The dependence of the SiO bond length on structural parameters in coesite, the silica polymorphs, and the clathrasils

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Abstract

Stepwise multiple regression analyses of the apparent $R(SiO)$ bond lengths were completed for coesite and for the silica polymorphs together with the clathrasils as a function of the variables $f_s(O)$, P (pressure), $f_s(Si)$, $B(O)$, and $B(Si)$. The analysis of 94 bond-length data recorded for coesite at a variety of pressures and temperatures indicates that all five of these variables make a significant contribution to the regression sum of squares with an R^2 value of 0.84. A similar analysis of 245 $R(SiO)$ data recorded for silica polymorphs and clathrasils indicate that only three of the variables ($B(O)$, $f_s(O)$, and P) make a significant contribution to the regression with an R^2 value of 0.90. The distribution of $B(O)$ shows a wide range of values from 0.25 to 10.0 $Å^2$ with nearly 80% of the observations clustered between 0.25 and 3.0 $Å^2$ and the remaining values spread uniformly between 4.5 and 10.0 $Å^2$. A regression analysis carried out for these two populations separately indicates, for the data set with $B(O)$ values less than three, that $f_s(O)$ $B(O)$, P, and $f_s(Si)$ are all significant with an R^2 value of 0.62. A similar analysis for the remaining data indicates that only $B(O)$ is significant with an R^2 value of 0.52. The relationships between these results and those published previously are discussed.

Introduction

The extent to which various parameters correlate with apparent SiO bond lengths, $R(SiO)$, observed for silicates has been the subject of debate since Cruickshank (1961) first proposed, from his $(d-p)\pi$-bonding model, that $R(SiO)$ should correlate inversely with $\angle SiOSi$. At that time, few precise bond-length and angle data were available, and so the correlation could not be tested. Following refinements of diffraction data recorded at room temperature and pressure for a number of silica polymorphs and feldspars, Brown et al. (1969) undertook a study of the apparent tetrahedral TO bond lengths, $R(TO)$, T = Al,Si, observed for these framework structures and concluded that $R(TO)$ correlates inversely with $\angle TOT$. Baur (1971) observed a similar correlation between $R(SiO)$ and $\angle SiOSi$ for the disilicates, but he ascribed it to a more fundamental correlation between $R(SiO)$ and p_O, the sum of the Pauling strengths of the bonds reaching each oxide ion bonded to Si. In the silica polymorphs, p_O has a constant value of 2.0, whereas it varies in both the feldspars and the disilicates. If the variation in $R(SiO)$ is not dependent upon $\angle SiOSi$ in silicates for which $p_O = 2.0$, as asserted by Baur (1971), then the correlation observed for the silica polymorphs would be a contradiction. However, Baur (1971) claimed that this is not a contradiction because data used to construct the correlation were either imprecise or not corrected for thermal motion. In support of his claim, he completed weighted and unweighted linear regression analyses on the same data set (omitting the imprecise data), with the tridymite data corrected for thermal motion using the riding model and data for four disilicates that have a constant p_O value of 2.0. As the resulting r^2 value was about zero, he concluded that the $R(SiO)$ vs. $\angle SiOSi$ correlation does not exist for crystal structures like the silica polymorphs for which $p_O = 2.0$. This result led him to question the validity of Cruickshank's (1961) $(d-p)\pi$-bonding model as a general bonding theory for the silicates. On the other hand, Taylor (1972) completed an unweighted regression analysis of the bond-length data for the silica polymorphs (without the keatite data), each measured at room temperature and for quartz, measured at high temperatures, all corrected for thermal motion again using the riding model. He found that the $R(SiO)$ vs. $\angle SiOSi$ correlation is significant at the 95% level with an r^2 value of 0.20.

