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OXYGEN COORDINATION AND THE Si-O BOND

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Abstract

The mean Si-O bond length in a silicate has been found to depend, in part, on the average cation coordination of oxygen and the predicted *s*-character of the metal-oxygen bonds. Individual Si-O(nbr) bond lengths in four *C*2/*m* amphiboles, which apparently deviate from this correlation, are discussed in terms of *d*-*p* π-bonding and the average electronegativity of the other cations bonded to O(nbr). A correlation exists between the Si-O(nbr) bond length in these amphiboles and the average electronegativity of the nontetrahedral cations bonded to O(nbr); longer Si-O(nbr) bonds are associated with the more electronegative cations.

Introduction

In structural refinements of low cordierite (Gibbs, 1966) and beryl (Gibbs, Breck, and Meagher, 1968), the Si-O bonds for oxygen anions coordinated by two cations were found, on the average, to be significantly shorter (1.595 Å) than those for oxygen anions coordinated by three (1.625 Å). Megaw, Kempster and Radoslovich (1962), Slaughter (1966) and McDonald and Cruickshank (1967a) have noted similar correspondences between tetrahedral bond lengths and oxygen coordination. These observations, suggesting that the Si-O distances in a silicate may depend, in part, on the coordination of the oxygen anion, have led to a review of the grand mean Si-O distance in terms of the mean coordination number of oxygen for a number of silicates (Gibbs and Brown, 1968).

Results and Discussion

Figure 1 is a scatter diagram showing the variation of $\overline{\text{Si-O}}$ (grand mean Si-O distance) with $\overline{\text{C.N.}}$ (mean coordination number of the oxygen anion bonded to Si) for 46 three-dimensionally refined structures (Table 1). Feldspar and zeolite data were not included in this study because of the difficulty encountered in making an unambiguous determination of the average coordination number of oxygen. Also, the data for Na_2SiO_3 (McDonald and Cruickshank, 1967b), α-$Na_2Si_2O_5$ (Pant and Cruickshank, 1968) and β-$Na_2Si_2O_5$ (Pant, 1968) were not included because of the highly electropositive nature of Na and the concomitant development of strong *d*-*p* π-bonding which, in these cases, apparently overrides the effect of cation coordination of oxygen on the Si-O bond. These effects are discussed in more detail below. The correlation coefficient for the data in Fig. 1 (0.78) indicates that about 60 percent of the variation can be explained in terms of a linear dependence of $\overline{\text{Si-O}}$

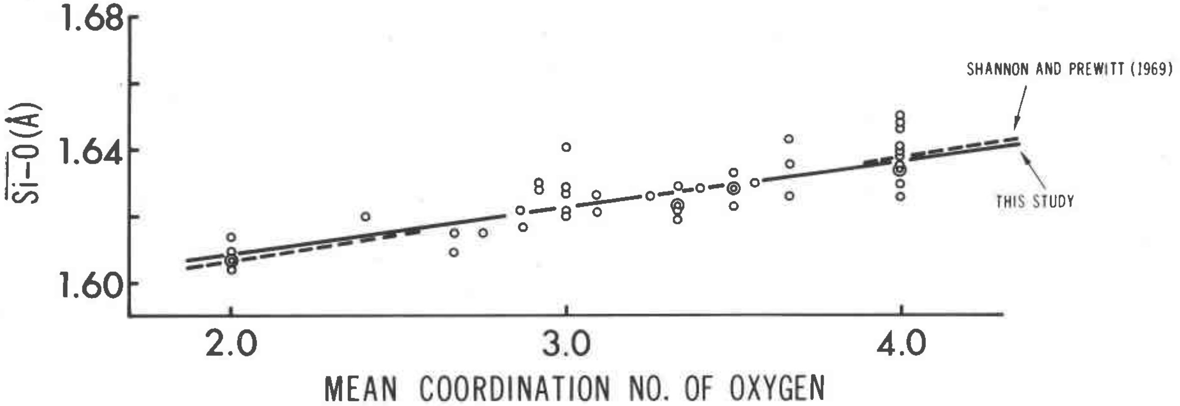

FIG. 1. Variation of grand mean Si-O bond length ($\overline{\text{Si-O}}$) with mean coordination number of oxygen ($\overline{\text{C.N.}}$) for 46 three-dimensionally refined silicate structures. The equation of the regression line is $\overline{\text{Si-O}}=0.015\ \overline{\text{C.N.}}+1.579$. Dashed line from Shannon and Prewitt (1969); solid line this study. Data and references are listed in Table 1.

