# THE PREDICTION OF BOND LENGTH VARIATIONS IN SILICON-OXYGEN BONDS

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## ABSTRACT

Individual silicon-oxygen bond lengths in many accurately determined silicate crystal structures vary from 1.55 to 1.72 Å. These variations in bond length are strongly correlated with the Pauling bond strength, $p_O$, received by the oxygen atoms. The individual variations in bond lengths $d(\text{Si-O})$ can be predicted using the expression $d(\text{Si-O})_{calc} = (d(\text{Si-O})_{mean} + 0.091\Delta p_O)$Å, where $d(\text{Si-O})_{mean}$ is the mean tetrahedral Si-O distance, 0.091 is an empirical constant, and $\Delta p_O$ is the difference in the bond strength received by the individual oxygen atom and the mean bond strength received by the oxygen atoms in the given silicate tetrahedron. The absolute mean deviation between 148 pairs of $d(\text{Si-O})_{obs}$ and $d(\text{Si-O})_{calc}$ taken from a sample of 26 crystal structures containing disilicate groups is found to be 0.010 Å. The correlation coefficient between the bond length variation and the bond strength variation $\Delta p_O$ is 0.92, which defines a very strong correlation. The dependence of $d(\text{Si-O})_{obs}$ on the angle Si-O-Si is found to be a corollary of the more basic correlation between bond length variation and $\Delta p_O$. In crystal structures in which $\Delta p_O = 0$ for all oxygen atoms, the $d(\text{Si-O})$ on $\angle$Si-O-Si dependence does not exist. Therefore $d$-$p$ $\pi$-bonding should be questioned as a general bonding theory for the silicates. An influence of the electronegativity of the non-tetrahedral cations on $d(\text{Si-O})_{obs}$ is not found in the case of four pairs of strictly isostructural pyroxenes. Such effects have been claimed in previous studies based on a comparison of not isostructural chainsilicates (McDonald and Cruickshank, 1967) and of not strictly isostructural clinoamphiboles (Brown and Gibbs, 1970). However, the bond length variations in these two cases, as well as for the pyroxenes, show a good correlation with the $\Delta p_O$-values.

The main difference between the extended electrostatic valence rule as applied here, and Cruickshank's (1961) $d$-$p$ $\pi$-bonding theory is that the former emphasizes the influence of all the coordinating cations on $d(\text{Si-O})_{obs}$, while the latter stresses the internal electronic structure within the isolated silicate groups. As this study shows it is not permissible to neglect the influence of the non-tetrahedral cations on the silicon-oxygen bond length. The silicate group cannot be viewed as an isolated entity within the crystal structure.

## INTRODUCTION

Recently, in an extension of earlier ideas on this subject (Baur, 1961), a large number of crystal structure data on borates, silicates, phosphates, sulfates, and titanates was analyzed with a view towards correlating, among other things, the variations of individual bond lengths, $d(A-X)$, with the bond strengths, $p_x$, received by the anions (Baur, 1970), One of the results of this study was formulated in rule 3, which states that in a given coordination polyhedron the deviation of an individual bond length $d(A-X)$ from the mean $\langle d(A-X)\rangle$ is proportional to $\Delta p_x$ and the bond lengths $d(A-X)$ can be predicted from equations of the form

$$d(A - X) = (\langle d(A - X)\rangle + b\Delta p_x)\text{Å} \tag{1}$$

where $\langle d(A-X) \rangle$ and $b$ are empirically derived constants for given pairs of $A$ and $X$ in a given coordination, and where $\Delta p_x$ is the difference between the individual $p_x$ and the mean $p_x$ for the coordination polyhedron. $A$ and $X$ stand respectively for cations and anions in ionic or partly ionic crystal structures. The empirical value of the slope $b$ in the above expression was found for the Si-O bond to be 0.091 Å/v.u., while the $\langle d(A-X) \rangle$ was obtained from Brown and Gibbs' (1969) expression

$$\langle d(\text{Si-O}) \rangle = (0.015 \, \overline{\text{C.N.}} + 1.579)\text{Å} \tag{2}$$

which relates the mean Si-O bond length within a silicate tetrahedron to the mean coordination number $\overline{\text{C.N.}}$ of the oxygen atoms bonded to silicon. This correlation is without doubt valid (see the documentation of this point by Shannon and Prewitt, 1969), but in many cases the discrepancy between observed and calculated mean Si-O distances is appreciable: for instance, in topaz it is 0.017 Å (Table 1, Gibbs and Brown, 1969). Predictions of bond lengths based on expression (1) could be affected by such inaccurate values chosen for $\langle d(A-X) \rangle$. The effect of $\Delta p_x$ on the individual bond lengths could be thus obscured. In order to avoid this complication in this paper the actually *observed* mean values of the Si-O bond lengths will be used in expression (1). In this way we will not test the ability of rule 3 to predict bond lengths, but instead its power to predict the deviations of the individual bond distances from their experimentally determined mean for a given silicate tetrahedron. This test of rule 3 is being applied to a clearly defined sample: to *all* crystal structures containing the disilicate group $Si_2O_7^{6-}$, provided: a) the structure determination is reasonably accurate, b) the error estimates of the positional parameters are given in the original papers, and c) the structure determination came to the attention of the author. Only the Si-O bond distances will be considered in this paper. The bonds from the oxygen atoms to all the other cations in these structures will not be discussed here.

Previous references to a possible relationship between bond length and bond strength in ionic or partly ionic crystals are scattered throughout the literature. The earliest discussion seems to be due to Smith (1953). Further literature on this subject is quoted in Baur (1970). In none of these earlier papers has this relationship been used for the prediction of bond lengths.

## DEFINITIONS

$p_x =$ sum of bond strengths received by an anion $X$ according to the electrostatic valence rule (Pauling, 1960; Baur, 1970).

$p_O =$ sum of bond strengths received by an oxygen atom.

$\Delta p_x$ = bond strength variation: difference between the $p_x$ of one individual anion in a coordination polyhedron around a cation and the mean $p_x$ of all anions in this coordination, $\Delta p_x = p_x - p_{x(\text{mean})}$ (rule 3, Baur, 1970).

v.u. = valence units, measure of $p_x$ and $\Delta p_x$. The bond strength given by a cation to an anion is the formal charge of the cation divided by its coordination number. The sum of these bond strengths received by an anion is called $p_x$. It corresponds approximately (with a change in sign) to the formal charge of that anion (electrostatic valence rule, Pauling, 1960).

$d(A-X)$ = interatomic distance from cation $A$ to anion $X$.

$\langle d(A-X) \rangle$ = mean observed $d(A-X)$ in a given coordination polyhedron.

$d(\text{obs})$ = experimentally observed distance between a cation and an anion.

$d(\text{calc})$ = distance calculated according to rule 3 (Baur, 1970) between cation and anion.

$\Delta d(\text{oc})$ = difference between the observed and the calculated distances.

$\Delta d(\text{om})$ = bond length variation: difference between $d(\text{obs})$ of one individual anion in a coordination polyhedron around a cation and the mean $d(\text{obs})$ of all anions in this coordination, $\Delta d(\text{om}) = d(\text{obs}) - \langle d(\text{A-X}) \rangle$.

$a$ = intercept of the linear regression equation.

$b$ = slope of the regression equation.

$r$ = correlation coefficient.

e.s.d. = estimated standard deviations of the bond lengths, mostly based on values supplied by the original authors. In a few cases these values had to be calculated from the e.s.d.'s of the positional parameters of the atoms because of misprints or mistakes in the original papers.

## BOND STRENGTH AND BOND LENGTH IN DISILICATE GROUPS

The only structure determinations considered here are those which resulted in mean estimated standard deviations of less than 0.03 Å for the Si-O bonds. In all these 26 structures the Si-O bonds are the strongest bonds present, because the silicon atoms have the highest formal charge of all cations present and/or because they have the smallest coordination number against oxygen. All crystal structures evaluated for this study are listed in Tables 1 and 2. The coordination numbers of the cations used for the calculation of the bond strengths are indicated as super-

Table 1. Chemical formulas and references for the synthetic disilicate compounds the data of which were used in this study. Mean e.s.d. refers to the mean estimated standard deviation of the Si-O bonds; mean $\Delta d_{OC}$ is the mean difference between an observed and a calculated Si-O bond length; mean $\Delta d_{OC}$/e.s.d. is the mean of the ratio of the individual e.s.d. and $\Delta d_{OC}$ for each bond length averaged over all bond lengths within the crystal structure.

| No. | chemical formula | mean e.s.d. | mean $\Delta d_{OC}$ | mean $\Delta d_{OC}$/e.s.d | Si-O-Si | C.N. of O(br) | reference |
|---|---|---|---|---|---|---|---|
| 1 | (Ca,Na)$_2^{[8]}$Al$^{[4]}$Si$_2$O$_7$ | 0.004Å | 0.002Å | 0.6 | 136.2(4)° | 4 | Louisnathan, 1970 |
| 2 | Yb$_2^{[6]}$Si$_2$O$_7$ | 0.005 | 0.006 | 1.6 | 180.0 | 2 | Smolin & Shepelev, 1970 |
| 3 | Er$_2^{[6]}$Si$_2$O$_7$ | 0.005 | 0.011 | 2.5 | 180.0 | 2 | Smolin & Shepelev, 1970 |
| 4 | Ba$_3^{[13]}$Nb$_6^{[6]}$O$_{12}$(Si$_2$O$_7$)$_2$ | 0.007 | 0.006 | 1.0 | 180.0 | 2 | Shannon & Katz, 1970 |
| 5 | Pr$_2^{[8]}$Si$_2$O$_7$ | 0.009 | 0.016 | 1.8 | 131.2(4) | 2 | Felsche, 1970, and personal communication |
| 6 | Li$_2^{[5]}$Li$_4^{[4]}$Si$_2$O$_7$ | 0.010 | 0.008 | 0.9 | 136.4(1.0) | 4 | Völlenkle et al., 1969 |
| 7 | Gd$_2^{[7]}$Si$_2$O$_7$ | 0.011 | 0.023 | 2.3 | 158.6(6) | 4 | Smolin & Shepelev, 1970 |
| 8 | Nd$_2^{[9]}$Si$_2$O$_7$ | 0.011 | 0.018 | 1.7 | 132.6(6) | 2 | Smolin & Shepelev, 1970 |
| 9 | Co$_4^{[6]}$OSi$_2$O$_7$ | 0.012 | 0.012 | 0.8 | 124.4(1.6) | 3 | Morimoto et al., 1970 |
| 10 | Sm$^{[7]}$Sm$^{[9]}$Si$_2$O$_7$ | 0.014 | 0.017 | 1.2 | 129.7(9) | 3 | Smolin et al., 1970 |
|  |  |  |  |  | 136.0(9) | 3 |  |