In a theoretical study of SiO bond length vs. $\angle SiOSi$ variations in silicates, Gibbs et al. (1972) undertook semiempirical molecular orbital calculations of the Mulliken overlap populations, $n(SiO)$, of the SiO bridging bonds in an $Si_2O_7^{-6}$ disilicate ion. They found that $n(SiO)$

correlates inversely with $-\sec\angle$SiOSi, despite the assumption in the calculations that all of the SiO bond lengths are constant. Since larger n(SiO) values are usually associated with shorter bonds, wider angles are predicted to involve shorter bonds. In a test of this prediction, Gibbs et al. (1977) collected a relatively precise set of diffraction data for the high-pressure silica polymorph coesite, which contains eight nonequivalent SiO bond lengths and five nonequivalent SiOSi angles. The coesite structure is an ideal system for testing the significance of a correlation between bond length and angle because its SiOSi angles exhibit a relatively wide range of values from 137 to 180°. A regression analysis of the resulting SiO bond-length and $-\sec\angle$SiOSi data shows that the correlation is highly significant, with an r^2 value of 0.96. Gibbs et al. (1977) also found that n(SiO) values calculated for the silicate tetrahedra in coesite serve to rank R(SiO) with shorter bonds involving larger overlap populations. In a study of a more recent refinement of the low tridymite structure, which yielded a relatively large number of bond-length and angle data, Baur (1977) undertook a regression analysis of the SiO bond length as a function of $-\sec\angle$SiOSi for a data set that included data for several silica polymorphs (including the more recent data set for low tridymite but omitting that for coesite) and for eight other silicates, all of which have a constant p_0 value of 2.0. As only 4% of the variation of R(SiO) could be explained in terms of a linear dependence on $-\sec\angle$SiOSi, he again concluded that the relationship between R(SiO) and $-\sec\angle$SiOSi could not be viewed as a general property of SiO bonds involving charged-balanced oxide ions. He also asserted that the correlation found by Gibbs et al. (1977) for coesite would "disappear when larger, less-biased samples are studied." Structural analyses completed for quartz (Levien et al., 1980), with data recorded at a number of pressures up to about 60 kbar, seemed to support his assertion, with R(SiO) observed to increase with increasing $-\sec\angle$SiOSi (Baur and Ohta, 1982). However, as will be shown later, when pressure is included as a variable in a multiple regression analysis with R(SiO) as the dependent variable, pressure becomes a highly significant independent variable along with $-\sec\angle$SiOSi. With the publication by Konnert and Appleman (1978) of a careful restrained-parameter refinement of the structure of a low tridymite crystal that provided more than 300 individual R(SiO) data, Hill and Gibbs (1979) undertook a regression analysis of these data and of those published for low quartz, low cristobalite, and coesite, all of whose structures were determined at room pressure. Their analysis of this data set indicates that the correlation is highly significant with 74% of the variation in R(SiO) being explained in terms of a linear dependence on $-\sec\angle$SiOSi.

In a nonempirical MO calculation of minimum-energy bond-length and angle data for the disilicic acid molecule $H_6Si_2O_7$, Newton and Gibbs (1980) obtained theoretical data for the molecule that showed that slightly more of the variation in R(SiO) is explained in terms of a linear

dependence on

$$f_s(O) = \frac{1}{1 - \sec\angle\text{SiOSi}}$$

than on $-\sec\angle$SiOSi. The parameter $f_s(O)$ was derived from hybridization theory (Coulson, 1952) and defines, for the SiO bonds of an SiOSi disiloxy group, the fraction of s character of the orbitals on the bridging O involved in bond formation. According to the theory, the greater the s character, the shorter the bond length.