TABLE 1. VARIATION OF GRAND MEAN Si-O DISTANCE WITH MEAN COORDINATION NUMBER

Silicate	$\overline{\text{Si-O}}$[a]	$\overline{\text{C.N.}}$[b]	Reference
low quartz	1.607Å	2.00	Young and Post (1962)
low quartz	1.607	2.00	Smith and Alexander (1963)
low quartz	1.609	2.00	Zachariasen and Plettinger (1965)
low cristobalite	1.604	2.00	Dollase (1965)
coesite	1.614	2.00	Zoltai (personal communication)
narsarsukite	1.620	2.40	Peacor and Buerger (1962)
beryl	1.609	2.67	Gibbs, Breck and Meagher (1968)
cordierite	1.615	2.67	Gibbs (1966)
sillimanite	1.615	2.75	Burnham (1963)
thortveitite	1.622	2.86	Cruickshank, Lynton and Barclay (1962)
protoamphibole	1.617	2.87	Gibbs (1969)
hemimorphite	1.628	2.92	McDonald and Cruickshank (1967a)
larsenite	1.630	2.92	Prewitt, Kirchner and Preisinger (1967)
andalusite	1.627	3.00	Burnham and Buerger (1961)
zircon	1.622	3.00	Robinson and Gibbs (personal communication)
tourmaline	1.621	3.00	Buerger, Burnham and Peacor (1962)
kyanite	1.628	3.00	Burnham (1963)
topaz	1.641	3.00	Ribbe and Gibbs (1969)
cummingtonite	1.627	3.09	Fischer (1966)
glaucophane	1.621	3.09	Papike and Clark (1968)
hodgkinsonite	1.626	3.25	Rentzeperis (1963)
orthoferrosilite	1.619	3.33	Burnham (1967)
clinoferrosilite	1.629	3.33	Burnham (1967)
spodumene	1.622	3.33	Clark, Appleman and Papike (1968)
iron spodumene	1.623	3.33	Clark, Appleman and Papike (1968)
bustamite	1.623	3.33	Peacor and Buerger (1962)
rhodonite	1.628	3.40	Peacor and Niizeki (1963)
jadeite	1.623	3.67	Prewitt and Burnham (1966)
cosmochlore	1.628	3.67	Clark, Appleman and Papike (1968)
acmite	1.628	3.67	Clark, Appleman and Papike (1968)
$NaInSi_2O_6$	1.633	3.67	Christensen and Hazell (1967)
pectolite	1.630	3.56	Prewitt (1967)
diopside	1.636	3.67	Clark, Appleman and Papike (1968)
johannsenite	1.644	3.67	Freed and Peacor (1967)
wollastonite	1.626	3.67	Prewitt and Buerger (1963)
monticellite	1.626	4.00	Onken (1965)
norbergite	1.630	4.00	Gibbs and Ribbe (1969)
forsterite	1.634	4.00	Birle, Gibbs, Moore and Smith (1968)
hyalosiderite	1.634	4.00	Birle, Gibbs, Moore and Smith (1968)
fayalite	1.638	4.00	Birle, Gibbs, Moore and Smith (1968)
hortonolite	1.639	4.00	Birle, Gibbs, Moore and Smith (1968)
pyrope	1.635	4.00	Gibbs and Smith (1965)
andradite	1.642	4.00	Novak and Gibbs (personal communication)
γ-Ca_2SiO_4	1.647	4.00	Smith, Majumdar and Ordway (1965)
uvarovite	1.649	4.00	Novak and Gibbs (1968)
grossular	1.651	4.00	Prandl (1966)

[a] Grand mean Si-O distance.

