

DISTORTIONS IN THE TETRAHEDRAL OXYANIONS OF
CRYSTALLINE SUBSTANCES, WITH CRYSTAL
STRUCTURE REFINEMENTS OF SLAWSONITE AND CELSIAN

by

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PART I

DISTORTIONS IN THE TETRAHEDRAL OXYANIONS
OF CRYSTALLINE SUBSTANCES

INTRODUCTION

High precision crystal structure refinements now available in large numbers have left no doubt that geometrically regular coordination polyhedra occur but rarely in minerals and other crystalline compounds. For this reason the value of expressing distortion quantitatively has long been recognized, and various approaches to the problem have been developed. Megaw, Kempster and Radoslovich (1962), Gibbs and Ribbe (1969), Gibbs, Ribbe and Anderson (1970), and Brown (1970) used "bond angle strain" (i.e., observed angle minus ideal angle) to characterize distortions in the feldspars, the humites, and the olivines; however, since each "strain" refers to only one angle, several are usually required to describe the distortion of any given polyhedron, and the method is quite unwieldy. Likewise "bond length strain" (Megaw *et al.*, 1962), bond length range (Burns, 1970; Walsh, Donnay and Donnay, 1974), and bond angle range (Walsh *et al.*, 1974) are cumbersome and generally too qualitative to permit meaningful comparisons. McDonald and Cruickshank (1967), Brown and Gibbs (1970), and Takeuchi (1975) have employed plots of tetrahedral edge length *vs.* the mean of the two adjacent T-O bonds; in these plots, each tetrahedron is represented by six points, the disposition of which provides only qualitative information about the nature of the distortion. One-parameter methods for quantitative description of distortions have been proposed by Robinson, Gibbs and Ribbe (1971), Shannon and Calvo (1973), Brown and Shannon (1973), Dollase (1974) and Phillips, Kroll, Pentinghaus and Ribbe (1974); Hamil (1974) has suggested a two-parameter

method, and a three-parameter characterization of tetrahedral distortions has been proposed by Baur (1974).

Although each of these methods may be useful for particular applications, only Baur's incorporates the fundamental notion that there are only two distinct ways by which polyhedral distortions may be effected. These are (1) deviation of the central atom from a reference position in a given polyhedron, and (2) deviation in the positions of the ligands from the apices of a reference polyhedron. Distortions of the first type will be called "bond-length distortions" and those of the second type "edge-length distortions" for reasons which will shortly become obvious. These two kinds of distortions may be characterized by two parameters, but not by only one; a third parameter -- angular distortion -- is redundant but sometimes useful. This study defines two easily-calculated and statistically meaningful distortion parameters that characterize bond-length and edge-length distortions in tetrahedra, and investigates the consequences of applying these parameters to the tetrahedral oxyanions of both transition and non-transition elements.

THE GEOMETRICAL NATURE OF TETRAHEDRAL DISTORTIONS

Bond-length and edge-length distortions

For any tetrahedron, regardless of its distortion, there exists a unique point equidistant from all four apices (though not necessarily within the tetrahedron). Since the apices of a tetrahedron (i.e., four non-coplanar points) define a sphere, the center of that sphere is the point equidistant from all four apices. Because this point is analogous to a "circumcenter" in plane geometry, it will be referred to likewise here. *Bond-length distortion* for a tetrahedron is defined as the distance from the circumcenter to the position of the central atom.¹

¹ Similar definitions may be devised for coordination numbers other than 4. For the special case of trigonal coordination in which the central atom is coplanar with its ligands (e.g., nearly all BO_3 groups), the definition of bond-length distortion is exactly analogous. For other cases of 3-coordination the distance of the central atom from the plane of the ligands would also need to be specified; that is, the displacement of the central atom from the circumcenter would have to be resolved into components perpendicular and parallel to the plane of the ligands, making a three-parameter specification necessary. For >4 coordination there is, in general, no point equidistant from all ligands, so that the definition of bond-length distortion must involve a "reference position" rather than a circumcenter.