In a more recent study of the correlation between R(SiO) and $\angle$SiOSi for the silica polymorphs, Baur and Ohta (1982) undertook a linear regression analysis of the bond-length and angle data recorded for low quartz for pressures up to about 60 kbar (Levien et al., 1980) and for low cristobalite (Dollase, 1965), synthetic low tridymite (Baur, 1977), $C2/c$ coesite (Gibbs et al., 1977) and $P2_1/a$ coesite (Kirfel et al., 1979), all recorded at 1 atm. Although the correlation between R(SiO) and $-\sec(\angle$SiOSi) was found to be highly significant, the calculations indicated that only 9% of the variation in the apparent bond lengths could be explained by such a model. The failure of the model to explain a larger percentage of the variation in R(SiO) may be ascribed to the fact that one or more essential parameters (such as pressure) were not included as independent variables in their analysis. The Konnert and Appleman (1978) data set for low tridymite was not included in the linear regression analysis because the Si-Si separations in its structure were constrained not to exceed 3.08 Å during its refinement.

In a molecular orbital modeling of the coesite structure as a function of pressure, Ross and Meagher (1984) observed that the R(SiO) vs. $-\sec\angle$SiOSi relationship holds for data collected at a fixed pressure. The inclusion by Baur and Ohta (1982) of the low quartz data recorded at a variety of pressures in their linear regression analysis without the presence of pressure as an independent variable may make it impossible to draw valid conclusions about the correlation. Smyth et al. (1987) have undertaken a refinement of coesite diffraction data recorded at 15 and 298 K and have observed that R(SiO) of the mineral and those recorded for cristobalite and quartz at a variety of temperatures are highly correlated with $-\sec\angle$SiOSi with an r^2 of 0.89. As the slope of the resulting regression equation (0.074) is about 50% greater than that calculated (0.048) for an $H_6Si_2O_7$ molecule (O'Keeffe et al., 1985), they concluded that such calculations are insufficient to give a complete explanation of the relations between bond length and angle. However, it should be noted that the discrepancy between the two slopes only amounts to about 1.5°. They went on to suggest that a better modeling of the bond length and angle relations might be obtained if the nonbonded repulsions between the O atoms of the next nearest silicate tetrahedra were included in the molecular modeling.

Thermal motion (dynamic disorder) and static disorder of the Si and O atoms in a silicate are other parameters

that may correlate with SiO bond length. Liebau (1985), for example, has observed that a significant percentage of the variation of $R(SiO)$ recorded for the silica polymorphs, and in particular for the clathrasils and low tridymite, can be explained in terms of a linear dependence on $B(O)$, the isotropic displacement factors of the oxide ions. We may expect that $B(O)$ will depend on the temperature at which a set of diffraction data is recorded. Also, as the various thermal models derived to correct $R(SiO)$ for thermal motion include terms that involve the mean square displacements for both Si and O (Busing and Levy, 1964), it follows that $R(SiO)$ may also correlate with $B(Si)$, the isotropic displacement factor of the Si atom. Thus, $B(O)$ and $B(Si)$ may be included in a multiple regression analysis of the bond-length and angle data observed for the silica polymorphs, particularly when their structures have been determined at a variety of temperatures. Indeed, Liebau (1985) observed that more than 50% of the variation of $R(SiO)$ in a combined data set for the silica polymorphs and the clathrasils can be explained in terms of a linear dependence on $B(O)$, a result that led him to conclude that the correlations between $R(SiO)$ and $-\sec \angle SiOSi$ reported for the silica polymorphs should be viewed with reservation.

In several refinements of the coesite structure, Gibbs et al. (1977), Smyth et al. (1987) and Geisinger et al. (1987) have also observed that shorter SiO bonds tend to involve wider OSiO angles. A study by Boisen and Gibbs (1987) of these angles in terms of a hybridization model shows that the parameter $f_s(Si)$, the fraction of s character of the valence orbitals on Si involved in forming an SiO bond, calculated from the observed OSiO angles of a silicate tetrahedron, correlates linearly with the observed $R(SiO)$ for a variety of silicates. Usually, the wider the three OSiO angles common to a SiO bond, the greater the value of $f_s(Si)$ and the shorter the bond. Thus, $\{f_s(O), P, f_s(Si), B(O), B(Si)\}$ are a set of parameters for which the apparent SiO bond lengths in the silica polymorphs may be expected to correlate (Geisinger et al., 1987).

