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Tetrahedral Bond Length Variations in Anorthite

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Abstract

With data from a refinement of primitive anorthite (Wainwright and Starkey, 1971), stepwise multiple linear regression analyses were undertaken to determine the factors most highly correlated with individual Si-O and Al-O bond lengths. All 4 calciums were assumed to be 7-coordinated, and 10 independent parameters were considered in the analyses of the 32 Si-O and 32 Al-O distances. Only two parameters $\Sigma[1/(Ca\text{-}O)^2]$ and $-1/\cos(Al\text{-}O\text{-}Si)$ were found to be statistically significant. These two parameters are positively correlated to Si-O and Al-O distances, yielding multiple correlation coefficients of 0.94 and 0.89 for the Si-O and Al-O populations, respectively.

Introduction

In a comparative structural study of orthoclase and sanidine, Cole, Sörum, and Kennard (1949) first suggested that differences in mean *T*–O distances in feldspar tetrahedra indicate differences in average Al/Si occupancy of the *T sites*. Using feldspar data available at that time, Smith (1954) and later Smith and Bailey (1963) determined a linear relationship between grand mean *T*–O distance and Al/(Al + Si). This relationship was updated by Jones (1968) and by Ribbe and Gibbs (1967, 1969), employing data from more recent feldspar refinements. The Al content of the *T* sites most strongly influences individual *T*–O bond lengths in feldspars; however, in a framework structure where all oxygens are linked to two *T* atoms, the type of linkage, Si–O → Si or Si–O → Al, also has a pronounced effect on the length of the Si–O bond (Clark and Papike, 1967; Brown, Gibbs, and Ribbe, 1969; Phillips, Colville, and Ribbe, 1971; Ribbe, Phillips, and Gibbs, 1973) with shorter Si–O bonds tending to be involved in Si–O → Al linkages.

The primitive anorthite structure, which consists of perfectly alternating Al- and Si-containing tetrahedra, provides an opportunity to examine other structural parameters related to individual *T*–O bond lengths. Assuming perfect order, the bond lengths can be subdivided into two groups, the Al–O and the Si–O populations; hence average Al occupancy is not a factor, and because all linkages are of the type Si–O–Al, the effect of linkage is constant within each group and therefore removed from consideration. Furthermore, structural parameters show a wide range of values even though there is only one kind of non-tetrahedral cation. Finally, there are a sufficient number of tetrahedral bond lengths (32 Si–O, 32 Al–O) with which to make statistically meaningful correlations. All structural data used in this study come from the Wainwright and Starkey (1971) refinement of primitive anorthite.

Selection of Variables

Because all calculations were made assuming a linear model, certain structural parameters were initially expressed by more than one variable in order to establish the best linear correlation between the parameter in question and the dependent variable, *T*–O bond length. Choice of *T*–O distance as the dependent variable does not imply that a cause and effect relationship necessarily exists among the structural parameters with *T*–O distance being the effect. This choice is merely considered a convenient approach to examine the correlations between *T*–O distance and the other parameters. The topology of the structure from which the ten independent variables considered in this study are derived is shown in Figure 1. These ten variables are listed in Table 2.

In an earlier study of primitive anorthite, Megaw, Kempster, and Radoslovich (1962) found that the number of calcium atoms to which an oxygen is bonded significantly influences the individual *T*–O distances (see analysis by Brown *et al,* 1969). Fleet, Chandrasekhar, and Megaw (1966) later found

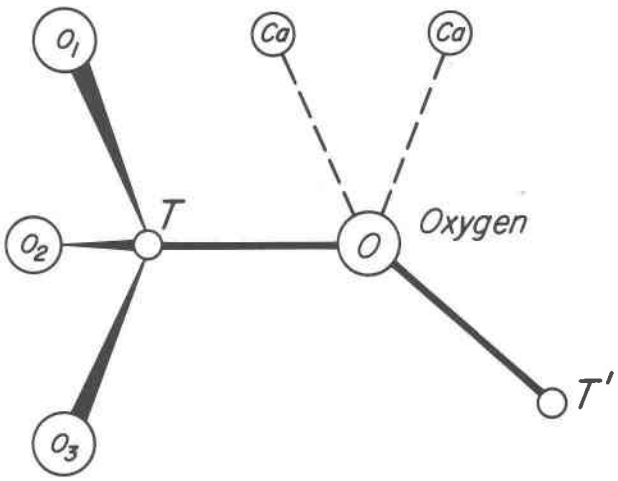

FIG. 1. A schematic representation of a portion of the anorthite structure. The distance T–O is considered as the dependent variable. The independent variables considered are listed in Table 2.