Table 2. Minerals with disilicate groups, for explanations see Table 1.

| No. | name | chemical formula | mean e.s.d. | mean $\Delta d_{oc}$ | $\Delta d_{oc}$/e.s.d. | mean Si-O-Si | C.N.of O(br) | Reference |
|---|---|---|---|---|---|---|---|---|
| 11 | lawsonite | $Ca^{[8]}Al_2^{[6]}(OH)_2(OH_2)Si_2O_7$ | 0.001Å | 0.003Å | 3.0 | 136.9(1)° | 3 | (1) |
| 12 | ilvaite | $Ca^{[7]}(Fe^{2+},Fe^{3+})_2^{[6]}(Fe^{2+})^{[6]}O(OH)Si_2O_7$ | 0.004 | 0.003 | 0.8 | 128.3(3) | 3 | (2) |
| 13 | hardystonite | $Ca_2^{[8]}Zn^{[4]}Si_2O_7$ | 0.005 | 0.007 | 1.6 | 138.5(5) | 4 | (3) |
| 14 | thortveitite | $Sc_2^{[6]}Si_2O_7$ | 0.005 | 0.009 | 1.7 | 180.0 | 2 | (4) |
| 15 | clinozoisite | $Ca^{[7]}Ca^{[8]}Al_3^{[6]}O(OH)(SiO_4)Si_2O_7$ | 0.006 | 0.007 | 1.2 | 164.3(5) | 2 | (5) |
| 16 | piemontite | $Ca^{[7]}Ca^{[8]}(Al,Mn,Fe)_3^{[6]}O(OH)(SiO_4)Si_2O_7$ | 0.006 | 0.011 | 1.8 | 151.0(3) | 2 | (6) |
| 17 | hemimorphite | $Zn_4^{[4]}(OH)_2(OH_2)Si_2O_7$ | 0.007 | 0.002 | 0.3 | 150.3(9) | 2 | (7) |
| 18 | epidote (high-Fe) | $Ca^{[7]}Ca^{[8]}(Al,Fe^{3+})_3^{[6]}O(OH)(SiO_4)Si_2O_7$ | 0.007 | 0.011 | 1.4 | 153.6(7) | 2 | (8) |
| 19 | zoisite | $Ca_2^{[7]}Al_3^{[6]}O(OH)(SiO_4)Si_2O_7$ | 0.011 | 0.006 | 1.0 | 172.6(8) | 2 | (5) |
| 20 | epidote (low-Fe) | $Ca^{[7]}Ca^{[8]}(Al,Fe)_3^{[6]}O(OH)(SiO_4)Si_2O_7$ | 0.012 | 0.003 | 0.3 | 159.4(5) | 2 | (9) |
| 21 | allanite | $Ca^{[7]}(RE,Ca)^{[8]}(Al,Fe^{3+})_3^{[6]}O(OH)(SiO_4)Si_2O_7$ | 0.014 | 0.013 | 0.9 | 145.1(1.3) | 2 | (8) |
| 22 | melilite | $(Ca,Na,K)_2^{[8]}(Mg,Al)^{[4]}Si_2O_7$ | 0.014 | 0.010 | 0.9 | 136.7(1.0) | 4 | (10) |
| 23 | barylite | $Ba^{[12]}Be_2^{[4]}Si_2O_7$ | 0.015 | 0.012 | 0.8 | 128.0(1.3) | 4 | (11) |
| 24 | pumpellyite | $Ca_2^{[7]}Al_2^{[6]}O(OH)_2(SiO_4)Si_2O_6OH$ | 0.022 | 0.010 | 0.6 | 133.5(1.2) | 3 | (12) |
| 25 | fresnoite | $Ba_2^{[10]}Ti^{[5]}OSi_2O_7$ | 0.024 | 0.019 | 0.8 | 144(3) | 4 | (13) |
| 26 | hancockite | $Ca^{[7]}(Pb,Sr,Ca)^{[8]}(Al,Fe)^{[6]}O(OH)(SiO_4)Si_2O_7$ | 0.025 | 0.019 | 1.0 | 161(2) | 2 | (8) |

(1) Khan & Baur, 1970, unpublished
(2) Tillmanns & Baur, 1970, unpublished
(3) Louisnathan, 1969
(4) Prewitt, 1970, personal communication
(5) Dollase, 1968
(6) Dollase, 1969
(7) McDonald & Cruickshank, 1967a

(8) Dollase, 1971
(9) Fang, 1970, personal communication
(10) Smith, 1953
(11) Cannillo et al., 1969
(12) Galli & Alberti, 1969
(13) Moore & Louisnathan, 1969

Table 3.  Example of a bond strength ($p_O$) calculation:
          $(Ca,Na)_2^{[8]}Al^{[4]}Si_2O_7$ (1., see Table 1). The contribution
          from (Ca,Na) to each oxygen atom is: $(0.5 \times 2.0 + 0.5 \times 1.0)/8 = 0.19$,
          from Al: $3.0/4$, from Si: $4.0/4$.

|        | $Ca_{0.5}Na_{0.5}$ | Al | Si | $p_O$ |
|--------|--------------------|-----|-----|-------|
| O(1)   | 2x0.19v.u.         |     | 2x1.00v.u. | 2.38 v.u. |
| O(2)   | 3x0.19             |     | 1.00 | 1.56 |
| O(3)   | 2x0.19             | 0.75v.u. | 1.00 | 2.13 |

scripts in square brackets. Since the Si-atoms are always 4-coordinated
their coordination number is omitted from the formulas. An example of
bond strength and bond length calculations, for synthetic soda melilite,
is presented in detail in Tables 3 and 4. Both the averages, of the sum
of bond strengths ($p_O$) and of the observed Si-O distances ($d$(obs)), are
taken for all four oxygen atoms in the silicate group, even when some of
them are symmetrically equivalent. The values of $d$(calc) were calculated
using expression (1) with $b = 0.091$ Å/v.u. For further details of the bond
strength calculations, especially concerning the way hydrogen bonds are
accounted for, see Baur (1970). The data derived for the other 25 crystal
structures are presented in Table 5. The values of $\Delta p_O$, $\Delta d$(oc) and
$\Delta d$(om) are not listed because they can be calculated easily from the
data of Table 5. Furthermore all values of $\Delta p_O$ and $\Delta d$(om) are displayed

Table 4.  Example of a bond length calculation:  $(Ca,NA)_2^{[8]}Al^{[4]}Si_2O_7$,
          see Tables 3 and 1, Table 1.  $\Delta p_O$ is defined in the
          text; $d_{calc} = (1.622 + 0.091\Delta p_O)$Å where 1.622Å is the mean
          observed Si-O distance (mean $d_{obs}$).  $\Delta d_{oc}$ is the
          difference between the observed and the calculated
          Si-O distance, while $\Delta d_{om}$ is the difference between
          the individual $d_{obs}$ and the mean $d_{obs}$.

|          | $p_O$     | $\Delta p_O$ | $d_{calc}$ | $d_{obs}$  | $\Delta d_{oc}$ | $\Delta d_{om}$ |
|----------|-----------|--------------|------------|------------|-----------------|-----------------|
| Si-O(1)  | 2.38v.u.  | 0.33v.u.     | 1.652Å     | 1.648(3)Å  | -0.004Å         | 0.026Å          |
| Si-O(2)  | 1.56      | -0.49        | 1.577      | 1.577(5)   | 0.000           | -0.045          |
| Si-O(3)  | 2.13      | 0.08         | 1.629      | 1.631(4)   | 0.002           | 0.009           |
| Si-O(3)  | 2.13      | 0.08         | 1.629      | 1.631(4)   | 0.002           | 0.009           |
| mean     | 2.05v.u.  |              |            | 1.622      | 0.002           |                 |

in Figure 1. Mean $\Delta d$(oc) values for each structure are listed in Tables 1 and 2.

In order to test the validity of rule 3 more extensively a weighted least squares linear regression of $\Delta d$(om) on $\Delta p_O$ was calculated. The inverse squares of the estimated standard deviations of the individual bond lengths were employed as weights. This decreased the contribution of the values with large e.s.d.'s. While most of the crystal structure data used in this study are fairly precise, the maximum ratio of the estimated standard deviations nevertheless is large: the least precisely determined Si-O bond length has an e.s.d. of 0.037 Å, the most precise one of 0.001 Å. One cannot expect to find meaningful correlations without taking these differ-

Table 5. Bond strengths and calculated and observed bond lengths for all disilicate groups of the compounds listed in Tables 1 and 2. The compounds are identified by number only, the individual SiO₄ groups differentiated by letters, and the bridging bonds are always listed first. The e.s.d.'s are indicated here, as elsewhere in the paper, in units of the last significant digits. The numbering of the atoms used in the original papers has been retained.