In a warning given by Baur and Ohta (1982), they state: "A least-squares model, however, in which an important independent variable has been omitted, is meaningless because part of the variation due to the omitted variable is falsely attributed to the included independent variable. Therefore, these simple regression models are unacceptable." It is clear that this caveat applies to the correlations presented by Baur and Ohta (1982) and by others, where pressure was omitted as an independent variable, and those presented by Liebau (1985), where the $\angle SiOSi$ angle was not included, and those presented by Smyth et al. (1987), where parameters like $B(O)$ and $B(Si)$ were not included. The decision as to whether a variable should be included in a regression model is a difficult one at best. Obviously, it depends on the experimental conditions that prevail when a particular set of diffraction data is recorded. If, for example, a set of data is recorded at a constant pressure and temperature, then it would be inappropriate to include pressure and temperature as variables, provid-

ed that there is no static disorder of the Si and O atoms. If, on the other hand, such a data set is recorded over a range of pressures, P, at room temperature, then pressure should be included as a variable, whereas $B(O)$ and $B(Si)$ should not be included unless, again, there is static disorder. Finally, if data are recorded over a range of temperatures and pressures, we should include P, $B(O)$, and $B(Si)$ as variables along with theoretically derived structural variables such as $f_s(O)$ and $f_s(Si)$. A study, to be presented in a later paper, of the mean-square displacement amplitudes of the T and O atoms in framework silicates and aluminosilicates will provide criteria for distinguishing between dynamic and static disorder.

STEPWISE LINEAR REGRESSION ANALYSES FOR COESITE

As the crystal structure of coesite has been precisely refined at least 12 times with diffraction data recorded for a range of temperatures from 15 K to 298 K and for a range of pressures from 1 atm to 51.9 kbar, we have the opportunity to examine the extent to which $R(SiO)$ in this mineral correlates with the parameters discussed above. For the study, we assembled a data set consisting of 94 SiO bond lengths (Gibbs et al., 1977; Levien and Prewitt, 1981; Kirfel and Will, 1984; Smyth et al., 1987; Geisinger et al., 1987). The $P2/a$ coesite data set reported earlier by Kirfel et al. (1979) was not included in our data set because the structure analysis was completed on a twinned crystal that yielded erroneous bond-length and angle data. To minimize the possibility of including incorrect bond lengths, angles, and thermal parameters in our data set, we wrote a Fortran 77 program, for use on a PC, called Metric, which calculates bond lengths and angles given the space group of the crystal and the positional parameters of the nonequivalent atoms. It also calculates equivalent isotropic displacement factors given a set of anisotropic displacement factors. The program is capable of handling data sets of virtually any size and for any space group and any setting. The size of the program was kept manageable by using the matrix generators of the space groups discussed in Chapter 7 of Boisen and Gibbs (1985), where it is shown that corresponding to each space group, G, there exists a set of no more than three matrices, R_1, R_2, and R_3, such that all of the remaining matrices in the group are of the form $R_1^i R_2^j R_3^k$. Using this fact, the coordinates of the atomic positions that are G-equivalent to a given atomic position are found by successively multiplying the given coordinate vector by the matrix generators in such an order as to move the given position to every symmetrically related position within the unit cell. This approach eliminates the need to store large numbers of matrices representing the group elements. Each of these positions is then translated to all equivalent positions in the 26 cells that adjoin the unit cell. This enables the program to find all of the nonequivalent bond lengths and angles as well as the geometries of all of the coordination polyhedra. Metric also calculates $f_s(T)$ for TX_4 tetrahedra in the manner discussed in Boisen

and Gibbs (1987) and $f_s(X)$ for corner-sharing tetrahedra (Newton and Gibbs, 1980). It also calculates p_X (Baur, 1970) for all of the X anions in the structure. With the cell dimensions and the atomic coordinates determined for coesite, Metric was used to calculate $R(SiO)$, $f_s(Si)$, $f_s(O)$, and the isotropic equivalent displacement factors.