[b] Average coordination number of oxygen bonded to silicon.

on $\overline{\text{C.N.}}$ The least-squares line shows that $\overline{\text{Si-O}}$ for individual structures increases from 1.608 Å for structures with a $\overline{\text{C.N.}}$ of two to 1.638 Å for those with a $\overline{\text{C.N.}}$ of four. The two-coordinated value agrees well with that (1.60 Å) quoted by Slaughter (1966); however, his value for three-coordinated oxygen (1.65 Å) is large and in poorer agreement with the value (1.622 Å) obtained in this study. Studies of aliphatic carbon compounds have revealed similar variations in C-C bond lengths as the number of adjacent atoms or bonds increases (Brown, 1959 and Stoicheff, 1962). The trend in Fig. 1 is further supported by Shannon and Prewitt's (1969) independent observation of increases in cation and anion radii with increases in coordination number for oxides and fluorides (see dashed line in Fig. 1). It is also consistent with the work of White and Gibbs (1967) and Dodd and Glen (1968, 1969) on the SiKβ band X-ray emission spectral shifts in crystalline silicates and aluminosilicate glasses. Their data suggest that the average strength of the Si-O bonds in a structure decreases (bonds lengthen) as the average coordination number of the oxygen anions in a structure increases.

Smith and Bailey (1963) attributed differences in $\overline{\text{Si-O}}$ to changes in the degree of polymerization of the SiO$_4$ tetrahedra but recognized that local environment must also be taken into account. The correlation between $\overline{\text{Si-O}}$ and $\overline{\text{C.N.}}$ is more general than that between $\overline{\text{Si-O}}$ and tetrahedral polmerization. For example, the coordination numbers of oxygen anions in a framework structure may vary from two to four with corresponding variations in individual $\overline{\text{Si-O}}$ distances. In anorthite $\overline{\text{C.N.}} = 3.0$ and in low quartz $\overline{\text{C.N.}} = 2.0$; this partly explains why the $\overline{\text{Si-O}}$ (1.614 Å) in anorthite (Megaw, *et al.*, 1962) is slightly longer than the $\overline{\text{Si-O}}$ (1.607 Å) in low quartz (Young and Post, 1962). On the other hand, the correlation of $\overline{\text{Si-O}}$ with tetrahedral polymerization (Smith and Bailey, 1963) predicts the same $\overline{\text{Si-O}}$ for all framework structures.

The correlation between $\overline{\text{Si-O}}$ and $\overline{\text{C.N.}}$ may be explained in part in terms of isovalent hybridization of the atomic orbitals of oxygen where the longer $\overline{\text{Si-O}}$ bond lengths associated with high coordination numbers reflect less s-character in the bond (Fyfe, 1954). For example, the data tabulated below for low quartz (Young and Post, 1962), zircon (Robinson and Gibbs, personal communication) and norbergite (Gibbs and Ribbe, 1969) illustrate the dependence of $\overline{\text{Si-O}}$ on the s-character of the bond predicted using mean M-O-M angles (Moore, 1962).

Mineral	$\overline{\text{Si-O}}$	$\overline{\text{C.N.}}$	$\overline{\text{M-O-M}}$	% s-character of bond
low quartz	1.607 Å	2.0	144°	~35%
zircon	1.622	3.0	120	~29%
norbergite	1.630	4.0	108	~25%

However, this is not the only possible explanation for the correlation of $\overline{\text{Si-O}}$ with $\overline{\text{C.N.}}$, as similar results are predicted by cation-cation repulsion, repulsion between adjacent bonds (Gillespie, 1963) and variation in the π-bond order of the Si-O bond as the bond angles at oxygen change.

