

THE NATURE AND THE VARIATION IN LENGTH OF THE Si-O AND Al-O BONDS IN FRAMEWORK SILICATES

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ABSTRACT

A detailed study of the bond distances and angles in framework silicates and aluminosilicates has shown that individual T -O distances ($T=Si,Al$) decrease with increasing T -O- T angle. In addition, the T -O bond length is affected by the types of T cations in the T -O- T linkages, by the number and types of cations coordinating oxygen and by the non-tetrahedral cation-oxygen distance(s). The dependence of T -O bond length on these factors can be qualitatively explained by a consideration of several bonding models including Cruickshank's (1961) d - p π -bonding model. Estimates of d - p π -overlap integrals for the SiO_4^{4-} (0.32) and AlO_4^{5-} (0.18) tetrahedral ions together with the correlations made between T -O bond lengths and T -O- T angles and data from X-ray emission studies suggest that the Si-O and Al-O bonds in framework aluminosilicates are similar in nature and that d - p π -bonding plays a significant role in their variation.

INTRODUCTION

In 1941 Schomaker and Stevenson revised the Pauling and Huggins' (1934) set of covalent radii and proposed an empirical equation for correcting the sum of the covalent radii of two bonded atoms for partial ionic character. However, application of this equation to the tetrahedral ions ClO_4^{1-} , SO_4^{2-} , PO_4^{3-} and SiO_4^{4-} gives single-bond distances 0.1 to 0.2 Å longer than the experimentally determined distances (Table 1). If the Schomaker-Stevenson equation gives a true prediction of single-bond distances, then these differences (Table 1) suggest that additional factors must be considered. Pauling (1952) has attributed these differences to π -bonding and has formulated empirical relationships based on single-multiple bond resonance which predict the amount of π -bond character for these TO_4^{n-} tetrahedral ions ($T=Cl,S,P,Si$) and which correct the single-bond distances for shortening due to d - p π -bonding (Table 1). The d - p π -overlap integrals of the T -O bonds in these ions have been calculated by Jaffe (1954) and are shown to be of sufficient magnitude to lead to appreciable bonding provided that the T cations maintain net positive charges. These values (Table 1) agree well with the percent π -bond character calculated using Pauling's equations. Craig *et al.* (1954) and Stone and Seyferth (1955) have also argued for d - p π -bonding in these ions resulting from back-donation of lone-pair electrons of oxygen to the $3d$ -orbitals of the T cation. More recently, Cruickshank (1961) has shown from group-theoretic considerations that only two strong π -bonding molecular orbitals may form between two $2p$ -orbitals of oxygen and two of the five $3d$ -orbitals of $T(3d_{x^2-y^2}$ and $3d_{z^2})$.

TABLE 1. OBSERVED, PREDICTED AND SINGLE-BOND LENGTHS AND PERCENT π -BOND CHARACTERS FOR TO_4^{n-} GROUPS

TO_4^{m-} group	$T-O$ (obs.)	$r_T^{cov} + r_O^{cov}$	Single-bond value ^c	Bond shortening ^d	Amount of π -bond character ^e	$d-p\pi$ overlap ^f	$T-O$ (predicted) ^g
AlO_4^{5-}	1.75 Å ^a	1.99 Å	1.81 Å	0.06 Å	0.20	0.15	1.72 Å
SiO_4^{4-}	1.62 ^a	1.91	1.76	0.13	0.32	0.33	1.63
PO_4^{3-}	1.54 ^b	1.84	1.71	0.17	0.44	0.46	1.55
SO_4^{2-}	1.49 ^b	1.78	1.69	0.20	0.54	0.52	1.51
ClO_4^{1-}	1.46 ^b	1.73	1.68	0.22	0.63	0.57	1.48

^a Smith and Bailey (1963).

^b Cruickshank (1961).

^c The Schomaker-Stevenson single-bond length $\equiv r_T^{cov} + r_O^{cov} - 0.09 |x_O - x_T|$.

^d The difference between columns 2 and 4.

^e The percent π -bond character calculated using Pauling's (1952) formulae.

^f The percent π -bond character from group overlap integrals (Jaffe, 1954).

^g Values calculated using Pauling's (1952) formula.

Cruickshank's $d-p$ π -bonding model permits the following predictions for crystals containing TO_4^{n-} groups:

a. the $T-O$ bond lengths should decrease nonlinearly with increasing π -bond order (Cotton and Wilkinson, 1966);¹

b. the length of the $T-O$ bond to non-bridging oxygens $O(nbr)$ should be shorter (higher π -bond order) than the bond to bridging oxygens $O(br)$ (lower π -bond order) [cf. Ramberg, 1952];

c. the $T-O(br)$ bond length and its π -bond order should vary directly with the $T-O-T$ angle, the length being shortest and the π -bond order being greatest at the 180° limit of the $T-O-T$ angle because this permits two $d-p$ π -bonds to be formed.

d. the $O-T-O$ angles should decrease in the order $O(nbr)-T-O(nbr) > O(br)-T-O(nbr) > O(br)-T-O(br)$ because the $T-O(nbr)$ bonds [higher π -bond order] should repel one another and $T-O(br)$ bonds more than the $T-O(nbr)$ bonds [lower π -bond order] repel one another (Gillespie, 1963). These predictions hold in a number of sulfates and phosphates (Cruickshank, 1961). However, the lack of accurate experimental data and the small variation of the Si-O bond length (Cruickshank, 1961; Smith and Bailey, 1963) have made it difficult to verify these predictions for silicates. Prediction (b) is obeyed by all Si-O bond lengths in a number of carefully refined chain silicates (wollastonite, Prewitt and Buerger, 1961;