We concluded that of the 96 bond lengths and their associated parameters recorded for coesite, two of the bond lengths had incorrect parameter values reported for them. In particular, we rejected both the Si2O2 bond-length data recorded by Gibbs et al. (1977) because the β_{33} value of O2 is incorrectly recorded, and the Si2O2 bond-length data recorded by Kirfel and Will (1984) because the coordinates of O2 seem to be incorrect. A stepwise regression analysis of $R(SiO)$ as a function of $f_s(O2)$, $P(kbar)$, $B(O)$, $B(Si)$ and $f_s(T)$ was computed using the data-analysis software Minitab. The results are given in the first 5 pairs of rows in Table 1. See the Appendix of Gibbs et al. (1972) for a discussion of stepwise regression analysis and Draper and Smith (1966) for a numerical example. The first line of each pair of rows in the table gives the estimated regression coefficients for each of the parameters considered in the analysis as well as the R^2 value (last column), and the second line gives the t values calculated for the null hypothesis that the regression coefficients are zero as well as the estimated standard deviation, s (last column), about the regression. A dash in a column indicates that the variable associated with that column was included as a candidate but was not chosen at that step in the regression analysis, according to the strategies set forth in the stepwise analysis of the data set. Asterisks in a column indicate that we did not include that variable in the analysis at that step.

An examination of these statistical data shows that each of the variables makes a significant contribution to the regression sum of squares.

Given the variables considered, the "best" regression equation for the coesite data set is

$$R(SiO) = 1.829 - 0.307f_s(O) - 0.00019P$$
$$- 0.297f_s(Si) - 0.656B(O) + 0.820B(Si) \quad (1)$$
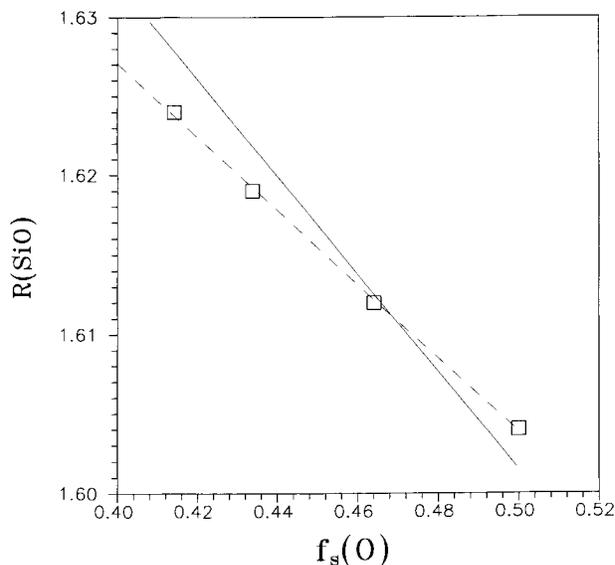

Fig. 1. The dashed line, $R(SiO) = 1.720 - 0.232f_s(O)$, is the line of regression for the data points calculated by O'Keeffe et al. (1985), Table III, which are represented by squares. The solid line, $R(SiO) = 1.755 - 0.307f_s(O)$, is based on the multiple regression (1) with P, $B(O)$ and $B(Si)$ each set to 0 and $f_s(Si)$ set to 0.25.