The coordination number of oxygen is only one of a number of factors that should be considered in explaining the variation of individual Si-O bond lengths. Brown, Gibbs and Ribbe (1969) discuss some of these other factors for the framework silicates and aluminosilicates, which contain only bridging oxygens, including the dependence of T-O bond lengths (T = Si,Al) on T-O-T angle, on the types of T cations coordinating oxygen and on the nontetrahedral cation-oxygen distances. In the chain silicates which contain both bridging, O(br), and nonbridging, O(nbr), oxygens, the Si-O(nbr) bonds to the three and four-coordinated oxygens may be shorter than the Si-O(br) bonds to two- and three-coordinated oxygens in contradiction to Figure 1. This is especially true when O(nbr) is bonded to one Si and to two or more relatively electropositive cations such as in tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$, where the mean Si-O(nbr) = 1.601 Å and the mean Si-O(br) = 1.640 Å (Papike, Ross, and Clark, 1969). Figure 1 predicts lengths of 1.633 and 1.615 Å respectively, for these bonds, in poor agreement with the observed lengths. However, the shorter Si-O(nbr) bonds to the three- and four-coordinated oxygens in tremolite, are expected if Cruickshank's (1961) d-p-π-bonding theory is applicable to the silicates. Furthermore, because of the relatively low electronegativity of Si, the length of the Si-O(nbr) bond should also depend on the electronegativity of the other cations bonded to O(nbr) (Pant and Cruickshank, 1967).

Few systematic studies have been made relating the variation of Si-O(nbr) bond lengths to the electronegativity of the other cations bonded to O(nbr). Papike and Clark (1968) have found for glaucophane, $Na_2Mg_{2.4}Al_{1.6}FeSi_8O_{22}(OH)_2$, that the Si-O(nbr) bond lengths are about 0.01 Å longer, on the average, than corresponding lengths in tremolite. Moreover, in grunerite, $Fe_2Fe_{4.2}Mg_{0.8}Si_8O_{22}(OH)_2$, (Finger, 1969) the Si-O(nbr) bonds are even longer than those in glaucophane reflecting the higher iron content, the greater average electronegativity of the M-cations, and the increase in the covalency of the M-O(nbr) bonds (cf. Ghose, 1961). Figure 2 illustrates the variation of individual Si-O(nbr) bond lengths with average electronegativity, $\bar{\chi}$, of the M-cations coordinating O(nbr) for four $C2/m$ amphiboles. The data for cummingtonite (Ghose, 1961) were not plotted in Figure 2 because of the uncertainty in its cell edges and chemical composition. However, a refinement of Ghose's data (Mitchell, personal communication) using corrected cell