¹ π -bond order as used here estimates the probability of finding a double bond between T and O ions in the tetrahedral linkage.

bustamite, Peacor and Buerger, 1962; protoamphibole, Gibbs, 1964; sodium metasilicate, McDonald and Cruickshank, 1967a; α - $\text{Na}_2\text{Si}_2\text{O}_5$, Pant and Cruickshank, 1968; β - $\text{Na}_2\text{Si}_2\text{O}_5$, Pant, 1968). In other recently refined chain-silicates (rhodonite, Peacor and Niizeki, 1963; cummingtonite, Ghose, 1961, and Fisher, 1966; haradaite, Takéuchi and Joswig, 1967; glaucophane, Papike and Clark, 1968) and the pyrosilicate, thortveitite, (Cruickshank *et al.*, 1962, Prewitt, pers. Commun.) prediction (b) does not hold for all Si-O bonds. These variant bond lengths may be due to the formation of partial covalent bonds between the oxygens and other cations, thereby reducing the Si-O d - p π -bond orders—a mechanism suggested by Cruickshank (1961) to explain the Si-O bond lengths in thortveitite.

Lazarev (1964) has cited spectroscopic data for the siloxanes and silicates which indicate that the Si-O-Si valence angles in these compounds depend primarily on the participation of d - p π -bonds. In addition, Cotton and Wilkinson (1966) have suggested that if d - p π -bonding is important in compounds containing T -O- T linkages, then increasing T -O- T angle should correlate with decreasing T -O bond length in agreement with prediction (c) above. A number of sulfates, phosphates and silicates have been discussed in terms of such a correlation (Cruickshank, 1961), but the study was limited by the lack of accurate experimental data. More recently Jones and Taylor (1968) pointed out the variation of selected Si-O bond lengths with Si-O-Si angles in four ordered alkali feldspar structures; however, they concluded that the details of these structures can be consistently explained using a model based on ionic bonding between K (or Na) and certain oxygen atoms.

The present study was undertaken to determine the degree to which the correlation between T -O bond length and T -O- T angle ($T = \text{Si}, \text{Al}$) exists in general for all of the precisely determined framework silicate and aluminosilicate structures (Brown, Gibbs and Ribbe, 1969a, b). Bonding models other than Cruickshank's (1961) d - p π -bonding model will be discussed and related to the observed bond lengths and angles in framework structures. The additional effects of (1) the cation coordination of oxygen, (2) the type of adjacent tetrahedral cation in the T -O- T linkage, (3) the type(s) of nontetrahedral A cations coordinating oxygen and (4) the A -O distance(s) on the T -O bond length will be examined. The relevance of recent X-ray emission spectral studies of the rock-forming silicates (White and Gibbs, 1967; Dodd and Glen, 1968; in press) will also be discussed. This study is restricted to the framework structures because (1) they exhibit a large range of T -O- T angles (120° – 180°); (2) the oxygens are bonded to two tetrahedral cations and zero, one or two nontetrahedral cations and therefore, are not complicated by the effects of nonbridging oxygens; (3) there are sufficient, precise structural data to make meaning-

ful correlations; and (4) many contain both Si and Al in tetrahedral coordination, permitting a comparison of the natures of the Si-O and Al-O bonds. It should be emphasized that no attempt will be made to evaluate the relative ionic and covalent character of these bonds.

THE Si-O AND Al-O BOND AND THE T -O- T ANGLE

Figure 1 shows seven scatter diagrams and linear regression lines of individual T -O bond lengths versus T -O- T angle for a number of framework structures all of which contain Si and/or Al in tetrahedral coordination. Figures 1a and 1b show the variation of Si-O bond lengths with Si-O-Si angle; Figures 1c and 1e the variation of Si-O with Si-O-Al angle; Figure 1d and 1f the variation of Al-O with Si-O-Al angle, and Figure 1g, the variation of $(\text{Si}_{0.75}\text{Al}_{0.25})\text{-O}$ with $(\text{Si}_{0.75}\text{Al}_{0.25})\text{-O-(Si}_{0.75}\text{Al}_{0.25})$ angle. The data for the Ca feldspar (anorthite) were plotted separately (Figure 1e, f) from those for the Na and K feldspars (Figures 1b, c, d) for reasons that will be discussed later. The sample correlation coefficients, slopes, T -O intercepts at T -O- T angles of 120° and 180° and estimated standard deviations (e.s.d.) of the slopes are listed in Table 2. The e.s.d.'s are poor estimates because they are biased by such systematic factors as the inductive effects of nontetrahedral cations and the coordination number of oxygen. The correlation coefficients are negative in all cases, agreeing with Cruickshank's prediction (c) and indicating that approximately 50 percent of the variation in T -O can be explained in terms of a linear dependence on T -O- T . The rest of the variation may be due to other factors to be discussed later.

In spite of the large scatter of data associated with each curve in Figure 1, there is a remarkable similarity in their respective slopes. The fact that a correlation can be made between T -O bond length and T -O- T angle suggests that d - p π -bonding is a distinct possibility in the framework silicates (Cotton and Wilkinson, 1966). Additional evidence for d - p π -bonding has been provided by Dodd and Glen's (1968a) interpretation of the SiK_β X-ray emission band of quartz where they assign a $3d$ (π^b)- $1s$ transition predicted by molecular orbital theory to a low intensity, poorly resolved shoulder on the higher energy side of the intense SiK_β band. This assignment agrees with Cruickshank's (1961) group theoretic analysis of the SiO_4^{4-} tetrahedral ion.