A regular tetrahedron is one whose ligand-ligand distances (i.e., edge lengths) are all equal -- ignoring for the moment the location of the central atom. For any four atoms disposed at the apices of an irregular tetrahedron, there exists a minimum total translation of one or more of them which will transform the arrangement to the apices of some regular tetrahedron. The edge-length distortion could be defined as the average (per atom) of these translations if the size of this regular tetrahedron bore a predictable relation to that of the distorted one. Since no such relationship is apparent, it is convenient to arbitrarily define the ideal tetrahedron as the one whose edge length is equal to the average edge length of the distorted tetrahedron; the *edge-length distortion* then becomes the minimum average translation per atom necessary to move the ligands to the apices of the ideal tetrahedron.²

Distortion parameters

The calculation of the actual values of bond-length and edge-length distortions are tedious at best. However, two easily-computed

² For 3-coordination the definition of edge-length distortion is analogous, with the replacement of "ideal tetrahedron" by "equilateral triangle." For >4 coordination, depending on the actual coordination number, there may be no "ideal" polyhedron with equal edge lengths.

parameters that are linearly related to the numerical values of these distortions may be defined as follows:

Bond-length distortion parameter (BLDP) =

$$\frac{1}{\langle T-O \rangle} \left\{ \frac{\sum_{i=1}^4 [(T-O)_i - \langle T-O \rangle]^2}{3} \right\}^{1/2} = \frac{1}{\langle T-O \rangle} [\hat{\sigma}(T-O)], \text{ and} \quad (1)$$

Edge-length distortion parameter (ELDP) =

$$\frac{1}{\langle 0 \cdots 0 \rangle} \left\{ \frac{\sum_{i=1}^6 [(0 \cdots 0)_i - \langle 0 \cdots 0 \rangle]^2}{5} \right\}^{1/2} = \frac{1}{\langle 0 \cdots 0 \rangle} [\hat{\sigma}(0 \cdots 0)] \quad (2)$$

where $T-O$ and $0 \cdots 0$ are individual bond lengths and edge lengths, $\hat{\sigma}$ represents an unbiased estimated standard deviation (e.s.d.), and "0" represents a ligand which, for the applications to be considered in this study, is oxygen. The terms $\langle T-O \rangle$ and $\langle 0 \cdots 0 \rangle$ are mean values for individual tetrahedra. Multiplication by $\frac{1}{\langle T-O \rangle}$ or $\frac{1}{\langle 0 \cdots 0 \rangle}$ serves to "normalize" each parameter so that distortions in tetrahedra of different sizes may be directly compared. A FORTRAN computer program, DISTORT, which provides actual values of distortion, distortion parameters, statistical analyses, and CALCOMP plots is included herein as Appendix A. The computational details are explained in comment statements within the program; the general procedures are as follows: For determination of the coordinates of the circumcenter incident to the computation of bond-length distortion, the circumcenter-to-oxygen distances are written

$$(C-O)^2 = (x_i - X)^2 + (y_i - Y)^2 + (z_i - Z)^2, \quad i = 1, 2, 3, 4 \quad (3)$$

where lower case cartesian coordinates refer to oxygen atoms 1 through 4, and upper case cartesian coordinates represent those of the circum-center. Subtraction of equation (3) from itself with $i = 1$ and 2, 2 and 3, and 3 and 4 gives three first-order equations in the three desired coordinates. Solving for these coordinates permits direct calculation of the bond-length distortion, since the coordinates of the cation are known. For the calculation of edge-length distortion, Dollase's (1974) computer program POLFT was extensively modified and included as subroutines in DISTORT. The method involves the least-squares optimization of the fit between two sets of atoms -- in this case, between the four ligands of the actual tetrahedral oxyanion and the four "ligands" (apices) of the ideal tetrahedron. Dollase used translation, rotation, and dilation to optimize the polyhedral fit. In the present work dilation has been eliminated so that the ideal tetrahedron maintains the same size throughout the calculation. Once the coordinates of the ideal tetrahedron are optimized to fit the real oxyanion, the average distance between corresponding ligands is calculated.