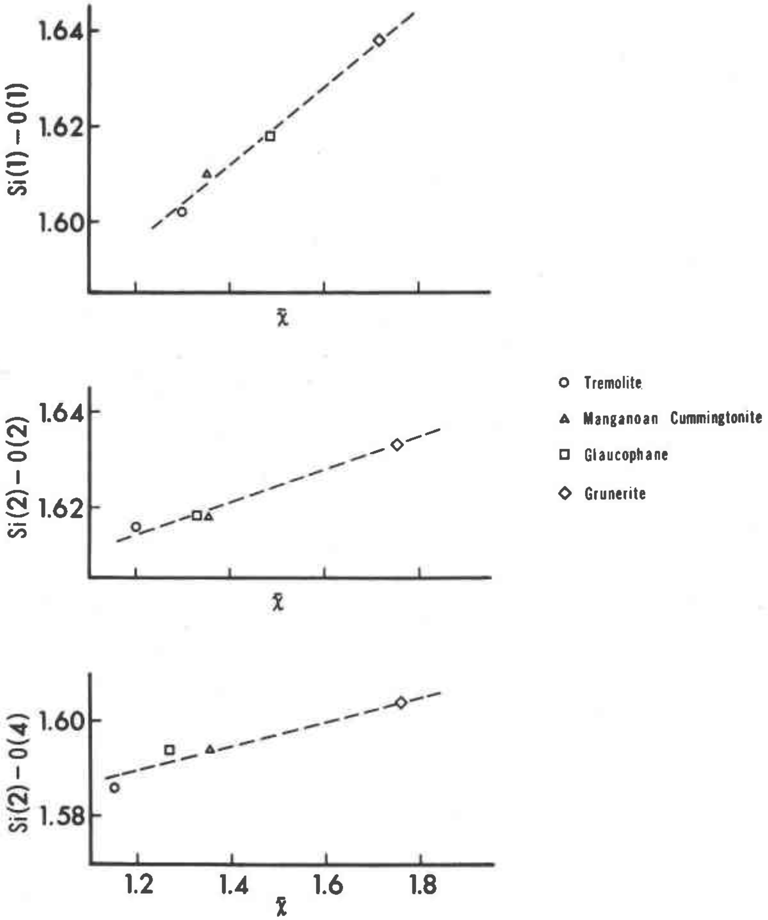

FIG. 2. Variation of Si(1)-O(1), Si(2)-O(2) and Si(2)-O(4) bond lengths for four *C*2/*m* amphiboles [tremolite (Papike, *et al.*, 1969); Managanoan Cummingtonite (Papike, *et al.*, 1969); Glaucophane (Papike and Clark, 1968); Grunerite (Finger, 1969)] with average electronegativity, $\bar{\chi}$, of the non-tetrahedral cations coordinating O(nbr). The amphiboles chosen are of the same structure type and lack cations in the A-site. The electronegativities for elements in various oxidation states were taken from Table 2.9, Douglas and McDaniel (1965).

edges (Ghose, personal communication) resulted in Si-O(nbr) bond lengths which are consistent with the trends in Figure 2. The correlations in Figure 2 are consistent with Noll's (1963), Lazarev's (1964), and McDonald and Cruickshank's (1967b) suggestion that the SiO_4^{4-} ion tends to lose some of its π-bonding potential by forming partial covalent bonds to the more electronegative cations, i.e., the individual Si-O(nbr) bonds should lengthen (π-bond orders decrease) as $\bar{\chi}$ increases. The data for the isostructural pyrophosphates β-$Mg_2P_2O_7$ and β-$Zn_2P_2O_7$ (Calvo, 1965) show this variation, with the P-O(nbr) bond lengths 0.01–0.02 Å longer in β-$Zn_2P_2O_7$ than in β-$Mg_7P_2O_7$.

As $\bar{\chi}$ of the cations coordinating O(1), O(2) and O(4) increases for the four amphiboles, the *M*-O bonds become more covalent, reducing the negative charges on O(1), O(2) and O(4). Part of the residual electron density, δ, remaining on these oxygens is then back donated into the Si-O *d-p* π-bond systems in accordance with the predictions of Pauling's (1948) electroneutrality principle (cf. Waser, 1968). Furthermore, the more residual electron density remaining on an oxygen after allowance is made for transfer of charge to the surrounding σ-bond systems, the greater the possible back donation of electrons from the orbitals on oxygen to the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals on silicon, resulting in shorter Si-O bonds. Figure 3 shows the expected decrease in the Si(1)—O(1), Si(2)—O(2) and Si(2)—O(4) bond lengths as δ on O(1), O(2) and O(4) increases.[1]

The slope of Si(1)—O(1) distance versus $\bar{\chi}$ is significantly greater than those for Si(2)—O(2) and Si(2)—O(4) versus $\bar{\chi}$ (Fig. 2). Similarly, the slope of Si(1)—O(1) distance versus $\delta_{O(1)}$ is more negative than those for Si(2)—O(2) and Si(2)—O(4) versus $\delta_{O(2)}$ and $\delta_{O(4)}$, respectively (Fig. 3). These observations imply that the bond developed between Si(1) and O(1) is weaker and more sensitive to a change in $\bar{\chi}$ than those between Si(2) and O(2) or O(4). This may be related to the fact that O(2) and O(4) are "underbonded" (Zachariasen, 1963), whereas O(1) maintains local charge balance according to Pauling's (1929) classical electrostatic valence rule. In fact, $\delta_{O(4)}$ for the four amphiboles is significantly greater than $\delta_{O(1)}$ or $\delta_{O(2)}$, reflecting the highly "underbonded" nature of O(4) in comparison to O(1) and O(2). The formation of d-p π-bonds between Si and O, in this case, between Si(2) and O(2) and Si(2) and O(4), is part of the mechanism whereby charge transfer and valency