By setting $B(O)$, $B(Si)$, and P at 0.0 and $f_s(Si)$ at an ideal value of 0.25, Equation 1 becomes $R(SiO) = 1.755 - 0.307f_s(O)$, which provides an estimate of $R(SiO)$ at absolute zero without zero-point vibration and for $P = 0$. As the bond lengths and angles obtained in the molecular orbital calculation on $H_6Si_2O_7$ were obtained for such conditions, we may compare this equation with that calculated for the molecule using the data in Table III of O'Keeffe et al. (1985) [$R(SiO) = 1.720 - 0.232f_s(O)$]. Although these two regression lines are not parallel (Fig. 1), the bond lengths estimated by both equations differ by at most 0.004 Å for the range of $\angle SiOSi$ values exhibited by coesite. It is noteworthy that the estimated standard deviation of the regression defined by Equation 1 is

TABLE 1. Stepwise regression analyses for coesite data

Intercept	$f_s(O)$	P	$f_s(Si)$	$B(O)$	$B(Si)$	$-sec\angle SiOSi$	R^2
1.748	−0.312	—	—	—	—	***	0.599
—	{−11.7}	—	—	—	—	***	0.007
1.764	−0.338	−0.00021	—	—	—	***	0.761
—	{−16.2}	{−7.8}	—	—	—	***	0.005
1.824	−0.329	−0.00021	−0.258	—	—	***	0.801
—	{−17.1}	{−8.4}	{−4.3}	—	—	***	0.005
1.831	−0.318	−0.00019	−0.277	−2.90	—	***	0.826
—	{−17.2}	{−8.0}	{−4.9}	{−3.6}	—	***	0.004
1.829	−0.307	−0.00019	−0.297	−0.656	0.820	***	0.841
—	{−17.0}	{−8.3}	{−5.4}	{−4.4}	{2.9}	***	0.004
1.621	***	−0.00020	−0.322	−0.717	0.910	0.0622	0.835
—	***	{−8.3}	{−5.8}	{−4.8}	{3.2}	{16.5}	0.004

Note: A dash indicates that the variable was included in the stepwise regression analysis, whereas asterisks indicate that the variable was not included.

TABLE 2. Stepwise regression analyses for silica polymorphs and clathrasils

Intercept	$f_s(O)$	$B(O)$	P	$f_s(Si)$	$B(Si)$	$-sec\angle SiOSi$	N	R^2
1.613	—	−0.0073	—	—	—	***	245	0.830
—	—	{−12.2}	—	—	—	***	—	0.009
1.735	−0.275	−0.0054	—	—	—	***	245	0.884
—	{−10.6}	{−22.1}	—	—	—	***	—	0.008
1.759	−0.324	−0.0054	−0.00019	—	—	***	245	0.900
—	{−12.7}	{−23.8}	{−6.2}	—	—	***	—	0.007
1.749	−0.320	—	—	—	—	***	193	0.437
—	{−34.4}	—	—	—	—	***	—	0.008
1.434	−0.273	−0.0048	—	—	—	***	193	0.503
—	{−10.3}	{−5.0}	—	—	—	***	—	0.007
1.757	−0.318	−0.0062	−0.00019	—	—	***	193	0.598
—	{−12.8}	{−7.0}	{−6.7}	—	—	***	—	0.007
1.799	−0.312	−0.0062	−0.00019	−0.180	—	***	193	0.619
—	{−12.9}	{−7.2}	{−6.8}	{−3.2}	—	***	—	0.006
1.583	***	−0.0062	−0.00020	−0.190	—	−0.064	193	0.613
—	***	{−7.1}	{−7.1}	{−3.4}	—	{−12.7}	—	0.007
1.559	—	−0.0054	***	—	—	***	52	0.520
—	—	{−7.4}	***	—	—	***	—	0.009

Note: A dash indicates that the variable was included in the stepwise regression analysis, whereas asterisks indicate that the variable was not included.

0.004 Å, indicating that the estimates of $R(SiO)$ based on the two lines are statistically identical. The average reported esd for the bond lengths in coesite is 0.003 Å, indicating that the regression model fits the data as well as can be expected. The coefficient for $f_s(Si)$ is statistically identical with that (−0.28) observed by Boisen and Gibbs (1987) in their study of the fractional s character of the SiO bonds recorded for a large number of silicates.