The slope of the regression line for quartz and other SiO_2 polymorphs (Fig. 1a) is steeper than those calculated for the other framework silicates, indicating that d - p π -bonding may be more important in the SiO_2 polymorphs than in structures containing nontetrahedral cations and tetrahedral Al. This is consistent with Lauser's (1968) observation of high energy SiK_β peaks for all of the SiO_2 polymorphs excepting coesite but not for other framework structures (Dodd, pers. commun.). The

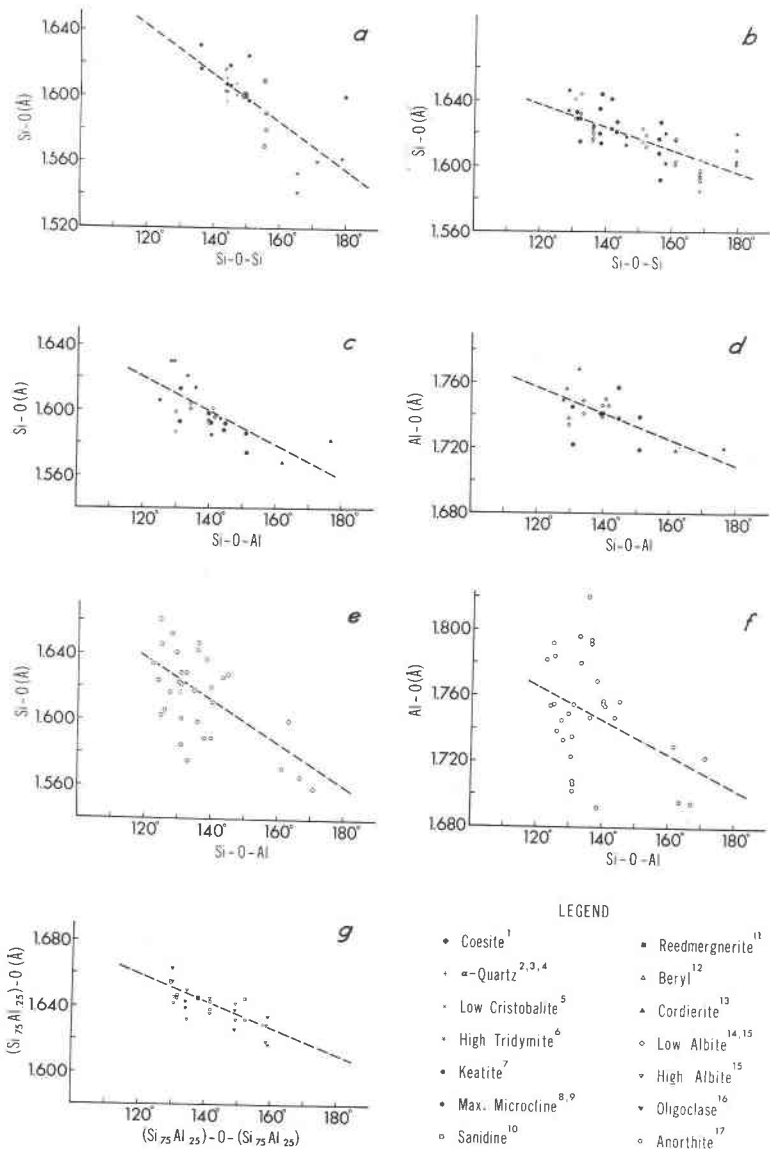


FIG. 1. Variations of T-O bond lengths with T-O-T angles for the framework structures listed in the legend. The superscripts after mineral names refer to the source of data:

- | | |
|-------------------------------------|-----------------------------------|
| 1 Zoltai (pers. comm.) | 5 Dollase (1965) |
| 2 Young and Post (1962) | 6 Dollase (1967) |
| 3 Smith and Alexander (1963) | 7 Shropshire <i>et al.</i> (1959) |
| 4 Zachariasen and Plettinger (1965) | 8 Finney and Bailey (1964) |

TABLE 2. REGRESSION LINES FOR TETRAHEDRAL BOND LENGTHS

Fig. 1	Type of linkage	T-O intercepts		Slope	Sample correlation coefficients
		T-O-T = 120°	T-O-T = 180°		
a	Si-O(\rightarrow Si) (SiO ₂ polymorphs)	1.64 ₃	1.55 ₈	-0.0014(3) ^a	-0.72
b	Si-O(\rightarrow Si)	1.63 ₈	1.59 ₅	-0.0007(1)	-0.74
c	Si-O(\rightarrow Al)	1.61 ₈	1.55 ₈	-0.0010(2)	-0.70
d	Al-O(\rightarrow Si)	1.75 ₅	1.71 ₆	-0.0006(2)	-0.58
e	Si-O(\rightarrow Al) (Anorthite)	1.63 ₈	1.56 ₁	-0.0013(3)	-0.61
f	Al-O(\rightarrow Si) (Anorthite)	1.76 ₆	1.70 ₄	-0.0010(4)	-0.40
g	(Si _{0.75} Al _{0.25})-O (\rightarrow Si _{0.75} Al _{0.25})	1.66 ₀	1.61 ₁	-0.0008(2)	-0.70

^a Estimated standard error referring to the last decimal place.

steeper slope is expected because the factors affecting T -O- T linkages in other framework structures are not present in the SiO₂ polymorphs (Noll, 1963).

In three ordered alkali feldspars whose mean T -O- T angle is 141°, Clark and Papike (1967) observed that the mean Si-O bond lengths in Si-O-Si linkages are significantly longer (~ 0.03 Å) than the mean Si-O bond lengths in Si-O-Al linkages. The corresponding Si-O bond lengths from Figures 1b and 1c differ by 0.025 Å at a T -O- T angle of 141°, bearing out their observation. The fact that the Si-O bond in Si-O (\rightarrow Si) linkages is longer than that in Si-O (\rightarrow T) linkages where T is a more electropositive tetrahedral cation than Si, *e.g.*, Al, suggests that Noll's (1963) ideas can be extended to include tetrahedral as well as nontetrahedral cations.