| | $p_O$ (v.u.) | $d_{calc}$ (Å) | $d_{obs}$ (Å) | | | $p_O$ (v.u.) | $d_{calc}$ (Å) | $d_{obs}$ (Å) |
|---|---|---|---|---|---|---|---|---|
| 2. Si-O(1) | 2.00 | 1.626 | 1.626(3) | 8a. Si(1)-O(1) | | 2.00 | 1.621 | 1.590(8) |
| Si-O(2) | 2.00 | 1.626 | 1.614(6) | Si(1)-O(2) | | 2.13 | 1.632 | 1.624(10) |
| 2xSi-O(3) | 2.00 | 1.626 | 1.632(5) | Si(1)-O(3) | | 2.13 | 1.632 | 1.638(11) |
| 3. Si-O(1) | 2.00 | 1.621 | 1.632(3) | Si(1)-O(4) | | 1.75 | 1.598 | 1.632(15) |
| Si-O(2) | 2.00 | 1.621 | 1.631(5) | 8b. Si(2)-O(1) | | 2.00 | 1.631 | 1.636(11) |
| Si-O(3) | 2.00 | 1.621 | 1.611(5) | Si(2)-O(5) | | 2.13 | 1.642 | 1.669(10) |
| Si-O(4) | 2.00 | 1.621 | 1.609(5) | Si(2)-O(6) | | 2.13 | 1.642 | 1.616(9) |
| 4. Si-O(1) | 2.00 | 1.612 | 1.599(6) | Si(2)-O(7) | | 1.75 | 1.608 | 1.604(10) |
| 3xSi-O(4) | 2.14 | 1.625 | 1.629(7) | 9. Si-O(2) | | 2.33 | 1.664 | 1.683(14) |
| 5a. Si(1)-O(1) | 2.00 | 1.614 | 1.599(9) | Si-O(3) | | 2.00 | 1.634 | 1.610(17) |
| Si(1)-O(2) | 2.13 | 1.626 | 1.650(9) | 2xSi-O(4) | | 2.00 | 1.634 | 1.636(10) |
| Si(1)-O(3) | 2.13 | 1.626 | 1.618(9) | 10a. Si(1)-O(4) | | 2.43 | 1.654 | 1.638(14) |
| Si(1)-O(4) | 1.75 | 1.591 | 1.587(9) | Si(1)-O(1) | | 2.10 | 1.624 | 1.615(14) |
| 5b. Si(2)-O(1) | 2.00 | 1.618 | 1.638(9) | Si(1)-O(2) | | 2.20 | 1.633 | 1.657(15) |
| Si(2)-O(5) | 2.13 | 1.630 | 1.614(9) | Si(1)-O(3) | | 1.76 | 1.593 | 1.595(15) |
| Si(2)-O(6) | 2.13 | 1.630 | 1.607(9) | 10b. Si(2)-O(4) | | 2.43 | 1.667 | 1.660(13) |
| Si(2)-O(7) | 1.75 | 1.595 | 1.613(9) | Si(2)-O(5) | | 1.67 | 1.598 | 1.580(15) |
| 6. Si-O(1) | 2.40 | 1.671 | 1.688(8) | Si(2)-O(6) | | 2.10 | 1.637 | 1.635(14) |
| Si-O(2) | 1.90 | 1.625 | 1.619(10) | Si(2)-O(7) | | 2.10 | 1.637 | 1.664(12) |
| 2xSi-O(3) | 1.95 | 1.629 | 1.625(10) | 10c. Si(3)-O(11) | | 2.33 | 1.643 | 1.622(15) |
| 7a. Si(1)-O(4) | 2.86 | 1.695 | 1.672(8) | Si(3)-O(8) | | 1.76 | 1.591 | 1.630(15) |
| Si(1)-O(1) | 1.86 | 1.604 | 1.604(13) | Si(3)-O(9) | | 2.20 | 1.631 | 1.605(15) |
| Si(1)-O(2) | 1.86 | 1.604 | 1.651(12) | Si(3)-O(10) | | 2.20 | 1.631 | 1.637(13) |
| Si(1)-O(3) | 1.86 | 1.604 | 1.581(9) | 10d. Si(4)-O(11) | | 2.33 | 1.658 | 1.665(15) |
| 7b. Si(2)-O(4) | 2.86 | 1.699 | 1.673(7) | Si(4)-O(12) | | 1.76 | 1.606 | 1.576(15) |
| Si(2)-O(5) | 1.86 | 1.608 | 1.588(13) | Si(4)-O(13) | | 1.67 | 1.598 | 1.624(15) |
| Si(2)-O(6) | 1.86 | 1.608 | 1.648(14) | Si(4)-O(14) | | 1.76 | 1.606 | 1.602(15) |
| Si(2)-O(7) | 1.86 | 1.608 | 1.614(9) | | | | | |

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| Table 5 cont. | $p_O$ (v.u.) | $d_{calc}$ (Å) | $d_{obs}$ (Å) | | $p_O$ (v.u.) | $d_{calc}$ (Å) | $d_{obs}$ (Å) |
|---|---|---|---|---|---|---|---|
| 11.   Si-O(1) | 2.25 | 1.648 | 1.653(1) | 19a.  Si(1)-O(9) | 2.00 | 1.631 | 1.645(11) |
| 2xSi-O(2) | 1.92 | 1.618 | 1.615(1) | 2xSi(1)-O(1) | 2.29 | 1.658 | 1.655(11) |
| Si-O(3) | 2.25 | 1.648 | 1.648(1) | Si(1)-O(7) | 1.57 | 1.592 | 1.585(12) |
| 12a.  Si(1)-O(5) | 2.29 | 1.657 | 1.653(4) | 19b.  Si(2)-O(9) | 2.00 | 1.619 | 1.620(11) |
| 2xSi(1)-O(2) | 2.04 | 1.634 | 1.633(3) | 2xSi(2)-O(3) | 2.07 | 1.626 | 1.621(11) |
| Si(1)-O(6) | 1.50 | 1.585 | 1.591(4) | Si(2)-O(8) | 1.50 | 1.574 | 1.582(13) |
| 12b.  Si(2)-O(5) | 2.29 | 1.660 | 1.660(4) | 20a.  Si(1)-O(9) | 2.00 | 1.624 | 1.625(15) |
| Si(2)-O(3) | 2.12 | 1.645 | 1.650(4) | 2xSi(1)-O(1) | 2.29 | 1.651 | 1.652(9) |
| 2xSi(2)-O(4) | 2.04 | 1.638 | 1.634(3) | Si(1)-O(7) | 1.54 | 1.582 | 1.580(13) |
| 13.   Si-O(1) | 2.50 | 1.658 | 1.649(3) | 20b.  Si(2)-O(9) | 2.00 | 1.628 | 1.628(15) |
| Si-O(2) | 1.75 | 1.590 | 1.583(6) | 2xSi(2)-O(3) | 2.04 | 1.632 | 1.627(9) |
| 2xSi-O(3) | 2.00 | 1.613 | 1.619(5) | Si(2)-O(8) | 1.50 | 1.583 | 1.595(15) |
| 14.   Si-O(1) | 2.00 | 1.622 | 1.605(1) | 21a.  Si(1)-O(9) | 2.00 | 1.633 | 1.652(14) |
| Si-O(2) | 2.00 | 1.622 | 1.627(2) | 2xSi(1)-O(1) | 2.15 | 1.646 | 1.644(14) |
| 2xSi-O(3) | 2.00 | 1.622 | 1.628(1) | Si(1)-O(7) | 1.63 | 1.599 | 1.582(14) |
| 15a.  Si(1)-O(9) | 2.00 | 1.622 | 1.628(6) | 21b.  Si(2)-O(9) | 2.00 | 1.633 | 1.627(14) |
| 2xSi(1)-O(1) | 2.29 | 1.649 | 1.652(6) | 2xSi(2)-O(3) | 2.13 | 1.645 | 1.632(14) |
| Si(1)-O(7) | 1.54 | 1.580 | 1.566(6) | Si(2)-O(8) | 1.36 | 1.575 | 1.603(14) |
| 15b.  Si(2)-O(9) | 2.00 | 1.624 | 1.627(6) | 22.   Si-O(1) | 2.46 | 1.668 | 1.654(8) |
| 2xSi(2)-O(3) | 2.04 | 1.628 | 1.620(6) | Si-O(2) | 1.69 | 1.598 | 1.592(16) |
| Si(2)-O(8) | 1.50 | 1.579 | 1.593(6) | 2xSi-O(3) | 2.06 | 1.632 | 1.643(16) |
| 16a.  Si(1)-O(9) | 2.00 | 1.626 | 1.638(7) | 23.   Si-O(4) | 2.33 | 1.652 | 1.661(10) |
| 2xSi(1)-O(1) | 2.29 | 1.653 | 1.654(5) | Si-O(1) | 1.83 | 1.607 | 1.623(14) |
| Si(1)-O(7) | 1.54 | 1.584 | 1.569(7) | Si-O(2) | 2.17 | 1.638 | 1.635(16) |
| 16b.  Si(2)-O(9) | 2.00 | 1.629 | 1.634(7) | Si-O(3) | 1.83 | 1.607 | 1.586(19) |
| 2xSi(2)-O(3) | 2.04 | 1.633 | 1.619(5) | 24a.  Si(1)-O(8) | 2.29 | 1.657 | 1.686(19) |
| Si(2)-O(8) | 1.50 | 1.584 | 1.608(7) | 2xSi(1)-O(1) | 1.79 | 1.611 | 1.604(25) |
| 17.   Si-O(4) | 2.00 | 1.628 | 1.627(4) | Si(1)-O(4) | 2.29 | 1.657 | 1.640(20) |
| 2xSi-O(1) | 2.00 | 1.628 | 1.626(6) | 24b.  Si(2)-O(8) | 2.29 | 1.658 | 1.657(19) |
| Si-O(2) | 2.00 | 1.628 | 1.631(10) | 2xSi(2)-O(2) | 2.07 | 1.638 | 1.634(24) |
| 18a.  Si(1)-O(9) | 2.00 | 1.626 | 1.640(7) | Si(2)-O(10) | 2.12 | 1.642 | 1.650(19) |
| 2xSi(1)-O(1) | 2.29 | 1.653 | 1.645(7) | 25.   Si-O(1) | 2.40 | 1.642 | 1.626(16) |
| Si(1)-O(7) | 1.54 | 1.584 | 1.586(7) | Si-O(2) | 1.60 | 1.569 | 1.607(37) |
| 18b.  Si(2)-O(9) | 2.00 | 1.619 | 1.628(7) | 2xSi-O(3) | 2.20 | 1.624 | 1.613(22) |
| 2xSi(2)-O(3) | 2.04 | 1.623 | 1.612(7) | 26a.   Si(1)-O(9) | 2.00 | 1.622 | 1.627(25) |
| Si(2)-O(8) | 1.50 | 1.574 | 1.588(7) | 2xSi(1)-O(1) | 2.29 | 1.649 | 1.629(25) |
| | | | | Si(1)-O(7) | 1.54 | 1.580 | 1.613(25) |
| | | | | 26b.  Si(2)-O(9) | 2.00 | 1.640 | 1.608(25) |
| | | | | 2xSi(2)-O(3) | 2.04 | 1.644 | 1.645(25) |
| | | | | Si(2)-O(8) | 1.50 | 1.595 | 1.627(25) |