The coefficient of P in Equation 1 can be used to estimate the bulk modulus of the silicate tetrahedra in coesite as discussed by Hazen and Finger (1982). The resulting bulk modulus of 280 Gpa is 40% larger than that (200 Gpa) measured for andradite (Hazen and Finger, 1989), suggesting that the silicate tetrahedra in a framework silicate like coesite are less compressible than those in a monosilicate like andradite. This result is expected inasmuch as the SiO bond lengths in coesite are significantly shorter than those in andradite.

As discussed above, theoretical calculations indicate that $f_s(O)$ should be more highly correlated with $R(SiO)$ than is $-sec(\angle SiOSi)$. A stepwise regression analysis that includes $-sec(\angle SiOSi)$ along with the other variables shows that it makes an insignificant contribution to the regression sum of squares in the presence of $f_s(O)$. If a stepwise regression is completed with $-sec(\angle SiOSi)$ replacing $f_s(O)$, then it is found that it is the most significant parameter and, together with P, $f_s(Si)$, $B(O)$, and $B(Si)$, the R^2 value is nearly as great as when $f_s(O)$ was used (see Table 1, the last pair of rows). This result seems to refute Baur's (1977) claim that the correlation between $R(SiO)$ and $-sec(\angle SiOSi)$ observed for coesite will "disappear when larger, less-biased samples are studied."

Of the two models discussed by Busing and Levy (1964) to correct bond lengths for thermal motion, the riding model, where the O atom is riding on the motion of the center of mass of the heavier Si atom, involves displacements for Si and O that have opposite signs, whereas the

uncorrelated model involves displacements for Si and O that have the same sign. The coefficients obtained in the regression analysis for $B(Si)$ and $B(O)$ are of opposite sign. This suggests that the riding model is to be preferred over the uncorrelated model. The expression for the lower bound, which corresponds to highly correlated parallel displacements of Si and O, also involve opposite signs and so may also be applicable. To decide which of these models may be applicable will require a study of anisotropic thermal displacement parameters.

STEPWISE LINEAR REGRESSION ANALYSES FOR SILICA POLYMORPHS AND THE CLATHRASILS

The silica polymorph and the clathrasil data set was constructed by adding 151 $R(SiO)$ values and their associated parameters recorded for low tridymite (Dollase, 1967; Baur, 1977; Kihara, 1977, 1978; Kihara et al., 1986a, 1986b), low cristobalite (Dollase, 1965; Peacor, 1973; Pluth et al., 1985), low quartz (Zachariasen and Plettinger, 1965; Le Page and Donnay, 1976; Levien et al., 1980; Lager et al., 1982), high quartz (Wright and Lehmann, 1981), melanophlogite (Gies, 1983), decadodecasil 3R (Gies, 1986), and decadodecasil 3C (Gies, 1984) to the coesite data set to give a total of 245 individual $R(SiO)$ values. As in the case of the coesite analysis, the bond lengths, $f_s(O)$, $f_s(Si)$, and the equivalent isotropic displacement factors for Si and O were calculated using Metric. As was done with the coesite data set, a stepwise regression analysis was calculated using Minitab. The estimated regression coefficients, the t, s, and R^2 values, are given in Table 2 in essentially the same format as those tabulated in Table 1. An additional statistic, N, the number of observations, is given in column 8 as an aid to the identification of the data sets.