Just as Al affects the Si-O bond in the linkage Si-O (\rightarrow Al), Si affects the Al-O bond in the same linkage. Therefore, the Al-O bond in the (Si \leftarrow)



- | | |
|-------------------------------|--|
| 9 Brown and Bailey (1964) | 14 Wainwright and Starkey (1968) |
| 10 Ribbe (1963) | 15 Ribbe <i>et al.</i> (1969) |
| 11 Appleman and Clark (1965) | 16 Colville and Ribbe (1966 and pers. comm.) |
| 12 Gibbs <i>et al.</i> (1968) | 17 Megaw <i>et al.</i> (1962) |
| 13 Gibbs (1966) | |

Table 2 contains slopes, intercepts and estimated standard deviations of these regression lines. Figure a was prepared using data for the SiO₂ polymorphs; Figures b, c and d, four ordered alkali feldspars, cordierite and beryl; Figures e and f, anorthite; and Figure g, sanidine, high albite and oligoclase.

O-Al linkage should be longer than the Al-O bond in the hypothetical Al-O(\rightarrow Al) linkage following Noll's reasoning. It should, therefore, be understood that estimates of pure Al-O bond lengths (Smith and Bailey, 1963; Jones, 1968; Ribbe and Gibbs, 1969) are, in reality Al-O bond lengths affected by Si in the (Si \leftarrow)O-Al linkages.

The slopes of the regression lines for the variation of individual Al-O bond lengths with Si-O-Al angle (Figs. 1d and 1f) are statistically identical to those calculated for the Si-O bond (Figs. 1b and 1c), indicating that the Al-O bond is very similar in character to the Si-O bond. Perhaps, therefore, it is not surprising that the Al-O single-bond length of 1.81 Å (Table 1) is ~ 0.06 Å longer than the observed value, suggesting that *d-p* π -bonding may also be important in determining its bond length. Estimates of the amount of *d-p* π -bond character of the AlO_4^{5-} ion (~ 0.20) and the single Al-O bond distance corrected for *d-p* π -bond shortening (1.72 Å) were made using the empirical equations formulated by Pauling (1952). Another estimate of the amount of π -bond character in the Al-O bond was obtained using the *d-p* π -overlap integrals calculated for ClO_4^{1-} , SO_4^{2-} , PO_4^{3-} and SiO_4^{4-} by Jaffe (1954). A near linear relationship exists between the magnitudes of these overlap integrals and the bond shortening observed for these ions (Fig. 2). Assuming that the relationship can be extrapolated to smaller values, and that the Al cation maintains a net positive charge, a bond shortening of 0.06 Å for the AlO_4^{5-} ion indicates a *d-p* π -overlap of 0.15 for the Al-O bond, a value in reasonable agreement

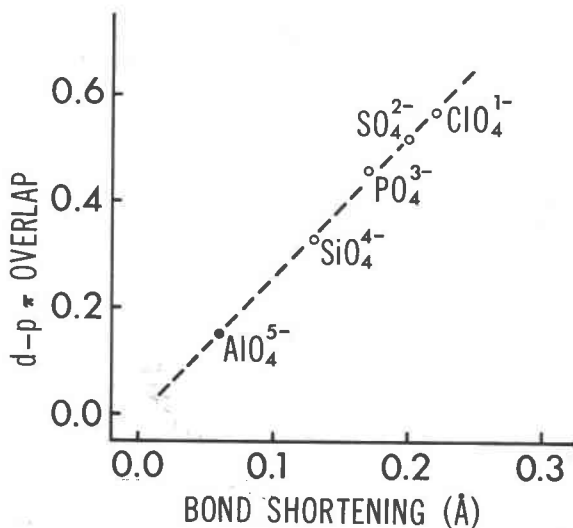


FIG. 2. The *d-p* π -overlap integrals of the TO_4^{n-} tetrahedral ions calculated by Jaffe (1954) (open circles) as a function of bond shortening. The overlap for AlO_4^{5-} (solid circle) was found by linear extrapolation to 0.06 Å bond shortening (see Table 1).

with 0.20 calculated using Pauling's equation. If the estimates for the amount of π -bond character for the AlO_4^{5-} ion obtained from Pauling's equations and the extrapolation of Jaffe's data are valid, and if d - p π -bonding is mainly responsible for the trends in Si-O bond length versus T -O- T angle (Figs. 1b, c, e), then it appears that d - p π -bonding also accounts for the trends observed in the plots of Al-O bond length T -O- T angle (Figs. 1d, f).

Dodd and Glen (1968a) have investigated the AlK_β X-ray emission band of the framework silicate cordierite and have found a slight shoulder on the high energy side of the K_β emission band which may also be attributed to a $3d(\pi^b)$ - $1s$ transition. Similar shoulders have been observed for nepheline, sodalite, feldspar and the AlPO_4 modifications of cristobalite, tridymite and quartz by Lauger (1968) and for sanidine by White and Gibbs (1969). The estimated energy difference ($\sim 3.5\text{eV}$) between the AlK_β band and its high energy peak (in cordierite) is smaller than the estimated energy difference ($\sim 5.0\text{eV}$) between the SiK_β band and its peak (in quartz). These values parallel the estimated d - p π -overlaps for the AlO_4^{5-} (0.18) and SiO_4^{4-} (0.33) ions.