Equations (1) and (2) have been written in terms of estimated standard deviations. Viewed from a philosophically different standpoint they could as well have been written as exact standard deviations with divisors of 4 and 6, respectively, instead of 3 and 5. The point in question is whether the four measured bond lengths and six measured edge lengths are treated as exactly-known populations or as samples of the populations of all possible $T-O$ and $O \cdots O$ measurements.

In the former case $\langle T-O \rangle$ and $\langle O \cdots O \rangle$ are population means; thus division by n ($= 4$ or 6) is appropriate. In the latter case $\langle T-O \rangle$ and $\langle O \cdots O \rangle$ are sample averages; thus division by $n-1$ ($= 3$ or 5) is necessary to give unbiased estimates of the population standard deviations. The second viewpoint has been taken in this work, although the first is recognized as equally valid.

Figure 1 shows plots of these parameters *vs.* distortions (as defined above) for the 489 TO_4 tetrahedra taken from references listed in Appendix B. In order to avoid "distortions" which were merely artifacts of poor structure refinements, the input data were carefully screened for high precision. With fewer than twenty exceptions tetrahedra were not used if the e.s.d.'s of individual bond lengths were in excess of $0.010 \text{ \AA}$; for the exceptional cases, the *averages* of the e.s.d.'s of the bond lengths were less than $0.010 \text{ \AA}$ and no individual bond length e.s.d. exceeded $0.013 \text{ \AA}$. In addition a few tetrahedra for which the $T-O$ distances were sufficiently precise had to be rejected because the e.s.d.'s of their bond angles exceeded $\sim 0.7^\circ$. Since the majority of the data available for selenates do not meet these requirements, the SeO_4^{2-} tetrahedra were omitted from Figure 1. A few unrefined spinels for which the chemical occupancy of the tetrahedral site was known were used in plots; since the site symmetry requires zero bond-length and edge-length distortions, and these tetrahedra were not used in calculations, this had no adverse effect on the overall precision of the data. The equations of the least-squares regression lines, for which correlation coefficients are given in

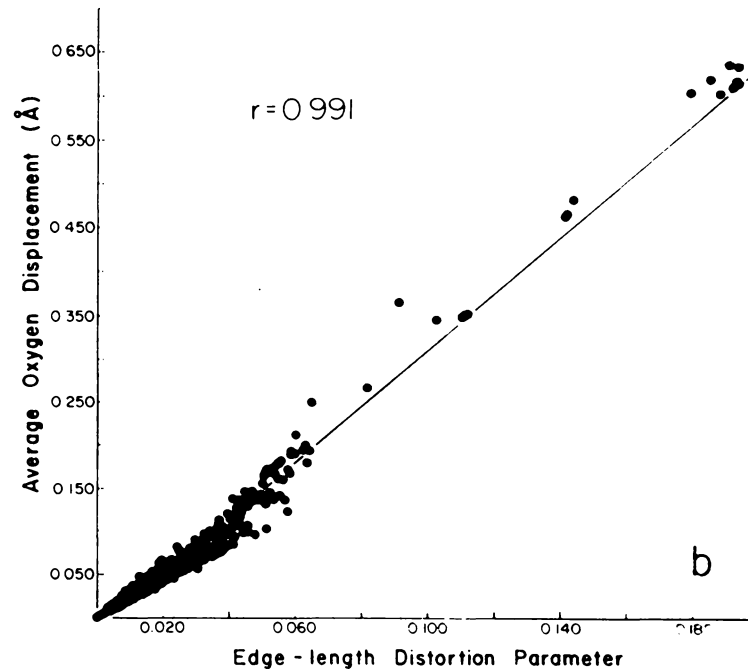
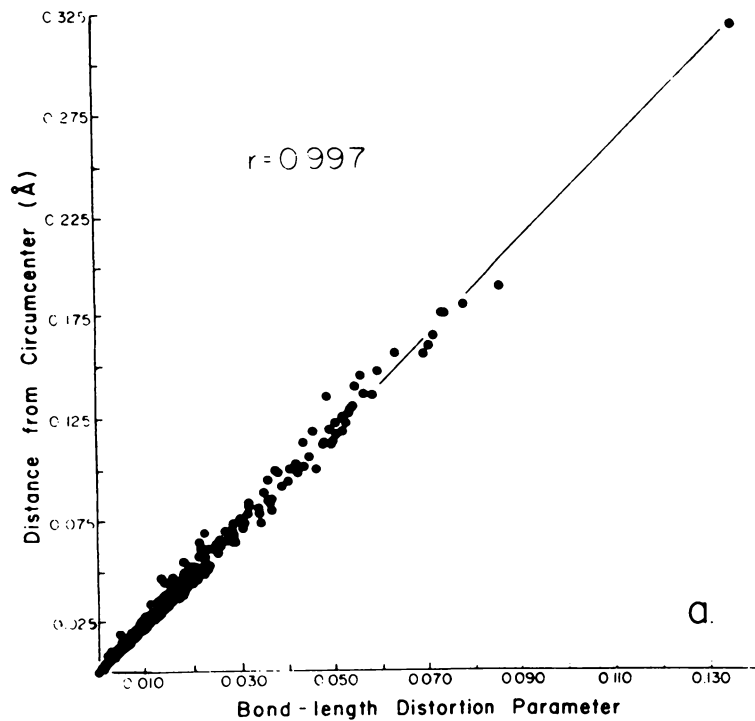