an inverse correlation between the Na/Ca–O and the T–O distances in bytownite. Thus it follows that some expression which takes into account not only oxygen coordination number ($\equiv$ CN(O)) but also individual Ca–O distances might be a more sensitive parameter. For this reason the variables $\Sigma[1/(\text{Ca–O})]$ ($\equiv \Sigma\text{Ca}$) and $\Sigma[1/(\text{Ca–O})^2]$ ($\equiv \Sigma\text{Ca}^2$) were defined.[1] Another variable related to oxygen coordination number is $\Delta\zeta(\text{O})$ ($\equiv \Delta p_o$ of Baur, 1970, 1971), where $\Delta\zeta(\text{O}) = \zeta(\text{O}) - \langle\zeta(\text{O})\rangle$. The symbol $\zeta(\text{O})$ represents the sum of electrostatic bond strengths received by an oxygen and $\langle\zeta(\text{O})\rangle$ is the mean value of $\zeta(\text{O})$ for the four oxygens of the tetrahedron containing the T–O bond under consideration. These four variables, CN(O), ΣCa, ΣCa^2 and $\Delta\zeta$(O), serve as gauges of coordination, bonding, and charge-balance effects.

The two angular parameters, T–O–T and O–T–O, are described by four variables: one pair in the form of the observed angles (T–O–T') and $\langle$O–T–O$\rangle_3$ ($\equiv \frac{1}{3}[(\text{O}_1\text{–}T\text{–O}) + (\text{O}_2\text{–}T\text{–O}) + (\text{O}_3\text{–}T\text{–O})]$, see Figure 1), the other pair in the form of the negative inverse cosine functions of these angles, $-1/\cos$ (T–O–T') and $-1/\cos\langle$O–T–O$\rangle_3$.

The variables $1/(\text{O–}T')$ and $1/(\text{O–}T')^2$ are used to account for any Pauling-Zachariasen type compensations (Zachariasen, 1963) that may occur in the T–O–T' linkages.

[1] Inasmuch as the oxygen atoms in anorthite are bonded to either 0, 1, or 2 calcium atoms and are thus involved in 0, 1 or 2 Ca-O bonds, ΣCa^2 (or ΣCa) will have values of zero, of $1/(\text{Ca-O})^2$, or of $[1/(\text{Ca}_1\text{-O})^2 + 1/(\text{Ca}_2\text{-O})^2]$, respectively. The abbreviations ΣCa and ΣCa^2 are introduced for convenience.

Calcium Coordination

In order to determine values for CN(O), ΣCa, ΣCa^2 and $\Delta\zeta$(O), it is necessary to assign coordination numbers to the four Ca atoms. Table 1 lists all the Ca-O distances less than 3.53Å. Although Ca(z00), Ca(0i0) and Ca(zi0) can clearly be thought of as 7-coordinated, Ca(000) may be considered to be 6-coordinated since the $\text{O}_C(0zi0)$ atom is 0.5Å more distant than the next nearest oxygen. This is and will remain a moot point, but for the purposes of this paper it was decided to test several Ca coordination models. The models were: (1) Ca–O < 2.84Å or CN(Ca) = 6, 7, 7, 7 for Ca(000), Ca(z00), Ca(0i0), and Ca(zi0) respectively; (2) Ca-O < 3.11Å or CN(Ca) = 7, 7, 7, 7; and (3) Ca–O < 3.35Å or CN(Ca) = 8, 8, 8, 8.

Model (2), which treats all calciums as 7-coordinated, gave the largest multiple correlation coefficients (and $|t|$ values) when a variety of independent variables, including ΣCa and ΣCa^2, were used in regression analyses with Al–O and Si–O distances as the dependent variables. It is for this reason only that model (2) was chosen over model (1), although the differences between the two are not significant.

It might be observed in passing that edges shared between the irregular Ca-polyhedra and the Al- and Si-containing tetrahedra are shorter than unshared edges, as expected from Pauling's Rules. In the case of Ca(000), inclusion of $\text{O}_C(0zi0)$ in the coordination polyhedron results in an additional shared edge (with $\text{O}_1(2000)$ in the $T_2(m000)$ tetrahedron).