Long range disorder of Al and Si does not significantly change the slope of T -O vs T -O- T (Fig. 1g) but only increases the T -O intercepts with respect to Si-O-Si linkages in proportion to the estimated Al content of the sites. As expected, the SiK_β wavelength does not vary significantly between ordered and disordered polymorphs (White and Gibbs, 1967; Dodd, pers. commun.).

Two bonding models besides Cruickshank's d - p π -model also qualitatively account for the observed slopes in Figure 1. The classic *valence bond theory* permits prediction of varying hybridization states (isovalent hybridization) of the oxygen atoms in the T -O- T linkages (*cf.* Fyfe, 1954). The variation of bond lengths with hybridization state appears well established for the C-C bond, with bond length decreasing as the s -content in the bonding orbital increases (Pauling *et al.*, 1935; Brown, 1959; Lide, 1962; Stoicheff, 1962). In other words, C-C single bonds, involving σ -overlap between two sp^3 hybrid orbitals (25% s -character) should be longer than if the overlap were between one sp^3 and one sp hybrid orbital (33% s -character). The T -O bonds in a T -O- T linkage may be similarly affected if the bonding orbitals of oxygen are assumed to exist in hybridization states varying continuously between sp^3 and sp types (it is convenient to assume that the hybridization state of T remains constant).¹ T -O- T angles near 120° suggest that the orbital hybridization of oxygen

¹ McDonald and Cruickshank (1967a) have discussed the effect of hybridization of the σ -bonds in O-T-O linkages on Si-O bond lengths and have concluded that orbital hybridization of the T cation is probably not of major importance in explaining variations in Si-O bond lengths.

is sp^2 whereas angles near 180° suggest sp hybridization (*cf.* Moore, 1962). Following the reasoning applied to C-C bonds, the decrease in T-O bond length as the T-O-T angle increases may be correlated with increasing s -content in the bonding orbitals of oxygen.

Ideally, an oxygen with two sp or three sp^2 hybrid orbitals would have two or three ligands, respectively. In framework aluminosilicates all oxygens are bonded to two tetrahedrally coordinated atoms, Si or Al, and for near sp^2 hybridization, most are bonded to a third cation, A . As the s -character of the σ -bond increases, the A -O distance should become increasingly longer, until, as T-O-T nears 180° , A may no longer be considered bonded to oxygen. Therefore, a negative correlation between T-O and A-O bond lengths and a positive correlation between T-O-T bond angle and A-O bond length should exist if the hybridization model is not to be discounted. Jones and Taylor (1968) have found correlations between K-O and Na-O distances and tetrahedral bond lengths for several ordered alkali feldspars when bonds between K (or Na) and oxygen in Si-O-Al linkages and between K (or Na) and oxygen in Si-O-Si linkages are distinguished. Rough correlations can also be made between Ca-O and T-O bond lengths (Fig. 3a and Megaw *et al.*, 1962) and Ca-O bond lengths and T-O-T angles (Fig. 3b) in anorthite and Na-O bond lengths and T-O-T angles in several Na feldspars (Fig. 3c). These correlations of A-O bond lengths ($A = K, Na, Ca$) with T-O bond lengths and T-O-T angles are consistent with the predictions based on the classic valence bond theory and support McDonald and Cruickshank's (1967a) suggestion that the silicate ions have a tendency to shed their negative charge through the formation of partial covalent bonds to nontetrahedral cations. Moreover, the sympathetic variation of T-O bond length with A-O bond length is consistent with the reasoning underlying the Pauling-Zachariasen method of the balancing of valences. On the other hand, Jones and Taylor (1968) have discussed the trends between K(Na)-O and T-O bond lengths in terms of ionic bonding between K(or Na) and oxygens in the Si-O-Al linkages. They also consider the contacts between K(or Na) and oxygens in the Si-O-Si linkages as nonbonding; these points will be considered in more detail later. Although several workers (Day and Selbin, 1962; Gillespie, 1963) have emphasized that a hybridization model can serve only as a convenient description of bonding and not as an explanation of bond length and angle variations, the fact that this model has been correlated with such success to bond length and bond angle variations in compounds involving carbon and other atoms, lends support to the hybridization model.

Predictions of the *valence-shell electron-pair repulsion theory* (VSEPR) of directed valency (Gillespie, 1963) are also consistent with Figure 1. In