ences in precision into account. The correlation coefficient for the regression of $\Delta d$(om) on $\Delta p_O$ for Si-O bonds in disilicates is 0.91 (Table 6, No. 1). This means that 83 percent of the variations of the individual bond lengths from their mean can be interpreted in terms of a dependence on $\Delta p_O$ (see Fig. 1). In view of the large spread of observed Si-O distances (1.57 to 1.69 Å) the close agreement between $\Delta d$(om) and $\Delta p_O$ is remarkable. The mean deviation (mean $\Delta d$(oc)) between $d$(obs) and
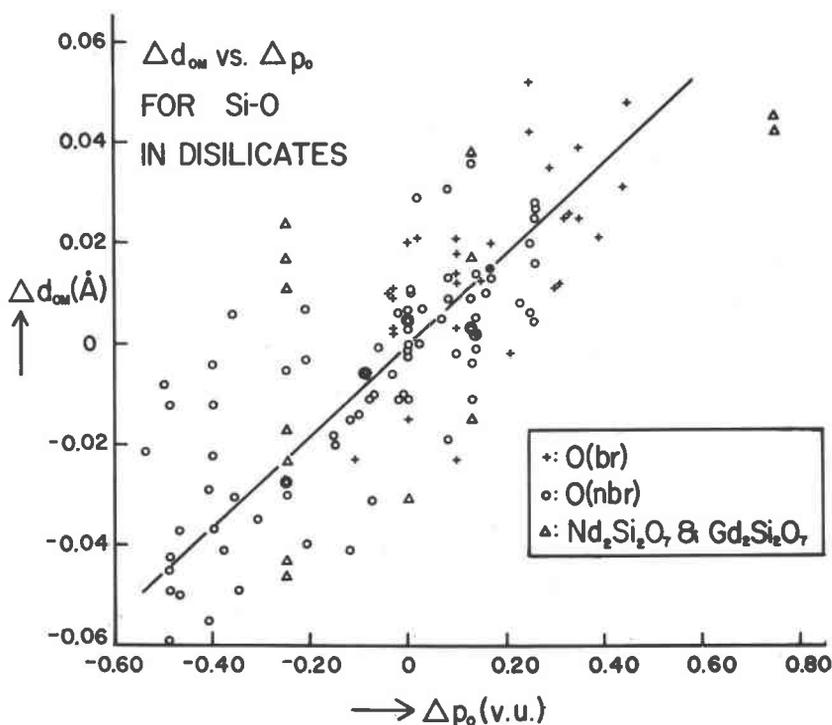
FIG. 1. Bond length variation $\Delta d(om)$ versus $\Delta p_0$ for silicon-oxygen bond lengths in 26 crystal structures containing disilicate groups.

$d$(calc) for all the data is only 0.011 Å and this includes the less accurately determined crystal structures in which the experimental error of the determination contributes heavily to the $\Delta d(oc)$ values. The correlation between mean $\Delta d(oc)$ and mean e.s.d. is 0.65 (Table 6, No. 4). This shows that a considerable part of the value of $\Delta d(oc)$ is caused by the experimental inaccuracy in the original structure determinations.

It is not necessary to explain all the deviations ($\Delta d(oc)$) by the imperfection of the model used. Moreover we can obtain an indication of the errors inherent in the method by observing the value of the intercept at e.s.d. $=0$. It is 0.004 Å and can be interpreted to mean that even for the case of Si-O bond lengths known without any experimental error we would find values of $\Delta d(oc)$ of this magnitude. Therefore it is not surprising that the values of the mean $\Delta d(oc)$/e.s.d. (Tables 1 and 2) are high for some of the more precisely determined crystal structures (*e.g.*, lawsonite) and low for many of the less precise structures (Nos. 9, 10, 19 to 26). However the poor agreement between observed and calculated

Table 6. Results of regression analyses, N = number of points in sample, a = intercept, b = slope of regression equation, r = correlation coefficient, % = percent variation explained, mean Δ = mean of all differences between observed and calculated values using the regression equations, uw = unit weights, iw = individual weights applied.

| No. | regression of | N | a (Å) | b | r | % | mean Δ (Å) | | remarks |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $\Delta d_{om}$ on $\Delta p_O$ | 164 | 0.0 | 0.087(3) | 0.91 | 83 | 0.011 | iw | data from Tables 4 and 5 |
| 2 | " | 148 | 0.0 | 0.090(3) | 0.92 | 85 | 0.010 | iw | as above, but excluding the Nd- and Gd-silicates. |
| 3 | " | 148 | 0.0 | 0.075(5) | 0.80 | 64 | 0.010 | uw | |
| 4 | mean $\Delta d_{oc}$ on mean e.s.d. | 24 | 0.004(2) | 0.52(13) | 0.65 | 42 | 0.003 | uw | data from Tables 1 and 2, excluding the Nd- and Gd-silicates |
| 5 | $\Delta d_{om}$ on ⅀Si-O-Si | 41 | 0.080(14) | -0.0004(1) | -0.58 | 34 | 0.013 | iw | data from Tables 1, 2, 4 and 5. |
| 6 | " | 57 | 0.087(12) | -0.0005(1) | -0.72 | 52 | 0.010 | iw | as above, but excluding the Nd- and Gd-silicates. |
| 7 | " | 37 | 0.10(2) | -0.0006(1) | -0.60 | 36 | 0.010 | uw | |
| 8 | d(Si-O) on ⅀Si-O-Si | 26 | 1.81(4) | -0.0014(3) | -0.71 | 51 | 0.011 | uw | data for SiO₂-polymorphs, as used by Brown et al., 1969. |
| 9 | " | 26 | 1.71(3) | -0.0007(2) | -0.59 | 34 | 0.013 | iw | |
| 10 | " | 26 | 1.617(18) | 0.0000(1) | -0.07 | 1 | 0.011 | iw | SiO₂-polymorphs with corrected tridymite-values and disilicates (Table 7). |
| 11 | $\Delta d_{om}$ on ⅀Si-O-Si | 26 | 0.006(16) | 0.0000(1) | -0.08 | 1 | 0.009 | iw | |

values for the crystal structures of $Gd_2Si_2O_7$ and $Nd_2Si_2O_7$ is surprising. Possible explanations for the discrepancy are to assume either that the e.s.d.'s are underestimated or that for these compounds the model is insufficient. As discussed at greater length previously (Baur, 1970) the Pauling bond strength is used here as an approximate measure of the potential of the cations on the anion-site in an undistorted coordination site. We should therefore expect deviations from rule 3, whenever this approximation is insufficient. This could happen when very irregular polyhedra are present, such as those found in $Gd_2Si_2O_7$ and $Nd_2Si_2O_7$ around the Gd-atoms and the Nd-atoms. The variation in $d$(Gd-O) is from 2.25 to 2.63 Å and in $d$(Nd-O) from 2.24 to 2.95 Å. However there is reason to believe that the first-mentioned explanation applies here. Smolin and Shepelev (1970) have refined $Nd_2Si_2O_7$ in space group $P2_12_12_1$. Felsche (1970) contests this assignment and claims that $Nd_2Si_2O_7$ is pseudo-orthorhombic and belongs to space group $P2_1/n$. The crystal structure of $Gd_2Si_2O_7$ was refined by Smolin and Shepelev both in space group *Pnam*, and then in *Pna2₁*. The final R-value of 0.073 for 1300 $F_{obs}$ in space group *Pna2₁* does not appear to be incontrovertible proof that the assignment of an acentric space group is correct (compare Baur and Tillmanns, 1970, for the discussion of a similar case). Since there is sufficient doubt about the correct space groups of both, $Gd_2Si_2O_7$ and $Nd_2Si_2O_7$, only the results of those calculations will be discussed below which exclude data points from these two compounds. Most of the points in Figure 1 which are not close to the regression line correspond to bond lengths with large e.s.d.'s, which do not contribute heavily to the correlation because they were given small weights. Using unit weights $r$ is 0.80 (Table 6, No. 3) which still defines a strong dependence of $\Delta d$(om) on $\Delta p_O$.

The value of the slope $b$ (0.090(3)Å/v.u.) is essentially identical with the value of the slope found previously ($b$=0.091(3)Å/v.u., Baur, 1970). For the calculation of bond lengths (in Tables 4 and 5) the latter value was used since it is based on a larger sample. It was derived by a least-squares linear regression of 293 observed Si-O distances (obtained from 45 silicate crystal structure determinations) on the bond strength, $p_O$, received by the oxygen atoms (rule 2), according to the expression:

$$d(A - X) = (a + bp_x)\text{Å} \qquad (3)$$

Rule 2 is a poorer approximation than rule 3 for the calculation of bond lengths but the slopes in both equations, (1) and (3) obviously have the same values. Both sets of data, the 45 silicates analyzed previously (Baur, 1970) and the 26 disilicates studied here, overlap slightly: bond length data from zoisite, clinozoisite, and piemontite (Dollase, 1968, 1969) were used both times.

The comparison of $d$(obs) and $d$(calc) (Tables 4 and 5), which agree on the average to within 0.010 Å, supports further the validity of rule 3. It can be stated confidently that rule 3 rationalizes in considerable detail the distortions encountered in the bond lengths of disilicate groups. Eighty-five percent of the variation in $\Delta d$(om) is explained by the dependence on the bond strength variation, $\Delta p_0$ (Table 6, No. 2). One can express this result differently and say that all the coordinating cations of every silicate oxygen atom determine the length of the silicon oxygen distance. Thus this empirical and quantitative approach emphasizes the influence of all the ligands on the bond lengths, in contrast to Cruickshank's (1961) approach which stresses the internal electronic structure within the isolated silicate groups.