Figure 1: Linear relationships between distortions and distortion parameters as defined in text.

- a. Distance of the central atom from the circumcenter *vs.* bond-length distortion parameter (BLDP). b. Average displacement of oxygen atoms from the apices of a regular tetrahedron *vs.* edge-length distortion parameter (ELDP).

Figures 1a and 1b, are

$$\text{Bond-length distortion} = 0.0 + 2.393(\text{BLDP}), \text{ and} \quad (4)$$

$$\text{Edge-length distortion} = -0.014 + 3.260(\text{ELDP}). \quad (5)$$

It is apparent that the dispersion of data points about the regression lines in both plots increases from the origin. For the BLDP plot this scatter reflects the fact that both $\langle T-O \rangle$ and $\hat{\sigma}(T-O)$ depend to a small extent on the direction of "displacement" of the central atom from the circumcenter (relative to the ligand positions), as well as on its distance from the circumcenter.³ The relatively greater amount of scatter seen in Figure 1b is presumably due to an analogous dependence of $\langle O \cdots O \rangle$ and $\hat{\sigma}(O \cdots O)$ on the relative directions, as well as distances, by which all four ligands must be shifted in order to attain an ideal geometrical configuration.

³ Since the average $T-O$ distance is not in general equal to the circumcenter-to-oxygen distance, a theoretically better parameter for estimating bond length distortion is

$$\text{BLDP}' = \frac{1}{C-O} \left\{ \frac{\sum_{i=1}^4 [(T-O)_i - (C-O)]^2}{3} \right\}^{1/2},$$

where $C-O$ is the circumcenter-to-oxygen distance. In fact, the differences in results obtained using this parameter and BLDP are insignificant. Additionally, two of the major advantages of BLDP are lost if BLDP' is used, namely, ease of computation and the statistical properties of an estimated standard deviation.

COMPARISON OF *BLDP* AND *ELDP* WITH OTHER DISTORTION PARAMETERS

In the following discussion, methods of characterizing tetrahedral distortions will be classified as Type I (single-parameter methods which depend upon bond angles), Type II (single-parameter methods which are independent of bond angles), and Type III (multiple-parameter methods).

