}(Be_3Si_9)O_{18}$. *Lithos,* **1,** 275–285.

———, AND G. E. BROWN (1969) Oxygen coordination and the Si-O bond. (abstr.) *Geol. Soc. Amer., Spec. Pap.* **121.**

GILLESPIE, R. J. (1963) The valence-shell electron-pair repulsion (VSEPR) theory of directed valency. *J. Chem. Educ.* **40,** 295–301.

———, AND E. A. ROBINSON (1964) Characteristic vibrational frequencies of compounds containing Si-O-Si, P-O-P, S-O-S, and Cl-O-Cl bridging groups: Force constants and bond orders for the bridge bonds. *Can. J. Chem.* **42,** 2496–2503.

GOLDSMITH, J. R. AND F. LAVES (1955) Cation order in anorthite ($CaAl_2Si_2O_8$) as revealed by gallium and gernamium substitutions. *Z. Kristallogr.* **106,** 213–226.

GUVEN, N., AND C. W. BURNHAM (1967) The crystal structure of 3T muscovite. *Z. Kristallogr.* **125,** 163–183.

ITO, T. (1934) The structure of epididymite, $HNaBeSi_3O_8$. *Z. Kristallogr.* **88,** 142–149.

——— (1947) The structure of eudidymite ($HNaBeSi_3O_8$). *Amer. Mineral.* **32,** 442–453.

JARCHOW, O. H (1964) Die Strukturverfeinerung des zweidimensional fehlgeordneter Natruimmetaphosphates, $Na_2H_2P_4O_{12}$. *Acta Crystallogr.* **17,** 1253–1262.

KAMB, B. (1960) The crystal structure of zunyite. *Acta Crystallogr.* **13,** 15–24.

LAZAREV, A. N. (1964) Polymorphism of molecules and complex ions in oxygen compounds of silicon and phosphorus report I. Nature of the Si-O-Si bonds and values of the valence angles of oxygen. *Izv. Akad. Nauks SSSR, Ser. Khim.* **2,** 235–241.

LOEWENSTEIN, W. (1954) The distribution of aluminum in the tetrahedra of silicates and aluminates. *Amer. Mineral.* **39,** 92–96.

LOPES-VIEIRA, A., AND Z. ZUSSMAN (1969) Further detail on the crystal structure of zussmanite. *Mineral. Mag.* **37,** 49–60.

LOUISNATHAN, S. J. (1969) The nature of Mg-Al-Si ordering in melilites, $(Ca, Na)_2$ (Mg,Al) $(Al,Si)_2O_7$ and the crystal structure of fresnoite, $Ba_2(TiO)Si_2O_7$, Ph.D. Thesis, University of Chicago.

MCADAM, A., K. H. JOST, AND B. BEAGLEY (1968) Refinement of the structure of sodium kurrol salt $(NaPO_3)_x$, Type A. *Acta Crystallogr.* **B24,** 1621–1622.

MCDONALD, W. S., AND D. W. J. CRUICKSHANK (1967a) A reinvestigation of the structure of sodium metasilicate, Na_2SiO_3. *Acta Crystallogr.* **22,** 37–43.

———, AND ——— (1967b) Refinement of the structure of hemimorphite. *Z. Kristallogr.* **124,** 180–191.

MEAGHER, E. P., AND G. V. GIBBS (1968) Tetrahedral magnesium in cordierite. [abstr.] *Geol. Soc. Amer. Spec. Pap.* **115.**

MEGAW, H. D., C. J. E. KEMSTER, AND E. W. RADOSLOVICH (1962) The structure of anorthite, $CaAl_2Si_2O_8$ II. Description and discussion. *Acta Crystallogr.* **15,** 1017–1035.

MEIER, W. M. (1960) The crystal structure of natrolite. *Z. Kristallogr.* **113,** 430–444.

MITCHELL, K. A. R. (1969) The use of outer d-orbitals in bonding. *Chem. Rev.* **69,** 157–178.

MOORE, P. B. (1969a) The crystal structure of sapphirine. *Amer. Mineral.* **54,** 31–49.

——— (1969b) Joesmithite: a novel amphibole crystal chemistry. *Mineral. Soc. Amer. Spec. Pap.* **2,** 111–115.

MROSE, M. E., AND D. E. APPLEMAN (1962) The crystal structures and crystal chemistry of väyrynerite $(Mn,Fe)BePO_4(OH)$ and euclase, $AlBeSiO_4(OH)$. *Z. Kristallogr.* **117,** 16–36.

NEGRO, A., G. ROSSI, AND L. UNGRETTI (1967) The crystal structure of meliphanite. *Acta Crystallogr.* **23,** 260–264.

NOLL, W. (1963) The silicate bond from the standpoint of electronic theory. *Angew. Chem.* [Int. ed.], **2,** 73–80.

ONDIK, H. M. (1964) The structure of the triclinic form of sodium tetrametaphosphate tetrahydrate. *Acta Crystallogr.* **17,** 1139–1145.