## Bond Length and the Angle Silicon-Oxygen-Silicon

Based on the simple $d$-$p$ $\pi$-bonding theory Cruickshank (1961) predicted that in an isolated disilicate group with an $\angle$ Si-O-Si of 180° the bridging Si-O(br) bond should have a length of 1.656 Å, while the non-bridging Si-O(nbr) bond lengths should be 1.621 Å. He assumes here that: a) the Si-O single bond has a length of 1.76 Å, b) the Si-O bond is 1.63 Å long, when it has a $\pi$-bond order of $\frac{1}{2}$, and c) the bridging oxygen has two $p$-orbitals available for $\pi$-bonding with the silicon atoms. As the angle $<$ Si-O-Si becomes smaller the bridging oxygen atom should lose its facility to engage in $\pi$-bonding with the silicon atom and consequently the Si-O(br) bonds should become weaker and longer, while the Si-O(nbr) bonds should become stronger and shorter. For the case of a metasilicate chain $(SiO_3)_\infty$ with $\angle$ Si-O-Si of 120°, Cruickshank gives an estimate of 1.70 Å and 1.56 Å for the inner (bridging) and outer (non-bridging) bonds. Presumably this relationship between the Si-O(br) bond length and the angle $\angle$ Si-O-Si should be most clearly displayed in the disilicate group itself. In more highly condensed silicates it possibly might be masked by constraints on the bonding geometry caused by mutual interactions of the tetrahedral groups.

In Figure 2 the $\Delta d$(om) for the Si-O(br) bonds are plotted versus $\angle$ Si-O-Si. The $\Delta d$(om) rather than the $d$(Si-O) are plotted in order to facilitate comparison with Figure 1. The correlation coefficient is $-0.72$ (Table 6, No. 6), which means that slightly more than half of the variation in the bridging bond lengths can be explained by the dependence on $\angle$ Si-O-Si. While it is obvious that a correlation between $\Delta d$(om) and the angle does exist, it is a) distinctly poorer than the correlation between $\Delta d$(om) and $\Delta p_0$ and b) it applies only to the bridging bonds, therefore it cannot be used to calculate the non-bridging silicon oxygen bonds, and is therefore of less practical value than the $\Delta d$(om) versus $\Delta p_0$ correlation. These two correlations seem to be related to each other. Whenever
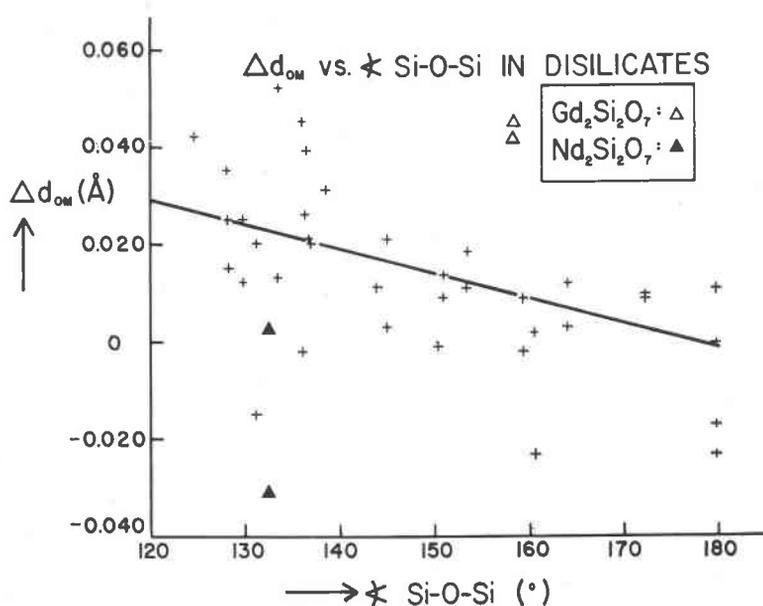
Fig. 2. Bond length variation $\Delta d(\text{om})$ versus $\sphericalangle$ Si-O-Si
for disilicate groups.

the O(br) atom is involved in a straight or large $\sphericalangle$ Si-O-Si it cannot be coordinated (because of steric reasons) to any additional cations and consequently receives a bond strength of 2.0 v.u., and therefore will form Si-O bonds of average length. However if the bridging oxygen atom is involved in a smaller $\sphericalangle$ Si-O-Si, it is more likely to engage in additional contacts to other cations, thus increasing the bond strength it receives, and therefore form bonds of more than average length. This is borne out by the data in Tables 1 and 2. The average $\sphericalangle$ Si-O-Si for all bridging O-atoms in 3- or 4-coordination is 134°, for all those in 2-coordination it is 154° (this excludes the cases with angles of 180°). However this does not mean that the bridging oxygen atom is 3- or 4-coordinated *because* the $\sphericalangle$ Si-O-Si is small or vice versa that the $\sphericalangle$ Si-O-Si is small *because* the oxygen atom is 3- or 4-coordinated. It is sufficient to say that both conditions do occur together and it is the higher coordination (which means larger $p_O$-values) which causes the longer Si-O distance and it is not necessarily the small $\sphericalangle$ Si-O-Si, which is responsible for the bond lengthening.

If this interpretation is correct and the $\Delta d(\text{om})$ on $\sphericalangle$ Si-O-Si correlation is only a corollary of the more basic $\Delta d(\text{om})$ on $\Delta p_O$ correlation then we should expect no correlation between Si-O(br) bond length (or $\Delta d(\text{om})$) and $\sphericalangle$ Si-O-Si in cases were all silicate oxygen atoms receive the

Table 7.    Angles Si-O-Si, distances Si-O and $\Delta d_{om}$ for crystal structures with
            $\Delta p_O = 0$ for all silicate oxygen atoms.

| | ⌡Si-O-Si | d(Si-O) | $\Delta d_{om}$ | reference |
|---|---|---|---|---|
| low cristobalite | 146.8° | 1.601(4)Å | -0.004Å | Dollase, 1965 |
| low cristobalite | 146.8 | 1.608(4) | 0.003 | Dollase. 1965 |
| coesite | 180.0 | 1.600(3) | -0.009 | Araki & Zoltai, 1969 |
| coesite | 143.8 | 1.608(3) | -0.009 | Araki & Zoltai, 1969 |
| coesite | 145.0 | 1.607(5) | -0.002 | Araki & Zoltai, 1969 |
| coesite | 145.0 | 1.619(6) | 0.002 | Araki & Zoltai, 1969 |
| coesite | 150.4 | 1.598(5) | -0.011 | Araki & Zoltai, 1969 |
| coesite | 150.4 | 1.625(5) | 0.008 | Araki & Zoltai, 1969 |
| coesite | 136.1 | 1.631(5) | 0.022 | Araki & Zoltai, 1969 |
| coesite | 136.1 | 1.617(5) | 0.000 | Araki & Zoltai, 1969 |
| quartz | 143.5 | 1.603(2) | -0.007 | Zachariasen & Plettinger, 1965 |
| quartz | 143.5 | 1.616(2) | 0.006 | Zachariasen & Plettinger, 1965 |
| keatite | 155.8 | 1.58(2) | -0.02 | Shropshire et al., 1959 |
| keatite | 155.8 | 1.59(2) | -0.01 | Shropshire et al., 1959 |
| keatite | 149.4 | 1.61(2) | 0.01 | Shropshire et al., 1959 |
| keatite | 149.4 | 1.61(2) | 0.02 | Shropshire et al., 1959 |
| keatite | 155.3 | 1.61(2) | 0.01 | Shropshire et al., 1959 |
| keatite | 155.3 | 1.57(2) | -0.02 | Shropshire et al., 1959 |
| high tridymite | 149.2 | 1.621(10) | 0.008 | Dollase, 1967 |
| high tridymite | 146.2 | 1.625(10) | 0.012 | Dollase, 1967 |
| high tridymite | 150.0 | 1.608(20) | -0.005 | Dollase, 1967 |
| high tridymite | 150.0 | 1.597(20) | -0.016 | Dollase, 1967 |
| $Yb_2Si_2O_7$ | 180.0 | 1.615(3) | 0.000 | Smolin & Shepelev, 1970 |
| $Er_2Si_2O_7$ | 180.0 | 1.621(3) | 0.011 | Smolin & Shepelev, 1970 |
| hemimorphite | 150.3 | 1.616(4) | -0.001 | McDonald & Cruickshank, 1967a |
| thortveitite | 180.0 | 1.593(5) | -0.017 | Prewitt, 1970, pers. comm. |

same bond strength and therefore $\Delta p_O$ for all oxygen atoms is zero. Cases among the disilicates with $\Delta p_O = 0$ are: Nos. 2, 3, 14, and 17. Since this is not sufficient for establishing the presence or absence of a correlation, the data from the $SiO_2$ polymorphs have to be included (Table 7). The average coordination number of the oxygen atoms in a silicate group is 2 in $SiO_2$, in the four disilicates it is 2.75. In order to make the two sets of bond lengths comparable, the values of the Si-O distances for the disilicates have been reduced by $0.75 \times 0.015 = 0.011$ Å (see expression 2). The bond length values of the Si-O bonds in tridymite are those corrected by

Dollase (1967) for the effects of thermal motion (riding model). This correction amounts to about 0.06 Å because the thermal movement of these oxygen atoms is extremely large and highly anisotropic. The values of the ∢Si-O-Si had to be corrected accordingly. For all other bond lengths the thermally uncorrected values are being used, since the possible corrections are estimated to be smaller than 0.01 Å. The bond lengths in keatite (Shropshire *et al.*, 1959) were assigned e.s.d.'s which are reasonable guesses, because no errors have been stated in the original paper. Likewise the errors of the *corrected* bond lengths in tridymite are estimated. Both estimates are probably too low. Correlations have been calculated for both: $d$(Si-O) versus ∢Si-O-Si, and $\Delta d$(om) versus ∢Si-O-Si. In neither case can a correlation between bond length variation and ∢Si-O-Si be proved (Table 6, Nos. 10 and 11). This result is at variance with the finding of Brown *et al.* (1969) who claim to have established a $d$(Si-O) versus ∢Si-O-Si correlation for the $SiO_2$ polymorphs (Table 6, Nos. 8 and 9). This discrepancy has two reasons: a) Brown *et al.* used unit weights for their least squares fit, thus giving undue weight to the demonstrably poor keatite data and to two of the tridymite points, and b) they used the uncorrected bond length values for tridymite, because they apparently overlooked the large and anisotropic thermal motion of the oxygen atoms in this compound.