TABLE 1. Ca-O Distances Less Than 3.53Å in Anorthite *

Ca(000)	Ca(z00)	Ca(0i0)	Ca(zi0)
O_A(2000) 2.292Å	O_A(2z00) 2.333Å	O_A(20i0) 2.337Å	O_A(2zi0) 2.300Å
O_B(0000) 2.377	O_D(0z00) 2.371	O_B(00i0) 2.425	O_B(0zi0) 2.405
O_D(0000) 2.389	O_B(0z00) 2.443	O_D(00i0) 2.432	O_D(0zi0) 2.438
O_A(1000) 2.514	O_B(mz00) 2.493	O_A(10i0) 2.448	O_A(1zi0) 2.454
O_D(m000) 2.538	O_A(1z00) 2.496	O_B(m0i0) 2.492	O_A(1zi0) 2.586
O_A(1000) 2.607	O_C(m0i0) 2.560	O_C(mz00) 2.563	O_D(mzi0) 2.715
	O_A(1z00) 2.732	O_A(10i0) 2.816	O_C(m000) 2.833
O_C(0zi0) 3.107			
O_C(mzi0) 3.269	O_A(2z00) 3.349	O_A(20i0) 3.254	O_B(mzi0) 3.302
O_A(2z00) 3.521			O_C(0000) 3.516

* Calculated using the positional parameters and unit cell data of Wainwright and Starkey (1971).

TABLE 2. Squares of the Correlation Coefficient of Variables Considered in the Regression Analyses of *T*-O Bond Lengths in Anorthite*

	ΣCa	ΣCa^2	$\Delta\zeta(O)$	T-O-T'	$\frac{-1}{\cos(T\text{-}O\text{-}T')}$	$\langle O\text{-}T\text{-}O\rangle_3$	$\frac{-1}{\cos\langle O\text{-}T\text{-}O\rangle_3}$	$\frac{1}{(O\text{-}T')}$	$\frac{1}{(O\text{-}T')^2}$	T-O
CN(O)	*.99*	*.96*	*.96*	*.16*	*.07*	*.51*	*.53*	*.61*	*.63*	*.76*
	.99	.96	.83	.16	.07	.27	.27	.73	.57	.60
ΣCa		*.99*	*.94*	*.18*	*.08*	*.54*	*.56*	*.66*	*.68*	*.79*
		.99	.85	.18	.08	.32	.32	.77	.62	.66
ΣCa^2			*.92*	*.20*	*.10*	*.57*	*.58*	*.70*	*.72*	*.82*
			.85	.20	.10	.38	.37	.80	.65	.70
$\Delta\zeta(O)$				*.16*	*.08*	*.53*	*.54*	*.56*	*.58*	*.78*
				.17	.09	.32	.29	.68	.56	.63
T-O-T'					*.88*	*.07*	*.08*	*.40*	*.41*	*.37*
					.88	.04	.06	.39	.38	.38
$\frac{-1}{\cos(T\text{-}O\text{-}T')}$						*.08*	*.09*	*.29*	*.30*	*.30*
						.06	.09	.30	.36	.28
$\langle O\text{-}T\text{-}O\rangle_3$							*.98*	*.26*	*.26*	*.55*
							.96	.35	.35	.40
$\frac{-1}{\cos\langle O\text{-}T\text{-}O\rangle_3}$								*.26*	*.27*	*.56*
								.36	.38	.36
$\frac{1}{(O\text{-}T')}$									*.99*	*.65*
									.83	.60
$\frac{1}{(O\text{-}T')^2}$										*.66*
										.50

* Numbers in italics are for the Si-O data; others are for the Al-O data.

This edge is longer than the other shared edges involving Si-containing tetrahedra, but shorter than any of the unshared edges in the structure.

Regression Analyses

A complete listing of the squares of the correlation coefficients (r^2) for the eleven variables is presented in Table 2. In each case the upper value refers to the Si–O and the lower value to the Al–O population. These data indicate that although many of the independent variables show a relatively strong linear correlation with the dependent variable *T*–O, there are also very high correlations among certain independent variables which define the same structural parameter, and these have been grouped as follows: (1) $1/(O\text{–}T')$ and $1/(O\text{–}T')^2$; (2) ΣCa, ΣCa^2, CN(O), and $\Delta\zeta$; (3) $-1/\cos\langle O\text{–}T\text{–}O\rangle_3$ and $\langle O\text{–}T\text{–}O\rangle_3$; and (4) $-1/\cos(T\text{–}O\text{–}T')$ and $T\text{–}O\text{–}T'$. In order to determine the most appropriate variable in each group, all ten were simultaneously tested in a stepwise multiple linear regression analysis which gauges the contribution of each independent variable to the regression sum of squares in the presence of the others.[2] The results for both the Al–O and Si–O populations indicate $1/(O\text{–}T')^2$, ΣCa^2, $\langle O\text{–}T\text{–}O\rangle_3$ and $-1/\cos(T\text{–}O\text{–}T')$ to be the most significant variables in groups (1)–(4) respectively. The remaining six variables are considered redundant and were omitted in subsequent calculations.