PANT, A. K. (1968) A reconsideration of the crystal structure of β-$Na_2Si_2O_5$. *Acta Crystallogr.* *B***24,** 1077–1083.

——— AND D. W. J. CRUICKSHANK (1967) A reconsideration of the structure of datolite, $CaBSiO_4(OH)$. *Z. Kristallogr.* **125,** 286–297.

——— AND, ——— (1968) The crystal structure of α-$Na_2Si_2O_5$. *Acta Crystallogr.* **B24,** 13–19.

PAPIKE, J. J., AND J. R. CLARK (1968) The crystal structure and cation distribution of glaucophane. *Amer. Mineral.* **53,** 1156–1173.

———, MALCOLM ROSS, AND JOAN R. CLARK (1969) Crystal-chemical characterization of clinoamphiboles based on five new structure refinements. *Mineral. Soc. of Amer. Spec. Pap.*, **2,** 117–136.

PAULING, LINUS (1929) The principles determining the structure of complex ionic crystals. *J. Amer. Chem. Soc.* **51,** 1010–1026.

——— (1933) The crystal structure of zunyite. *Z. Kristallogr.* **84,** 442–447.

PEACOR, D. R. (1967) Refinement of the crystal structure of a pyroxene of formula M_IM_{II} $(Si_{1.5}Al_{0.5})O_6$, *Amer. Mineral.* **52,** 31–41.

——— AND, M. J. BUERGER (1962b) The determination and refinement of the structure of narsarsukite, $Na_2TiOSi_4O_{10}$. *Amer. Mineral.* **47,** 539–556.

———, AND ——— (1962a) Determination and refinement of the crystal structure of bustamite, $CaMnSi_2O_6$. *Z. Kristallogr.* **117,** 331–343.

———, AND N. NIIZEKI (1963) The redetermination and refinement of the crystal structure of rhodonite, $(Mn,Ca)SiO_3$. *Z. Kristallogr.* **119,** 98–116.

PREWITT, C. T. (1967) Refinement of the structure of pectolite, $Ca_2NaHSi_3O_9$. *Z. Kristallogr* **125,** 298–316.

———, AND M. F. BUERGER (1963) Comparison of the crystal structures of wollastonite and pectolite. *Mineral. Soc. Amer., Spec. Pap.*, **1,** 293–302.

———, AND C. W. BURHNAM (1966) The crystal structure of jadeite, $NaAlSi_2O_6$. *Amer. Mineral.* **51,** 956–975.

RIBBE, P. H., H. D. MEGAW, AND W. H. TAYLOR (1969) The albite structures. *Acta Crystallogr.* **B25,** 1503–1518.

ROBERTSON, B. E., AND C. CALVO (1967) The crystal structure and phase transformation of α-$Cu_2P_2O_7$. *Acta Crystallogr.* **22,** 665–672.

——— (1968) Crystal structure of β-$Cu_2P_2O_7$. *Can. J. Chem.* **46,** 605–612.

SCHOMAKER, V., AND D. P. STEVENSON (1941) Some revisions of the covalent radii and the additivity rule for the lengths of partially ionic single covalent bonds. *J. Amer. Chem. Soc.* **63,** 37–40.

SCHRAMM, V., AND K. F. FISHER (1970) Refinement of the crystal structure of laumontite. Advances in Chemistry series.

SHANNON, R. D., AND C. T. PREWITT (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.* **B24,** 925–946.

SMITH, J. V. (1953a) Reexamination of the crystal structure of melilite. *Amer. Mineral.* **38,** 643–661.

——— (1953b) The crystal structure of tilleyite. *Amer. Mineral.* **6,** 9–18.

———, AND S. W. BAILEY (1963) Second review of Al-O and Si-O tetrahedral distances. *Acta Crystallogr.* **16,** 801–811.

SOLOVIEVA, L. P., AND N. V. BELOV (1961) Crystal structure of bertrandite. *Dokl. Akad. Nauk SSSR* **140,** 685–688.

STEWART, D. B., AND P. H. RIBBE (1969) Structural explanation for variations in cell parameters of alkali feldspar with Al/Si ordering. *Amer. J. Sci.,* **267A,** 444–462.

SVANSON, S. E. (1969) π-Electron charge density on boron in the borate structures. *Acta Scand.* **23,** 2005–2015.

TAKEUCHI, Y., AND W. JOSWIG (1967) The crystal structure of haradaite and a note on the Si-O bond lengths in silicates. *Mineral. J.* [Tokyo] **5,** 98–123.

URCH, D. S. (1969) Direct evidence for $3d$-$2p$ π-bonding in oxy-anions. *J. Chem. Soc., A,* 3026–3028.

ZACHARIASEN, W. H. (1968) The crystal structure of monoclinic metahoric acid. *Acta. Crystallogr.* **16,** 385–389.

ZAGAL' SKAYA, Y. G., AND N. V. BELOV (1962) The crystal structure of zunyite. *Kristallografiya,* **8,** 533–538. [Transl, *Sov. Phys. Crystallogr.* **8,** 429–432.]

Manuscript received, January 26, 1970; accepted for publication, March 9, 1970.