In this context Brown and Gibbs' (1970) proposal regarding the ordering of tetrahedral cations in silicates should be discussed. They state that "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." It is thus argued by these authors that the di- and tri-valent tetrahedral cations 'prefer' tetrahedral sites with smaller T-O-T angles. If one turns the reasoning around it makes sense as a consequence of Pauling's electrostatic valence rule. Since oxygen atoms bonded to Al, B, Be, or Mg will generally have relatively small contributions to their $p_O$ from the tetrahedral cations, the angle T-O-T must be small, so that additional contacts to non-tetrahedral cations can be made, thus increasing the $p_O$-values of these oxygen atoms. This proposal is therefore a corollary of the electrostatic valence rule.

## Bond Lengths and Electronegativity

The difficulty of reconciling the observed bond distances in certain silicates with the $d$-$p$ $\pi$-bonding theory has led McDonald and Cruickshank (1967a,b) to make additional assumptions. In hemimorphite (1967a) they had to assume the formation of covalent bonds between zinc and oxygen atoms. They pointed out that the bond angles around the oxygen atoms O(1) and O(2) (both non-bridging) are close to 120°.
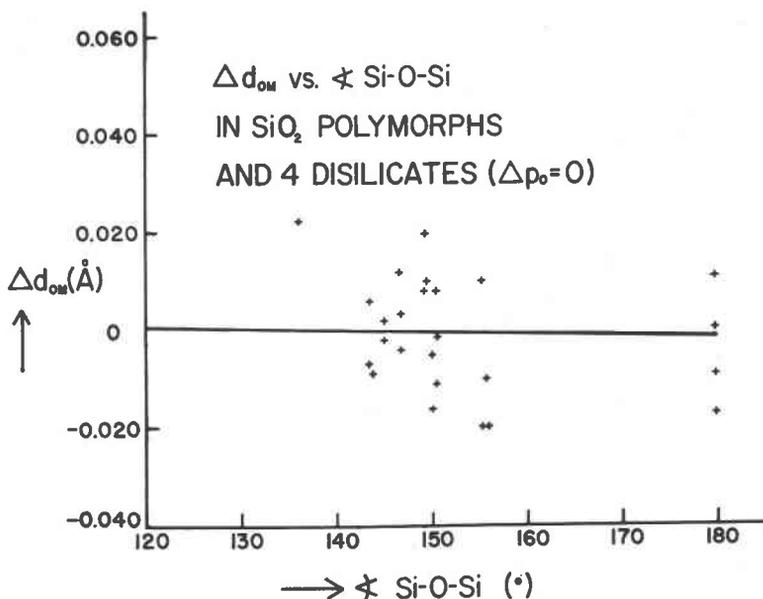
FIG. 3. Bond length variation $\Delta d$(om) versus $\angle$Si-O-Si for silicates in which $\Delta p_O$ equals zero for all oxygen atoms.

thus indicating $sp^2$ hybridization. This reasoning cannot be easily ex-tended to include the bridging oxygen atoms in the disilicates, because the average angle Si-O-Si (Tables 1 and 2) for three-coordinated O(br) is 131.5° (mean of 6) and for four-coordinated O(br) it is 136.6° (mean of 6). It is of interest that these numbers are very close to those for three- and four-coordinated oxygen atoms in anorthite, (132.0° and 136.9°, averages of 19 and of 4 values, Megaw et al., 1962). This means that one cannot generally assume $sp^2$ and $sp^3$ hybridization in these cases, since the values of the angles should then be close to 120° and 109.5°.

In their discussion of chain-silicates McDonald and Cruickshank (1967) went one step further and suggested that the different electro-positive character of the cations in the series of structures listed in Table 8 could be related to the formation of partially covalent bonds of differ-ent strengths between these cations and the oxygen atoms of the silicate group. Because of these covalent bonds the silicate 'ions' would lose part of their $\pi$-bonding potential. The more the silicate groups would thus 'shed' their negative charge the smaller would the differences ($\Delta d$(obs)) between the Si-O(br) and the Si-O(nbr) bond distances become. Accord-ing to McDonald and Cruickshank (1967b) the decreasing values of $\Delta d$(obs) in Table 8 should therefore be caused by 'the lower electroposi-
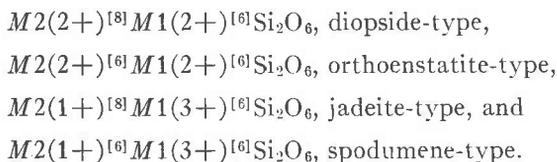
Table 8. Observed and calculated mean distances from silicon to bridging and to non-bridging oxygen atoms in five chain silicates. The $\Delta d$ is the difference between the mean of $d(Si-O(br))$ and the mean of $d(Si-O(nbr))$.

| | mean $d(Si-O(br))$ | | mean $d(Si-O(nbr))$ | | $\Delta d$ | | range of $\Delta p_O(br)$ | mean $\Delta d_{oc}$ |
|---|---|---|---|---|---|---|---|---|
| | obs | calc | obs | calc | obs | calc | | |
| Na-metasilicate, (1) | 1.672Å | 1.659Å | 1.592Å | 1.605Å | 0.080Å | 0.054Å | 0.30 v.u. | 0.013Å |
| wollastonite, (2) | 1.655 | 1.647 | 1.598 | 1.604 | 0.057 | 0.043 | 0.18-0.28 | 0.011 |
| rhodonite, (3) | 1.648 | 1.650 | 1.608 | 1.613 | 0.040 | 0.037 | 0.17-0.29 | 0.011 |
| bustamite, (4) | 1.642 | 1.638 | 1.604 | 1.605 | 0.038 | 0.033 | 0.0 -0.33 | 0.008 |
| stokesite, (5) | 1.630 | 1.629 | 1.612 | 1.614 | 0.018 | 0.015 | 0.00-0.17 | 0.008 |

(1) $Na_2$[5]$SiO_3$, McDonald & Cruickshank, 1967b

(2) $Ca_2$[6]$Ca$[7]$(SiO_3)_3$, Prewitt & Buerger, 1963

(3) $Mn_3$[6]$(Mn,Mg,Fe)$[5]$(Ca,Mn)$[7]$(SiO_3)_5$, Peacor & Niizeki, 1963

(4) $Ca$[6]$Mn$[6]$(SiO_3)_2$, Peacor & Buerger, 1962

(5) $Ca$[6]$Sn$[6]$(SiO_3)_3 \cdot 2H_2O$, Vorma, 1963

tive character of calcium, manganese and tin compared with sodium.'
However it seems that this decrease in $\Delta d$(obs) can just as well be corre-
lated with decreasing $\Delta p_O$-values of the bridging and non-bridging oxygen
atoms in this series of chain-silicates. The main results of detailed calcu-
lations of the same type as presented earlier for the disilicates are shown
in Table 8 for the five chain silicates. The values of $\Delta d$(calc) closely
parallel those of $\Delta d$(obs). Since the full details of the calculations are not
presented here, at least the range of the $\Delta p_O$(br) is given in Table 8. It is
obvious that the diminishing differences between Si-O(br) and Si-O(nbr)
are related to the diminishing $\Delta p_O$ values. While it cannot be ruled out
completely that the electropositive character of the cations is also some-
how connected with these differences, this series of compounds is a poor
sample for testing this hypothesis, because the compounds are not iso-
structural and the different oxygen atoms receive widely different bond
strengths.

The four pairs of strictly isostructural pyroxenes listed in Table 9 pro-
vides the basis for a better comparison. The pyroxenes used represent
four different structural types of pyroxene:

$$M2(2+)^{[8]}M1(2+)^{[6]}Si_2O_6, \text{ diopside-type,}$$

$$M2(2+)^{[6]}M1(2+)^{[6]}Si_2O_6, \text{ orthoenstatite-type,}$$

$$M2(1+)^{[8]}M1(3+)^{[6]}Si_2O_6, \text{ jadeite-type, and}$$

$$M2(1+)^{[6]}M1(3+)^{[6]}Si_2O_6, \text{ spodumene-type.}$$

Even the three clinopyroxenes are not strictly isostructural, because they
contain cations of different valence states in the $M$-sites, and have dif-
ferent coordination numbers for the cations in the $M2$-site. As a conse-
quence of this, the coordination numbers of the individual oxygen atoms
and their $\Delta p_O$-values vary appreciably. Therefore a test for the influence
of the electronegativity can only be made within each given pair. The
electronegativity-values in question are: Li, 1.0; Na, 0.9; Mg, 1.2; Al, 1.5;
Ca, 1.0; Mn, 1.5, and Fe, 1.8 (Pauling, 1960). In Table 9 the pyroxenes
with the more electronegative $M1$-cations (Mn, Fe) are listed on the
right side, those with the less electronegative $M1$-cations (Mg, Al) on the
left side. The oxygen atoms O(1) are coordinated twice to $M1$, the O(2)-
atoms only once. In orthoenstatite and orthoferrosilite the $M2$-site is
occupied by Mg and Fe respectively; each oxygen atom has one contact
to the $M2$-site. No unambiguous trend attributable to electronegativities
is apparent between the bond lengths of the pyroxenes on going from the
left to the right side of Table 9. The mean tetrahedral distances Si-O in-
crease (Nos. 1 and 3), decrease (No. 2), or do not change (No. 4). The Si-
O(1) distances decrease (Nos. 2a, 3 and 4) or do not change (Nos. 1 and

Table 9. Observed and calculated d(Si-O) in four different pyroxene structure types. The $p_O$ and $\Delta p_O$ are in v.u., all other numbers in Å.