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[1] A number of well known chemists consider the use of electronegativity values, to predict the polar character of bonds, as suspect and theoretically unsound. A summary of these opinions as well as a review of past and present electronegativity scales, their applications and imperfections is given by Pritchard and Skinner (1955, *Chem. Rev.*, **55,** 745–786). The correlations presented above between bond lengths and the quantities $\bar{\chi}$ and δ depend wholly on the electronegativity scale of Allred and Rochow (1958, *J. Inorg. Nucl. Chem.*, **5,** 264–268) and on Pauling's widely used method of predicting the relative covalent and ionic characters of bonds. Even though the criticisms of the electronegativity scale and its applications are in most cases justified, the concept of electronegativity has enabled the correlation and explanation of a large number of observations including those discussed above. Nevertheless, the tenuous position of this concept and its applications should be remembered.

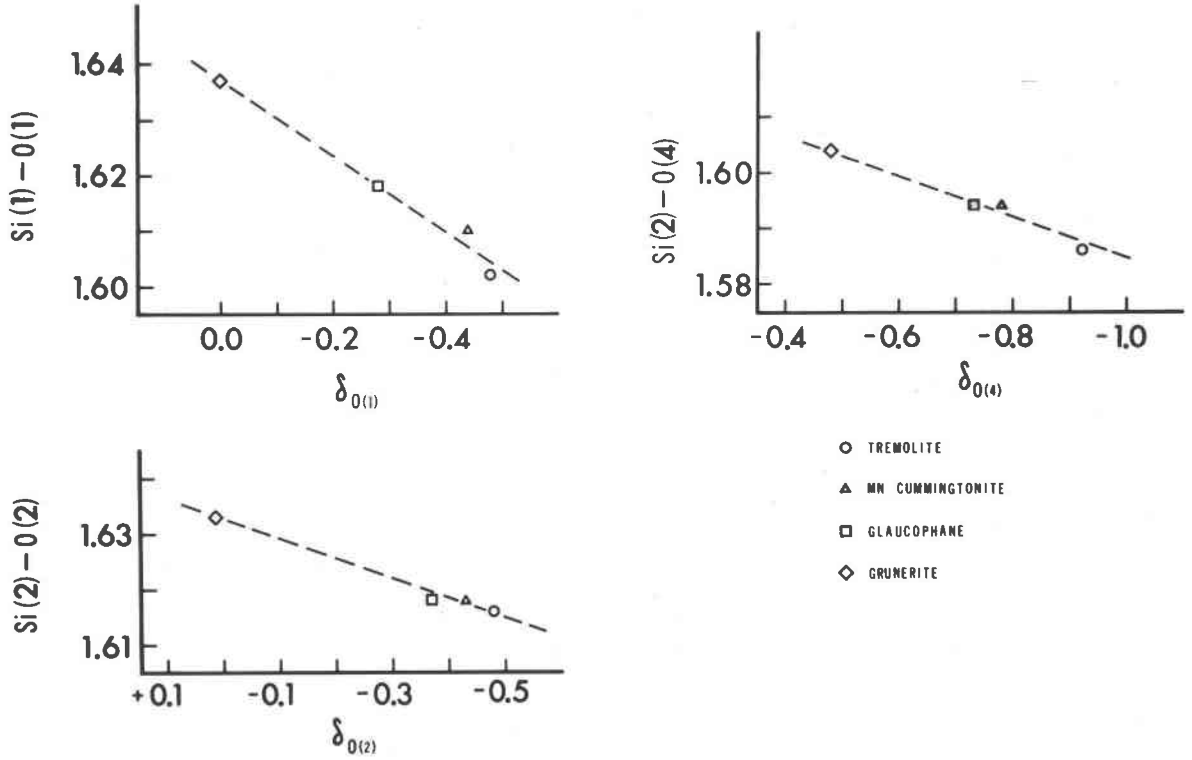

FIG. 3. Correlation between Si(1)-O(1), Si(2)-O(2) and Si(2)-O(4) bond lengths and residual electron density, δ, on O(1), O(2) and O(4) for the four *C*2/*m* amphiboles listed in the caption of Fig. 2. The residual charges on the oxygens were estimated following Pauling's (1948) electroneutrality principle.

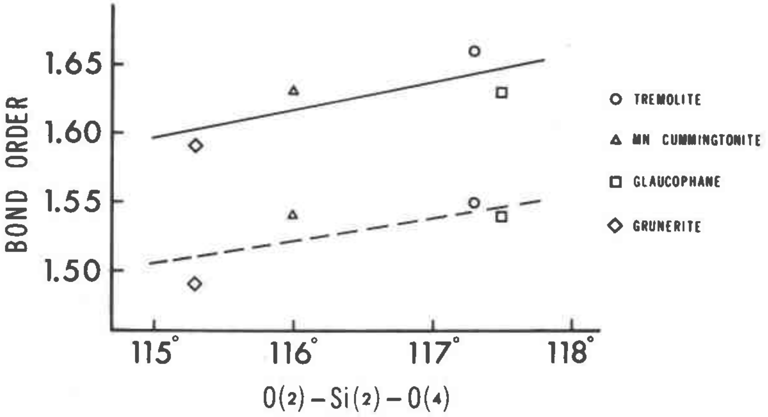

FIG. 4. Si(2)-O(2) (dashed line) and Si(2)-O(4) (solid line) bond orders plotted against the O(2)-Si(2)-O(4) tetrahedral bond angles for the four $C2/m$ amphiboles listed in the caption of Fig. 2. The bond orders were calculated using the bond order-bond length relationship for the Si-O bond developed by Robinson (1963).