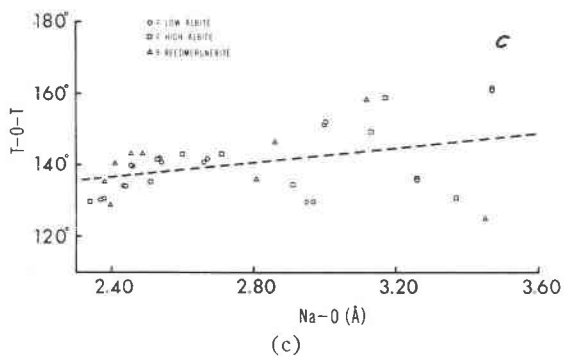
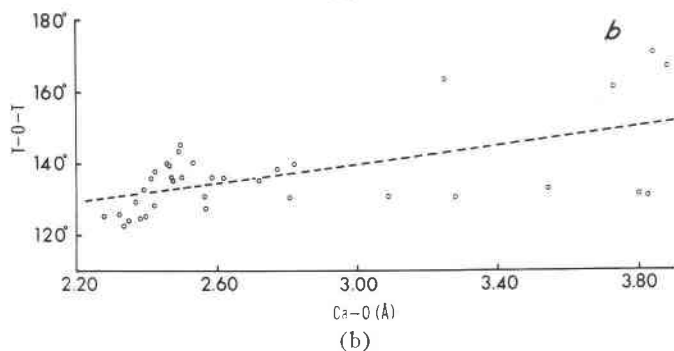
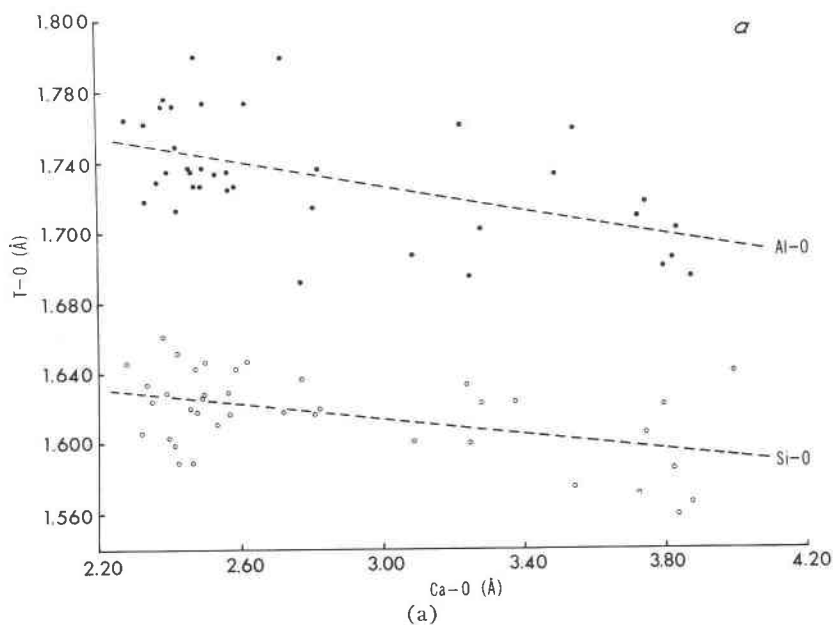


FIG. 3. (a) Linear regression lines showing $T-O$ bond lengths as a function of $Ca-O$ interatomic distances (up to 4.0\AA) for Al- and Si-rich tetrahedra in anorthite. (b) Regression line relating $T-O-T$ angle and $Ca-O$ distances in anorthite. Data for (a) and (b) from Megaw *et al.* (1962). (c) Regression line relating $T-O-T$ angle and $Na-O$ distances for three ordered Na feldspars. See legend of Fig. 1 for references.

part this theory states that repulsions between two bonding electron-pairs or between bonding electron-pairs and nonbonding electron-pairs (lone pairs) strongly influence the bond angles in a molecule. In addition, repulsions between bonds are predicted to increase as the order of these bonds increase. Applying this idea to *T-O-T* linkages in framework aluminosilicates, the decrease in *T-O* bond lengths as *T-O-T* angles increase is consistent with an increase in bond repulsions as the percent π -bond character of the *T-O* bonds increase. However, it should be emphasized that the VSEPR theory as well as the valence bond theory are of little quantitative usefulness in explaining the variations in *T-O* bond lengths.

EFFECT OF NONTETRAHEDRAL CATIONS ON Si-O AND Al-O BONDS

As indicated earlier about 50 percent of the variation in *T-O* bond length cannot be explained in terms of a linear dependence on *T-O-T* angle and may be due to additional factors such as the cation coordination of oxygen (Megaw *et al.*, 1962; Burnham, 1963; McDonald and Cruickshank, 1967b; Gibbs and Brown, 1968) the inductive effects of nontetrahedral cations, (Noll, 1963; Lazarev, 1964; Pant and Cruickshank, 1967; Jones and Taylor, 1968), the degree of Al/Si disorder in the tetrahedral site, (Smith and Bailey, 1963) and other effects yet unknown.

In a review of about 45 carefully refined silicate structures (Gibbs and Brown, 1968) the grand mean Si-O distances were found to increase linearly with average coordination number of the oxygen anions from 1.608 Å for two coordinated to 1.638 Å for four-coordinated oxygen anions. Similar variations in *T-O* bond lengths are expected in the framework aluminosilicates where the coordination numbers of oxygen generally range from two to four. Table 3 is a listing of the observed and predicted mean *T-O* bond lengths (*T-O*) for two-, three-, and four-coordi-

TABLE 3. OBSERVED AND PREDICTED MEAN *T-O* BOND LENGTHS FOR TWO-, THREE-, AND FOUR-COORDINATED OXYGENS IN ANORTHITE

Coordination about oxygen ^a			Mean <i>T-O-T</i> ^a	Si-O			Al-O		
Si	Al	Ca		Observed	Predicted ^b	δ	Observed	Predicted ^b	δ
1	1	0	148.5°	1.588 Å	1.600 Å	-0.012	1.719 Å	1.736 Å	-0.017
1	1	1	131.9°	1.622	1.623	-0.001	1.755	1.753	+0.002
1	1	2	136.9°	1.632	1.616	+0.016	1.780	1.747	+0.033

^a Megaw, Kempster and Radoslovich (1962).

^b Predicted using Figures 1e, f.