**1)**

| | $p_O$ | $\Delta p_O$ | $d_{calc}$ | diopside, $CaMgSi_2O_6$ Clark et al., 1969 $d_{obs}$ | $\Delta d_{oc}$ | $\Delta d_{om}$ | $d_{calc}$ | johannsenite, $CaMnSi_2O_6$ Freed and Peacor, 1967 $d_{obs}$ | $\Delta d_{oc}$ | $\Delta d_{om}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Si-O(1) | 1.92 | -0.21 | 1.616 | 1.602(2) | -0.014 | -0.033 | 1.625 | 1.604(6) | -0.021 | -0.040 |
| Si-O(2) | 1.58 | -0.55 | 1.585 | 1.585(1) | 0.000 | -0.050 | 1.594 | 1.594(6) | 0.000 | -0.050 |
| Si-O(3) | 2.50 | 0.37 | 1.669 | 1.664(2) | -0.005 | 0.029 | 1.678 | 1.683(7) | 0.005 | 0.039 |
| Si-O(3) | 2.50 | 0.37 | 1.669 | 1.687(2) | 0.018 | 0.052 | 1.678 | 1.693(7) | 0.015 | 0.049 |
| mean: | 2.13 | | | 1.635 | 0.009 | | | 1.644 | 0.010 | |

**2a)**

| | $p_O$ | $\Delta p_O$ | $d_{calc}$ | orthoenstatite, $Mg_2Si_2O_6$ Morimoto & Koto, 1969 $d_{obs}$ | $\Delta d_{oc}$ | $\Delta d_{om}$ | $d_{calc}$ | orthoferrosilite, $Fe_2Si_2O_6$ Burnham, 1967 $d_{obs}$ | $\Delta d_{oc}$ | $\Delta d_{om}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| SiA-O1A | 2.00 | -0.08 | 1.623 | 1.614(8) | -0.009 | -0.016 | 1.607 | 1.581(9) | -0.026 | -0.033 |
| SiA-O2A | 1.67 | -0.42 | 1.592 | 1.598(8) | 0.006 | -0.032 | 1.576 | 1.594(10) | 0.018 | -0.020 |
| SiA-O3A | 2.33 | 0.25 | 1.653 | 1.673(10) | 0.020 | 0.043 | 1.637 | 1.644(9) | 0.007 | 0.030 |
| SiA-O3A | 2.33 | 0.25 | 1.653 | 1.635(10) | -0.018 | 0.005 | 1.637 | 1.638(9) | 0.001 | 0.024 |
| mean: | 2.08 | | | 1.630 | 0.013 | | | 1.614 | 0.013 | |

**2b)**

| | $p_O$ | $\Delta p_O$ | $d_{calc}$ | $d_{obs}$ | $\Delta d_{oc}$ | $\Delta d_{om}$ | $d_{calc}$ | $d_{obs}$ | $\Delta d_{oc}$ | $\Delta d_{om}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| SiB-O1B | 2.00 | -0.08 | 1.634 | 1.619(8) | -0.015 | -0.022 | 1.617 | 1.611(8) | -0.006 | -0.013 |
| SiB-O2B | 1.67 | -0.42 | 1.603 | 1.596(9) | -0.007 | -0.045 | 1.586 | 1.573(9) | -0.013 | -0.051 |
| SiB-O3B | 2.33 | 0.25 | 1.664 | 1.663(10) | -0.001 | 0.022 | 1.647 | 1.664(10) | 0.017 | 0.040 |
| SiB-O3B | 2.33 | 0.25 | 1.664 | 1.687(9) | 0.023 | 0.046 | 1.647 | 1.647(9) | 0.000 | 0.023 |
| mean: | 2.08 | | | 1.641 | 0.012 | | | 1.624 | 0.009 | |

**3)**

| | $p_O$ | $\Delta p_O$ | $d_{calc}$ | jadeite, $NaAlSi_2O_6$ Prewitt & Burnham, 1966 $d_{obs}$ | $\Delta d_{oc}$ | $\Delta d_{om}$ | $d_{calc}$ | acmite, $NaFeSi_2O_6$ Clark et al., 1969 $d_{obs}$ | $\Delta d_{oc}$ | $\Delta d_{om}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Si-O(1) | 2.13 | 0.07 | 1.629 | 1.637(2) | 0.008 | 0.014 | 1.634 | 1.629(2) | -0.005 | 0.001 |
| Si-O(2) | 1.63 | -0.43 | 1.584 | 1.590(2) | 0.006 | -0.033 | 1.589 | 1.598(2) | 0.009 | -0.030 |
| Si-O(3) | 2.25 | 0.19 | 1.640 | 1.628(2) | -0.012 | 0.005 | 1.645 | 1.637(2) | -0.008 | 0.009 |
| Si-O(3) | 2.25 | 0.19 | 1.640 | 1.636(2) | 0.004 | 0.013 | 1.645 | 1.646(2) | 0.001 | 0.018 |
| mean: | 2.06 | | | 1.623 | 0.008 | | | 1.628(2) | 0.006 | |

**4)**

| | $p_O$ | $\Delta p_O$ | $d_{calc}$ | spodumene, $LiAlSi_2O_6$ Clark et al., 1969 $d_{obs}$ | $\Delta d_{oc}$ | $\Delta d_{om}$ | $d_{calc}$ | $LiFeSi_2O_6$ Clark et al., 1969 $d_{obs}$ | $\Delta d_{oc}$ | $\Delta d_{om}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Si-O(1) | 2.17 | 0.13 | 1.630 | 1.638(2) | 0.008 | 0.020 | 1.632 | 1.629(2) | -0.003 | 0.009 |
| Si-O(2) | 1.67 | -0.37 | 1.584 | 1.586(2) | 0.002 | -0.032 | 1.586 | 1.596(3) | 0.010 | -0.024 |
| Si-O(3) | 2.17 | 0.13 | 1.630 | 1.622(2) | -0.006 | 0.004 | 1.632 | 1.626(2) | -0.006 | 0.006 |
| Si-O(3) | 2.17 | 0.13 | 1.630 | 1.626(2) | -0.004 | 0.008 | 1.632 | 1.627(2) | -0.005 | 0.007 |
| mean: | 2.04 | | | 1.618 | 0.006 | | | 1.620 | 0.006 | |

2b). The Si-O(2) distances increase (Nos. 1, 3, and 4), decrease (No. 2b) or do not change (No. 2a). Likewise there is no clearcut correlation between the $\Delta d$(om) and the electronegativities of the cations in the $M$1- and $M$2-sites. On the other hand the correlation between $\Delta d$(om) and $\Delta p_O$ is excellent and offers a reasonable interpretation for the differences in the bond lengths of the four different types of pyroxenes (see also the discussion of clinopyroxenes by Clark *et al.*, (1969). Brown and Gibbs (1969, 1970) and Mitchell *et al.* (1970) attempted to correlate the Si-O bond length differences in four clinoamphiboles with the electronegativities of the non-tetrahedral cations and with $\angle$Si-O-Si. The four amphiboles in question with their type formulas are:

tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$, Papike *et al.* (1969):

$$M(2+)_2^{[8]}M(2+)_3^{[6]}M(2+)_2^{[6]}Si_8O_{22}(OH)_2$$
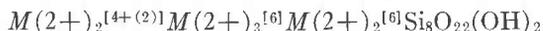
Mn-cummingtonite, $(Mg, Mn, Fe)_7Si_8O_{22}(OH)_2$, Papike et al. (1969):

$$M(2+)_2^{[4+2]}M(2+)_3^{[6]}M(2+)_2^{[6]}Si_8O_{22}(OH)_2$$

glaucophane, $Na_2(Mg, Fe, Al)_5Si_8O_{22}(OH)_2$, Papike & Clark (1968):

$$M(1+)_2^{[8]}M(2+)_3^{[6]}M(3+)_2^{[6]}Si_8O_{22}(OH)_2$$

and grunerite, $Fe_7Si_8O_{22}(OH)_2$, Finger (1969):

$$M(2+)_2^{[4+(2)]}M(2+)_3^{[6]}M(2+)_2^{[6]}Si_8O_{22}(OH)_2$$

Similarly to the case of the pyroxenes, no two of these four amphiboles are strictly isostructural. Cationic valences and coordination numbers vary distinctly. The greatest similarity is between Mn-cummingtonite and grunerite, but the latter has a rather odd four plus two coordination of oxygen atoms around the $Fe^{2+}$-atoms which is essentially a one-sided four coordination (Fe-O: $2 \times 1.99$, $2 \times 2.14$, and $2 \times 2.76$ Å). Consequently the number and valence state of the ligands of the silicate oxygen atoms vary so much between these four amphiboles that it is impossible to ascribe the silicon-oxygen bond length variations to the electronegativity differences of the non-tetrahedral cations. However the $\Delta d$(om) correlate well with the $\Delta p_O$ (see Table VI, in Baur, 1970, where the results of the bond lengths calculations for three of these amphiboles are shown). Since Brown and Gibbs (1969, 1970) and Mitchell *et al.* (1970) do not make the comparisons between strictly isostructural amphiboles, their discussion of Si-O bond lengths versus electronegativity (and $\measuredangle$ Si-O-Si) is not convincing.

The experience with the strictly isostructural pairs of pyroxenes indicates that the search for a dependence of Si-O bond lengths on the electronegativity of the other cations might be futile. In principle, and apart from the Si-O case, one would think that such a dependence would be most pronounced whenever an oxygen atom is involved in two bonds o-very unequal strength: the weaker bond should be affected by the electrof negativity of the cation forming the strong bond to the oxygen atom. For instance in cases like: $\overset{.}{X}$-O---H-O or $X$-O-H---O, where $X$ is P, V, or As the hydrogen bond distance should be influenced by the substitutions in isostructural compounds. Three such cases have been investigated lately: a) $Na_2(OH_2)_7(PO_3OH)$ and $Na_2(OH_2)_7(AsO_3OH)$ (Baur and Khan, 1970), b) $Na_8F(OH_2)_{18}(NaH_2O)(AsO_4)_2$ and $Na_8F(OH)_{18}(NaH_2O)$ $(PO_4)_2$ (Tillmanns and Baur, 1970, and unpublished results) and c) $[Na_{12-13}(OH)_{0-1}(OH)_{48}](XO_4)_4$ with $X = P$, V, or As (Tillmanns and

Baur, 1971). However the substitutions of As or V for *P did not show any effect* on the average hydrogen bond lengths.