At this point unweighted multiple linear regression analyses were performed on various combinations of the remaining four independent variables. Tests based on $|t|$ values obtained in these analyses (see Table 3) indicate that only two variables, ΣCa^2 and $-1/\cos(T\text{–}O\text{–}T')$, can be retained as significantly contributing to *T*–O bond distance when tested at a 99 percent confidence level.

Graphs of the observed Si–O and Al–O distances versus those calculated using the variables ΣCa^2 and $-1/\cos(T\text{–}O\text{–}T')$ are shown as dots in Figure 2. The ends of the vertical lines opposite the dots represent the values predicted by ΣCa^2 alone. Horizontal lines represent the estimated standard errors in the observed distances reported by Wainwright and Starkey (1971).

Discussion

Baur (1971) found that a strong correlation can be made between $\Delta\zeta(O)$ and Si–O distance for a variety of silicates. Our study substantiates this for both the Si–O ($r^2 = 0.78$) and the Al–O ($r^2 =$

[2] For a discussion of the statistical methods used in this paper see Chapter 6, Draper and Smith (1966).

TABLE 3. $|t|$ Values and Multiple Correlation Coefficients (r) for T-O Distances in Anorthite

		Si-O			
ΣCa^2	4.36	7.45	7.76	12.11	11.24
$-1/\cos(T\text{-}O\text{-}T')$	3.90	4.37	4.54	4.43	
$1/(O\text{-}T')^2$	0.78		1.36		
$\langle O\text{-}T\text{-}O\rangle_3$	-0.64	-1.28			
r	0.946	0.944	0.945	0.941	0.899
		Al-O			
ΣCa^2	5.58	5.98	5.95	8.34	8.57
$-1/\cos(T\text{-}O\text{-}T')$	3.87	3.43	3.50	3.43	
$1/(O\text{-}T')^2$	1.71		1.22		
$\langle O\text{-}T\text{-}O\rangle_3$	-2.04	-1.65			
r	0.911	0.901	0.897	0.891	0.843

0.63) distances in anorthite. Despite these strong correlations $\Delta\zeta(O)$ was found not to contribute significantly to the regression sum of squares when run in the presence of ΣCa^2, which, as discussed above, apparently models interatomic forces in anorthite more sensitively.

As expected, plots of the variable ΣCa^2 against observed Al–O and Si–O distances show that the data are grouped into three populations on the basis of the coordination number of oxygen (Ribbe *et al,* 1973, Figure 3). Examination of data for 3-coordinated oxygen atoms shows that the trend *within* this group is the same as that for all data, although the slope of the regression line for CN(O) = 3 data is somewhat steeper than that for all data. This observation confirms the fact that a term involving the Ca–O distances describes the variation of tetrahedral bond lengths in anorthite better than either CN(O) or $\zeta(O)$.

Furthermore, as demonstrated graphically by Brown *et al* (1969, Fig le,f) for all data and by Ribbe *et al* (1973, Fig. 4) for data grouped according to the coordination number of oxygen, the trends of Al–O and Si–O bond lengths with T–O–T angle in anorthite are consistent with those predicted by Cruickshank (1961): wider T–O–T angles are associated with shorter T–O bonds. [Baur's (1971) arguments against these trends have been countered by Gibbs, Hamil, Louisnathan, Bartell, and Yow (1972) and Taylor (1972)]. This statistical study has confirmed the significance of the effect of T–O–T angle: vertical bars on data points in Figure 2 indicate the magnitude of the effect when