The first three pairs of rows of Table 2 show that only three of the five variables [$B(O)$, $f_s(O)$, and P] make a highly significant contribution to the regression sum of

squares. The coefficients calculated for $f_s(O)$ and P for the silica polymorph and the clathrasil data set are statistically identical with those obtained for the coesite data set. However, the stepwise regression analysis indicates that the parameter $f_s(Si)$ does not make a significant contribution to the regression sum of squares. Also, unlike the coesite data set, $B(O)$ makes a larger contribution to the regression sum of squares than does $f_s(O)$, whereas $B(Si)$ makes an insignificant contribution. The reason for these differences is not clear, but it may be related to the static disorder exhibited by the Si and O atoms making up the framework structures of the clathrasils and low tridymite. It is known that the equivalent isotropic displacement factors recorded for the O and Si atoms of these materials are much larger than those recorded for coesite, low cristobalite, and quartz. Liebau (1985) has ascribed these unusually high displacement factors to a static disorder of the framework atoms. A histogram (Fig. 2) of the $B(O)$ values recorded for the silica polymorphs and the clathrasils shows a relatively wide range of values from 0.25 to 10.0 Å². It also shows a relatively high concentration of 193 observations between 0.25 and 3.0 Å² with the remaining 52 observations spread uniformly between 4.5 and 10.0 Å². The removal of these 52 observations from the data set may reduce, at least in part, the number of observations that are strongly affected by static disorder. A stepwise regression analysis of the resulting data set shows (see pairs of rows 4–7 of Table 2), in addition to $B(O)$, $f_s(O)$, and P, that $f_s(Si)$ makes a highly significant contribution to the regression sum of squares.

As observed by Liebau (1985), static disorder of the type exhibited by the clathrasils has a significant effect on $R(SiO)$ and $\angle SiOSi$. The apparent SiO bond lengths are significantly shorter (1.56 Å) and the SiOSi angles are significantly wider (175°), on average, than those observed (1.608 Å, 144°) for the silica polymorphs. Static disorder does not, however, appear to affect the mean $\angle OSiO$ of a silicate tetrahedron, which is 109.47°, but it does seem to have had a significant effect on the individual OSiO angles, with the range of angles in the clathrasils being 2 to 3 times larger than those in the silica polymorphs. Such a range of values, if in error, would yield a set of erroneous $f_s(Si)$ values, which in turn may explain why this hybridization parameter fails to make a significant contribution to the regression. A similar argument can be made for the range and the values for $\angle SiOSi$ and $f_s(O)$. A stepwise regression of the 52 data exhibiting $B(O)$ values between 4.5 and 10.0 Å² seems to support this assertion. The data composing this population includes all of the bond-length data for the clathrasils, those for the tridymite samples studied by Kihara (1977, 1978) and Kihara et al. (1986a, 1986b), those for high quartz (Wright and Lehmann, 1981), and several from the data for tridymite obtained by Dollase (1965). A stepwise regression analysis of these data shows that only $B(O)$ makes a significant contribution to the regression sum of squares when considered in the presence of the other variables.
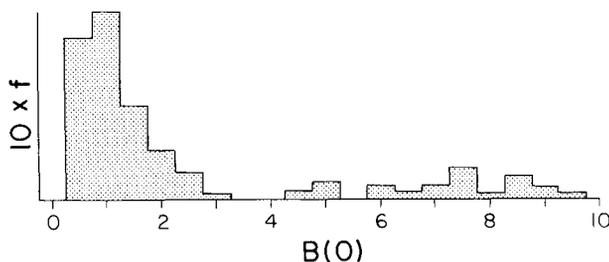

Fig. 2. A histogram of the average equivalent isotropic displacement factor for the oxygen atom, $B(O)$, in silica polymorphs and clathrasils.

A regression analysis completed with $-\sec(\angle SiOSi)$ replacing $f_s(O)$ again shows, as observed for the coesite data set, that this parameter makes a significant contribution to the regression sum of squares. Moreover, as in the case of coesite, it is not as significant as $f_s(O)$. The regression coefficient (0.064) calculated for $-\sec(\angle SiOSi)$ matches that (0.068) calculated by Hill and Gibbs (1979) for the silica polymorphs and the low tridymite data. In other words, the constraints employed by Konnert and Appleman (1978) in their refinement of the structure resulted in crystal-structure parameters whose bond-length and angle trends match those obtained in this study of the silica polymorphs.

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