## APPLICATIONS

The prediction of individual bond lengths has, apart from its intrinsic interest, practical applications. It allows us to compare actually observed bond distances with the calculated ones so that we:

a) have an additional criterion for the correctness or accuracy of crystal structure determinations. Such was the case in $Zn_3(BO_3)_2$ where the Zn-O distances varied from 1.86 to 2.13 Å and the B-O distances varied from 1.22 to 1.54 Å when the structure was refined in the acentric space group $Ic$ by Garcia-Blanco and Fayos (1968). Since the $\Delta p_O$ were zero for all oxygen atoms such range was unusual. Refinement of the structure in space group $I2/c$ reduced the bond length spread to 1.91 to 2.02 Å for Zn-O, 1.33 to 1.40 Å for B-O (Baur and Tillmanns, 1970). In this case the use of the Pauling-Zachariasen method of balancing valences (Zachariasen, 1963) would not have shown that this structure was refined in the wrong space group, because this method has no predictive value. It deduces bond strengths from the observed bond lengths, and therefore one cannot use it for the prediction of bond lengths unless one wishes to reason in a circle.

b) can detect more complicated and interesting bonding phenomena *after* we are certain to have taken into account the simple effects of $\Delta p_O$ on the bond lengths. While it is unlikely after the foregoing discussions, that the ∢ Si-O-Si or the electronegativities of certain ligands have pronounced effects on Si-O bond lengths, it is nevertheless certain that many other factors influence bond lengths (*e.g.,* Jahn-Teller effect, lone pairs of electrons on certain cations, subtle asymmetries in the $d$-electron configuration as in the rutile-type phases, Baur and Khan, 1971).

c) can predict bond lengths in poorly known crystal structures, provided we know the coordinations of anions and cations around each other. Actually it seems reasonable to assume that the $d$(calc) in Table 5 for Nos. 7 to 10, and 21 to 26 are closer to the true bond lengths Si-O in these compounds than the $d$(obs) are. A similar prediction made for ilvaite (Baur, 1970) has been verified recently as can be seen in Table 10 (Tillmanns and Baur, 1970, unpublished data). The predicted values in column 2 were based on equation (1) with the $\langle d(\text{Si-O})\rangle$ taken from equation (2). Since this underestimated the $\langle d(\text{Si-O})\rangle$ for the Si(2)-tetrahedron the deviations be-

tween columns 2 and 3 are for this tetrahedron all in one direction. This detailed prediction of individual bond lengths approaches in its accuracy (mean $\Delta d(oc) = 0.01$ Å) the precision of modern crystal structure determinations.

d) can get additional information on the crystal chemistry of certain compounds. An example is pumpellyite (No. 24, Table 2) the chemical formula of which is traditionally written in such a way as to indicate the presence of water molecules in this mineral:

$$Ca_2Al_2(Mg, Fe, Al)(SiO_4)Si_2O_7(OH)_2(H_2O, OH).$$
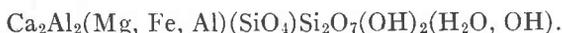
Upon calculation of the bond strengths for this mineral it is immediately obvious that no oxygen atoms in this structure receives a bond strength of less than 1.00 v.u., when the contributions of the hydrogen atoms are disregarded. This excludes the possibility that any one of these oxygen atoms represents a water molecule. Secondly the oxygen atom O(10) receives from Si(2) and one Ca-atom a bond strength of only 1.29 v.u., while the Si(2)-O(10) distance is 1.650(18) Å. Assuming O(10) not to be a hydroxyl group, the bond length calculation for the Si(2) tetrahedron would be as presented in Table 11. Very obviously the $d$(calc) computed this way disagree completely with the $d$(obs) (mean $\Delta d(oc) = 0.032$ Å). When the calculations are based on the assumption that O(10) is a hydroxyl group, the mean $\Delta d(oc)$ equals 0.006 Å (Table 5, No. 24b). Therefore it has to be concluded that pumpellyite actually contains $Si_2O_6(OH)$ groups and not $Si_2O_7$-groups, and that the chemical formula should be written as

$$Ca_2Al_2(Al, Mg, Fe)(O, OH)(OH)_2 (SiO_4)Si_2O_6OH,$$

where the nonsilicate oxygen atoms are most likely disordered with OH-groups in the sites O(7) and O(11), and are replaced by OH to the same degree as divalent cations are replacing aluminum atoms.

## CONCLUSIONS

1. The extended electrostatic valence rule (rule 3, Baur, 1970), has been found to give a reasonable interpretation of the bond length variations in the disilicates, the pyroxenes and other silicate structures.

2. The dependence of $d$(Si-O) (and $\Delta d$(om)) on $\measuredangle$ Si-O-Si has been found to be a secondary consequence of the extended electrostatic valence rule. In crystal structures where $\Delta p_O$ equals zero for all silicate oxygen atoms, this dependence does not seem to exist. Therefore the simple $d$-$p$ $\pi$-bonding approach as discussed by Cruickshank (1961) and Brown *et al.* (1969) should be discarded as a general bonding theory for silicates.

Table 10. Comparison of observed and predicted Si-O bond length in ilvaite. $\Delta d_{31}$ and $\Delta d_{32}$ are the differences between column 3 and 1, and 3 and 2.

| | Belov & Mokeeva, 1951, $d_{obs}$ | Baur, 1970. prediction, $d_{calc}$ | Tillmanns & Baur, unpublished, $d_{obs}$ | $\Delta d_{31}$ | $\Delta d_{32}$ |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | | |
| Si(1)-O(5) | 1.74Å | 1.66Å | 1.653Å | -0.09Å | -0.01Å |
| Si(1)-O(2)(2x) | 1.61 | 1.63 | 1.633 | 0.02 | 0.00 |
| Si(1)-O(6) | 1.60 | 1.58 | 1.591 | -0.01 | 0.01 |
| Si(2)-O(5) | 1.79 | 1.65 | 1.660 | -0.13 | 0.01 |
| Si(2)-O(3) | 1.66 | 1.63 | 1.650 | -0.01 | 0.02 |
| Si(2)-O(4)(2x) | 1.66 | 1.63 | 1.634 | -0.03 | 0.01 |
| mean: | | | | 0.04 | 0.01 |

Table 11. Calculation of $d_{calc}$ for the Si(2)-tetrahedron in pumpellyite based on the assumption that O(10) is not a hydroxyl group.

| | | | | | |
|---|---|---|---|---|---|
| Si(2)-O(2) | 2.07 v.u. | 0.14 v.u. | 1.657Å | 1.634(24)Å | -0.023Å |
| Si(2)-O(2) | 2.07 | 0.14 | 1.657 | 1.634(24) | -0.023 |
| Si(2)-O(8) | 2.29 | 0.36 | 1.677 | 1.657(19) | -0.020 |
| Si(2)-O(10) | 1.29 | -0.64 | 1.586 | 1.650(18) | 0.064 |
| mean: | 1.93 | | | 1.644 | 0.032 |

3. Brown and Gibb's (1970) proposal regarding the ordering of tetrahedral Al, B, Be, and Mg in silicates as a function of $T$-$O$-$T$ angle is a corollary of the electrostatic valence rule.

4. The dependence of $d$(Si-O) (and $\Delta d$(om)) on the electronegativity of other cations bonded to the silicate oxygen atoms (McDonald and Cruickshank, 1967b; Brown and Gibbs, 1969; 1970) has not been proved. The previous workers overlooked that one would have to compare strictly isostructural compounds in order to establish such a relationship. Effects attributed by them to the dependence on electronegativity have been interpreted here as the consequence of $\Delta p_O$-variations.

5. The extended electrostatic valence rule, while it is useful as a tool for predicting individual bond lengths in many crystalline compounds of course cannot replace a detailed bonding theory based on the electronic structure of the atoms. Attempts to establish such a theory should start preferably where the extended electrostatic valence rule fails: in cases where all the oxygen atoms have $\Delta p_O = 0$. Since in these cases no bond length variations can be attributed to $\Delta p_O$-variations, rule 3 cannot be used to predict bond lengths, and therefore other effects can be studied in detail without the interference from $\Delta p_O$-effects. Among silicon containing compounds not only the $SiO_2$-polymorphs, but also olivine, kyanite, and many other minerals, usually with simple crystal structures, fall into this group. A future detailed bonding theory of the silicates and of other oxy-compounds, will have to take into account not only the electronic structure within certain groups of atoms, such as the silicate- or phosphate-tetrahedra but also their relationships to all neighboring cations. Meanwhile we can use the extended electrostatic valence rule and simple geometrical considerations for a semiquantitative prediction of bond lengths.

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*Note added in proof.* In my literature survey, I had overlooked the crystal structure of kornerupine (Moore and Bennett, 1968), which also contains $Si_2O_7$ groups. The agreement between observed and calculated bond lengths Si-O is in this case $\Delta d(oc) = 0.004$ Å, using $p_0$-values of 1.83 v.u. for O(3) and O(4), and 2.17 v.u. for O(9). The bond strength values stated by Moore and Bennett in their Table 3 are partly in error.

An application of the extended electrostatic valence rule to kinoite (Laughon, 1971) shows that this new mineral should not be formulated as $Cu_2Ca_2Si_3O_{10} \cdot 2H_2O$ as proposed by Laughon. If Laughon's formula is accepted, the water molecule oxygen, O(7), would be accepting a bond strength of 2.90 v.u. (from two Cu-ions, one Ca-ion, and two hydrogen atoms), while O(6) would receive 1.33 v.u. from one Si- and one Ca-atom, and the calculated Si-O bond lengths would completely disagree with the $d(Si-O)_{obs}$. These inconsistencies can be removed by assuming that O(6) and O(7) are both hydroxide groups. Therefore the correct formulation should be

$$Cu_2Ca_2(OH)_2Si_3O_8(OH)_2,$$
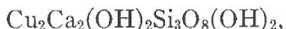
with discrete $Si_3O_8(OH)_2$ groups in the structure.

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