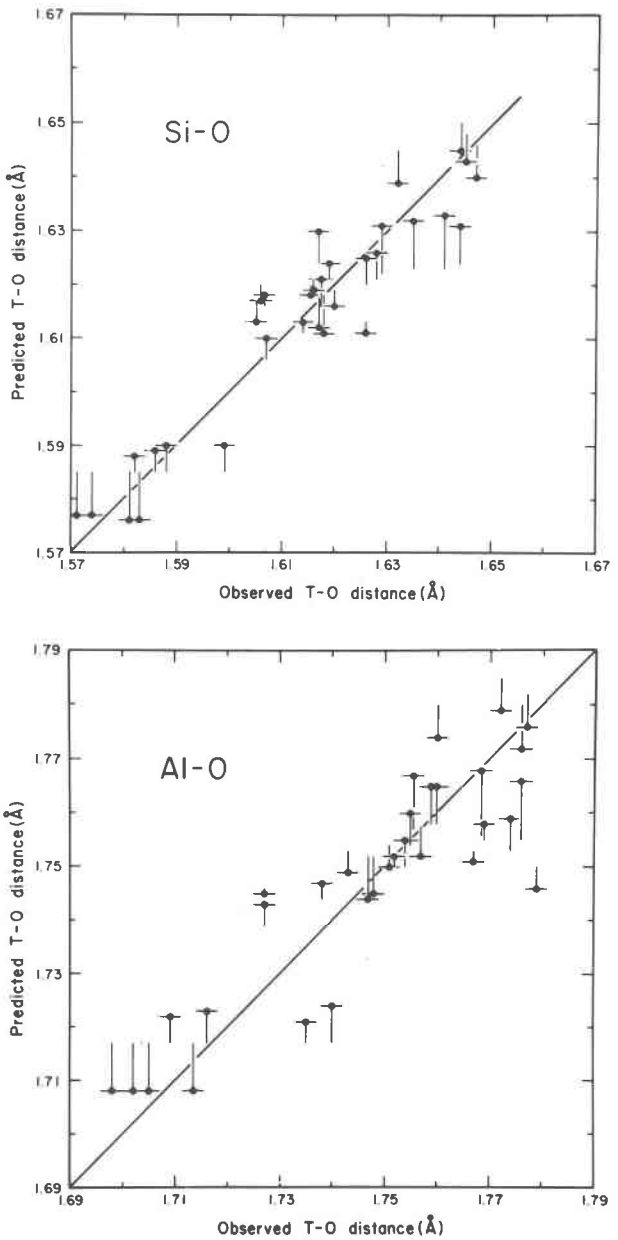

FIG. 2. Graphs of the observed Si-O and Al-O distances against those calculated using the variables ΣCa^2 and $-1/\cos(T\text{-}O\text{-}T')$. The dots represent the values obtained using both variables, while the ends of the vertical lines opposite them represent the values predicted by ΣCa^2 alone. The horizontal lines represent the standard errors in the observed distances reported by Wainwright and Starkey (1971). The equations used to calculate the distances are:

$$(Si\text{-}O)_{calc} = 1.548 + 0.182\Sigma[1/(Ca\text{-}O)^2] + 0.028[-1/\cos(T\text{-}O\text{-}T')]$$

$$(Al\text{-}O)_{calc} = 1.673 + 0.189\Sigma[1/(Ca\text{-}O)^2] + 0.032[-1/\cos(T\text{-}O\text{-}T')]$$

$-1/\cos(T\text{–O–}T')$ is used with ΣCa^2 in multiple linear regression analysis (see also Table 3).

Inverse correlations have been observed between the variables $\langle O\text{–}T\text{–}O\rangle_3$ and individual Si–O and Al–O bond lengths in anorthite by Gibbs, Louisnathan, Ribbe, and Phillips (1973, Figs. 4c and 4i); however, our regression analyses indicate these relationships can be rejected at a 99 percent confidence level. The contributions of these angular parameters to the regression analyses are understandably small, inasmuch as the $\langle O\text{–Si–}O\rangle_3$ and $\langle O\text{–Al–}O\rangle_3$ angles show ranges of only 4° and 12° respectively, whereas the T–O–T angles vary between 123° and 170°.

In conclusion, the individual T–O bond lengths in anorthite can be described in terms of the parameters $\Sigma[1/(Ca\text{–}O)^2]$ and T–O–T' angle linearized to $-1/\cos(T\text{–O–}T')$. The former is the more important in ordered anorthite because of the divalent nature of the Ca atom; electrostatic forces are clearly more pronounced than in postassium-rich fieldspars (Phillips and Ribbe, 1973) and sodic plagioclases (Ribbe *et al,* 1973). The contribution of the T–O–T' angular parameter is secondary in anorthite and monoclinic K-feldspar, and assumes even less importance in the ordered sodic plagioclases, where Al content of the tetrahedral site and the linkage factor become the dominant factors influencing T–O bond lengths.

Acknowledgments

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