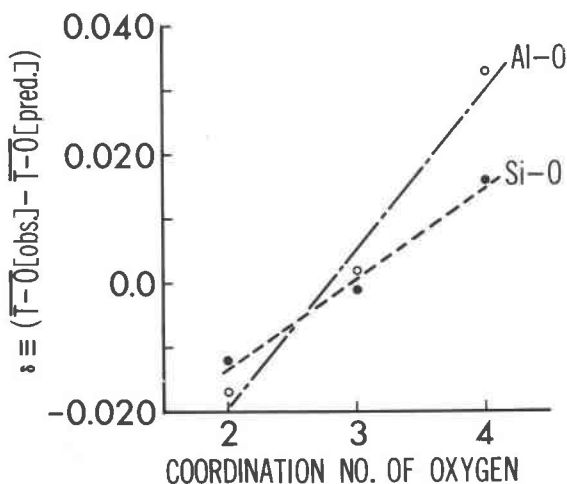


FIG. 4. Variation of δ with coordination number of oxygen in anorthite for Al- and Si-rich tetrahedra. Values of $\overline{T-O}$ [obs.] are from Megaw *et al.* (1962); values of $\overline{T-O}$ [pred.] are from Figs. 1e, f (*cf.* Table 3).

nated oxygens in anorthite. The dependence of $T-O$ distance on $T-O-T$ angle and type of tetrahedral cation has in effect been subtracted out in Figure 4 which shows the variation of $\delta = (T-O \text{ [observed]} - T-O \text{ [predicted]})$ with coordination number of the oxygen. The δ values for both Si- and Al-rich tetrahedra are negative, near zero and positive for the two-, three- and four-coordinated oxygens, respectively, reflecting the effect of the number of nontetrahedral Ca cations on the $T-O$ bond. The curves (Figs. 1e, f) used in the prediction of these $T-O$ distances are based on structures in which the oxygen coordination is ~ 3 , on the average. This explains why the δ 's are near zero for three-coordinated oxygens in anorthite. For four-coordinated oxygens the two Ca neighbors result in a lengthening of the observed $\overline{T-O}$ bond with respect to the predicted $\overline{T-O}$ distances, causing average increases of $\sim 0.035 \text{ \AA}$ in the $\overline{Al-O}$ bond and $\sim 0.015 \text{ \AA}$ in the $\overline{Si-O}$ bond. The fact that $\delta(\overline{Al-O})$ is about twice as large as $\delta(\overline{Si-O})$ for oxygen coordinated by two Ca cations is consistent with the greater $d-p \pi$ -character predicted for the $\overline{Si-O}$ bond (see Table 1). For the two-coordinated oxygens in anorthite, there are no nontetrahedral cations to perturb the $T-O-T$ linkage, just as in the SiO_2 polymorphs, where observed bond lengths (Fig. 1a) are shorter than those predicted using Figure 1b. For the Na and K feldspars no correlations could be made between δ and oxygen coordination. This lack of correlation may be related in part to the differences in character of the Na-O, K-O, and Ca-O bonds imposed by the electroneutrality principle (Pauling, 1960) and to the dif-

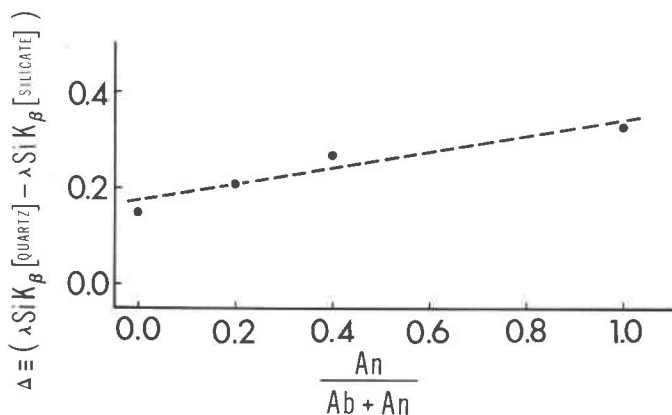


Fig. 5. Variation of Δ with mole percent anorthite for albite, oligoclase andesine and anorthite, using data from White and Gibbs (1967).

ferences in charge density (= formal charge of ion/volume of ion) of the cations ($K=0.10$; $Na=0.25$; $Ca=0.40$ electrons/ \AA^3). The greater charge density of Ca may also explain why the $T-O$ bond lengths in Ca feldspars tend to be slightly longer at narrow $T-O-T$ angles (120°) than those in Na and K feldspars (Fig. 1). For these reasons, the data for the Ca feldspars were plotted separately in Figure 1.

Further evidence supporting the above discussion of Figure 4 comes from White and Gibbs' (1967) study of the SiK_β X-ray-emission shifts of 45 naturally occurring silicates. Figure 5 shows that a correlation can be made between $\Delta \equiv (\lambda SiK_\beta [\text{quartz}] - \lambda SiK_\beta [\text{silicate}])$ and the ratio $An/Ab + An$ for albite, oligoclase, andesine and anorthite. The degree of shift of the SiK_β line for any silicate from the SiK_β line of quartz reflects the differences in the nature of the Si-O bonds in the two silicates. Figure 5 indicates that increasing replacement of Na by Ca and Si by Al causes increasing deviation of the nature of the Si-O bond from that in quartz. The data cited in the present study, together with the extension of Noll's (1963) ideas and Clark and Papike's (1967) observations discussed previously, suggest that an increase in the Al/Si ratio should result in a shortening of $\overline{Si-O}$. However, $\overline{Si-O}$ in low albite and anorthite are 1.613 \AA and 1.614 \AA , respectively, even though anorthite contains more tetrahedral Al than low albite does. This implies that nontetrahedral Ca counteracts the effect of tetrahedral Al on the Si-O bond in Si-O (\rightarrow Al) linkages for the plagioclase feldspars.