Type I methods

Perhaps the most widely used parameters in this category are mean quadratic elongation and tetrahedral angle variance (Robinson *et al.*, 1971), respectively defined as

$$\langle \lambda_{\text{tet}} \rangle = \frac{4}{\sum_{i=1}^4 (\ell_i / \ell_o)^2} \quad \text{and} \quad (6)$$

$$\sigma_{\theta(\text{tet})}^2 = \frac{6}{\sum_{i=1}^6 (\theta_i - 109.47^\circ)^2} \quad (7)$$

Here ℓ_i and θ_i are the i^{th} bond length and bond angle, while ℓ_o is the circumcenter-to-oxygen distance of the ideal tetrahedron whose volume is the same as that of the actual tetrahedron. Since 109.47° is generally not the true mean angle, $\sigma_{\theta(\text{tet})}^2$ is not a true variance; thus a more appropriate name might have been chosen. A more serious shortcoming, in terms of the types of distortions being considered in this study, arises from angular dependence. The dependence of $\sigma_{\theta(\text{tet})}^2$ on bond angles is obvious; $\langle \lambda_{\text{tet}} \rangle$ is also a function of bond angles in that the volume of the tetrahedron, from which ℓ_o is calculated, depends on both bond lengths and bond angles. Any parameters

which involve bond angles and which are used as one-parameter distortion measurements combine bond-length and edge-length distortions so that their independent effects are unresolvable. This limitation does not make such parameters any the less valuable for certain applications, but it does obscure some interesting phenomena to be discussed later. Of course an angular distortion parameter such as $\sigma_{\theta(\text{tet})}^2$ could be substituted for either BLDP or ELDP in a two-parameter method of characterizing distortions; however the relationships between $\sigma_{\theta(\text{tet})}^2$ and BLDP or ELDP are sufficiently complicated that the recovery of quantitative information about the third parameter would be intractable in most cases.

Robinson *et al.* (1971) demonstrated the high linear correlation between $\langle \lambda_{\text{tet}} \rangle$ and $\sigma_{\theta(\text{tet})}^2$ for a large variety of tetrahedral oxyanions, but observed that there are some cases in which $\sigma_{\theta(\text{tet})}^2$ might not give a reliable estimate of $\langle \lambda_{\text{tet}} \rangle$. A comparison of the values of BLDP, ELDP, $\sigma_{\theta(\text{tet})}^2$, and $\langle \lambda_{\text{tet}} \rangle$ for the tetrahedra used in Figure 1 shows that, for most species of tetrahedral oxyanions, $\sigma_{\theta(\text{tet})}^2$ and $\langle \lambda_{\text{tet}} \rangle$ are very highly correlated with ELDP, but not with BLDP. There are two types of tetrahedral oxyanions that deviate markedly from the foregoing. The first type comprises those oxyanions which exhibit large ranges in BLDP and small ranges in ELDP (i.e., BO_4^{5-} , PO_4^{3-} , and SO_4^{2-} , as discussed below); these show good correlations between $\langle \lambda_{\text{tet}} \rangle$ or $\sigma_{\theta(\text{tet})}^2$ and BLDP, but poor correlations with ELDP. The second type consists of those oxyanions whose O-T-O angles tend to be close to 109.47° (i.e., VO_4^{3-} , CrO_4^{2-} , and MoO_4^{2-} , as discussed below); for these $\sigma_{\theta(\text{tet})}^2$

is generally very small, and is not correlated well with BLDP, ELDP, or $\langle \lambda_{\text{tet}} \rangle$. Robinson *et al.* (1971) have given other examples of the failure of $\sigma_{\theta(\text{tet})}^2$ to accurately predict $\langle \lambda_{\text{tet}} \rangle$. Since $\langle \lambda_{\text{tet}} \rangle$ is difficult to compute, is not always accurately predicted by $\sigma_{\theta(\text{tet})}^2$, and cannot resolve edge-length and bond-length distortions, its use is not recommended. On the other hand, $\sigma_{\theta(\text{tet})}^2$ is useful for determining the bond angle deviation from ideality, even though it is not a statistical variance.

Phillips *et al.* (1974) have defined a parameter σ , where

$$\sigma^2 = \frac{6}{\sum_{i=1}^6} [(O-T-O)_i - \langle O-T-O \rangle]^2 / 6 \quad (8)$$

If $\langle O-T-O \rangle$ is considered as an exact population mean, then σ^2 is a true population variance. This parameter differs conceptually from $\sigma_{\theta(\text{tet})}^2$ in that $\langle O-T-O \rangle$ is the mean angle rather than the ideal angle. Like $\sigma_{\theta(\text{tet})}^2$, however, σ^2 cannot be used alone to resolve the separate effects of bond-length and edge-length distortions.