balance is achieved (Pant, 1968). Additional evidence for the strong d-p π-bonds developed between Si(2) and O(2) and O(4) are the wide O(2)—Si(2)—O(4) angles (115°–117°) in all four amphiboles in comparison to the other O-Si-O angles (103°–112°) (cf. Gibbs. 1969). In fact, as the bond orders of these bonds increase from grunerite to tremolite, the O(4)—Si(2)—O(2) angles widen (Fig. 4) as expected (Gillespie, 1963) because of increased repulsion between the increased electron densities in the Si(2)—O(4) and Si(2)—O(2) d-p π-bond systems. This trend is also consistent with a similar correlation found between S-O bond orders and O-S-O angles in the sulphuryl and thionyl compounds by Gillespie and Robinson (1963).

As more systematic studies are carried out, such as those now in progress at VPI on the inductive effects of non-tetrahedral cations on the Si-O(nbr) bond in the olivines, garnets and humites, more of the factors affecting the Si-O bond should become evident.

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NOTE Added in Proof: Morimoto and Koto (1969, *Z. Kristallogr.*, **129,** 65–83) have recently published several plots showing a decrease in mean Si-O distances with increasing replacement of Mg by Fe in the isostructural series orthoenstatite-orthoferrosilite. This trend is opposed to the one presented above, indicating a decrease in mean Si-O distances as the nontetrahedral cations become more electronegative rather than an increase. However, if the individual Si-O(br) and Si-O(nbr) bond lengths of orthoenstatite, hypersthene and orthoferrosilite are examined, no consistent trends can be found. Similarly, with the exception of Si-O(2), the Si-O bond lengths in eight recently refined, ordered clinopyroxenes (Clark, *et al.*, 1968) show no consistent variation with average electronegativities of the *M* cations.

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