DISCUSSION

Attention has recently been drawn to the Pauling-Zachariasen method of the balancing of valences (Pauling, 1929; Zachariasen, 1963) by Pant

and Cruickshank's (1967) interpretation of the datolite structure and by Pant's (1968) reconsideration of the β - $\text{Na}_2\text{Si}_2\text{O}_6$ structure. In essence this method involves the assignment of Pauling's bond strengths followed by the balancing of oxygen valences through the "shortening" of underbonded-oxygen cation distances and the "lengthening" of overbonded-oxygen cation distances. This qualitative method is successful because it implicitly depends on all the factors discussed earlier. In fact, Pant (1968) has pointed out that the d - p π -bonding theory and the method of balancing of valences for the Si-O bonds "... are not exclusive" and that "... π -bonding in Si-O bonds may be part of the mechanism whereby valency balance is achieved." Pant and Cruickshank (1967) were careful to emphasize that the successful application of this method does not necessitate that the nature of the bonds be purely ionic or purely covalent. In this connection, Jones and Taylor's (1968) discussion of the bond lengths in ordered alkali feldspars in terms of purely ionic bonds between K (or Na) and certain of the oxygen atoms is without justification. Moreover, their use of the term "nonbonding" is not consistent with its accepted usage, especially when applied to the K (or Na)- O_A2 contact which is the *shortest* A-O bond in all feldspars. In light of this discussion and the reasoning underlying the Pauling-Zachariasen method, it appears that the valency of a bridging oxygen in a Si-O-Si linkage is not necessarily balanced. Valency balance in this case probably depends both on the Si-O bond lengths and the Si-O-Si angle.

The data cited in this study indicate that individual T -O bond lengths ($T = \text{Si}, \text{Al}$) vary directly with T -O- T angle, coordination number of oxygen, types of nontetrahedral cations A ($= \text{Ca}, \text{Na}, \text{K}$), A -O distance, and with types of T cations in the T -O- T linkages besides variation due to disordered Al/Si distributions. The scatter of data in Figures 1 and 3 probably is related to systematic errors due primarily to these factors. A multiple linear regression analysis is planned by GEB and GVG to determine the relative importance of each of these factors.

The predictions of the hybridization and VSEPR models in addition to Cruickshank's d - p π -bonding model have been discussed and are consistent with the trends observed in Figure 1. On the basis of data presented in this paper and in Dodd and Glen's recent studies of the X-ray emission bands of silicates, it appears that Cruickshank's d - p π -bonding model best explains the trends observed in Figure 1. Figure 1 indicates that bonding electron-pair repulsions are more important than nonbonded repulsions between the T cations in T -O- T linkages. If π -bonding explains the shortening of the Si-O bond as proposed by Pauling (1952) and Cruickshank (1961), then the similarities between the Si-O and Al-O bonds found in this study and in Dodd and Glen's (1968a, b) work indicate that the shortening of the Al-O bond is probably due to π -bonding as

well. In the past, predictions of the Al/Si content of tetrahedra in silicates have been made using $\overline{T-O}$ bond lengths exclusively (Smith and Bailey, 1963). However, this study shows that $\overline{T-O}$ is dependent not only on chemistry but also on the factors outlined above. For example, if the structures used to prepare Figure 1b are completely ordered, then the Si-O distances in Si-O-Si linkages can vary from ~ 1.64 Å at a Si-O-Si angle of 120° to ~ 1.60 Å at 180° . Similarly, the Al-O distance can vary from ~ 1.76 Å at a Si-O-Al angle of 120° to ~ 1.71 Å at 180° (Fig. 1d). Figures 1 and 3 are not intended to be used as determinative curves for predicting the dimensional details of a tetrahedron or A-O distances in framework structures. However, it is hoped that the proposed multiple linear regression analysis will yield an empirical relationship that will predict individual T-O distances as a function of T-O-T angle, coordination number of oxygen, type of tetrahedral and nontetrahedral cation and A-O distance.

In conclusion, it is important to maintain an open mind concerning bonding theories and their applicability to silicates. Our ultimate goal is to predict the structural details of a silicate given its chemical composition. Along this line, Cruickshank (pers. commun.) indicates that the Pauling-Zachariasen method of the balancing of valences gives necessary conditions for the bond lengths of a structure but is of little use in their prediction and that the VSEPR theory, although containing important truths, also does not predict lengths. On the other hand, the *d-p* π -bonding model has been found to be of some use in the prediction of bond lengths in the tetrahedral portions of a structure (Cruickshank, 1961). However, Cruickshank (pers. commun.) believes that "... the real competition is not between π -bonding and one of these other theories, but between π -bonding and theory X." His present guess is that theory X will prevail, because he doubts that π -bonding can energetically explain all of the structural details of a silicate. Nevertheless, until theory X is developed, the π -bonding model may be retained until additional systematic studies of the type presented here provide the facts necessary to formulate theory X.

ACKNOWLEDGMENTS

The writers are grateful to Prof. D. W. J. Cruickshank and his colleagues whose research on the bonding in silicates provided the stimulus for this study. The following individuals are gratefully acknowledged for their critical reviews of this manuscript: Prof. D. W. J. Cruickshank, the University of Manchester Institute of Science and Technology; Dr. Joan Clark, U.S. Geological Survey, Washington, D. C.; Profs. J. G. Dillard and P. E. Field, Chemistry Department., Virginia Polytechnic Institute; Prof. C. T. Prewitt, Department of Earth and Space Sciences, State University of New York at Stony Brook; and Prof. J. V. Smith, Department of Geophysical Sciences, University of Chicago. Thanks are also due to Drs. C. G. Dodd, Phillip Morris Research Laboratory, Richmond, Virginia and

D. B. Stewart, U.S. Geological Survey, Washington, D. C. for several informative and stimulating discussions. This work was supported in part by N.S.F. Grant No. GA-1133.

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Manuscript received, December 19, 1968; accepted for publication, April 28, 1969.