Type II methods

Brown and Shannon (1973) and Shannon and Calvo (1973) have suggested the use of a distortion parameter for octahedra, defined as

$$\text{Distortion} = \left(\frac{\Delta R}{\bar{R}} \right)^2. \quad (9)$$

Applied to tetrahedra and rewritten, equation (9) becomes

$$\left(\frac{\Delta R}{\bar{R}} \right)^2 = \frac{1}{4} \frac{\sum_{i=1}^4 [(T-O)_i - \langle T-O \rangle]^2}{\langle T-O \rangle^2} = \frac{1}{\langle T-O \rangle^2} \sigma^2(T-O) = 0.75(\text{BLDP})^2. \quad (10)$$

It is apparent that $\left(\frac{\Delta R}{\bar{R}} \right)^2$ is a true population variance if the $(T-O)_i$

are considered exact determinations of the entire population of bond lengths instead of a sample of all possible bond length measurements. As mentioned previously, the contrary viewpoint has been taken in this work. These authors did not suggest a distortion parameter analogous to ELDP.

Perhaps the most versatile one-parameter distortion characterization to be suggested thus far is that of Dollase (1974); it involves the determination of the least-squares optimum fit (through translation, rotation, and dilation) between the real polyhedron and a similar one of any desired symmetry. The inclusion of both the central atom and ligands, however, unavoidably combines bond-length and edge-length distortions, so that this method is also subject to the limitations pointed out for Type I methods. Nevertheless, as Dollase has demonstrated, his approach provides a means for studying changes in polyhedral orientations in related structures, for quantifying the degree of approximation of a real polyhedron to one with any desired symmetry, and for investigating some other types of problems not tractable by other methods of distortion characterization.

Type III methods

The two parameters of Hamil (1974) are longitudinal distortion, α , and angular distortion, ψ , which are defined as follows:

$$\alpha = \sum_{j=1}^N \log \ell_j / \ell_i \quad (11)$$

$$\psi = \sum_{j=1}^{3N-6} \tan \theta_i, \quad (12)$$

where N is the number of bonds, ℓ_j and ℓ_i are observed and ideal bond lengths, respectively, and θ_i is the difference between observed and ideal angles. From the foregoing discussions it is clear that α and ψ are generally not independent parameters.

Baur (1974) has proposed a three-parameter characterization of tetrahedral distortions, using the following distortion indices:

$$DI(TO) = \frac{1}{\langle T-O \rangle} \left[\frac{\sum_{i=1}^4 |(T-O)_i - \langle T-O \rangle|}{4} \right], \quad (13)$$

$$DI(OTO) = \frac{1}{\langle O-T-O \rangle} \left[\frac{\sum_{i=1}^6 |(O-T-O)_i - \langle O-T-O \rangle|}{6} \right], \text{ and} \quad (14)$$

$$DI(OO) = \frac{1}{\langle O \cdots O \rangle} \left[\frac{\sum_{i=1}^6 |(O \cdots O)_i - \langle O \cdots O \rangle|}{6} \right]. \quad (15)$$

It is obvious that $DI(TO)$ and $DI(OO)$ measure the same quantities as do BLDP and ELDP, respectively, whereas $DI(OTO)$ is analogous to σ^2 of Phillips *et al.* (1974). Baur's (1974, p. 1196) statement that "it is not possible for a tetrahedral group to have two distortion indices equal to zero and one different from zero" leads to the conclusion already stated above, that angular distortion is a function of both bond-length and edge-length distortion. The use of BLDP, ELDP, and σ^2 instead of Baur's distortion indices may be advantageous in cases where statistical testing is intended, since the former are statistically unbiased. Certainly Baur's $DI(TO)$ and $DI(OO)$ bear the same kinds of relationships to bond-length and edge-length distortion, respectively, as do BLDP and ELDP.

ANALYSIS OF OBSERVED DISTORTIONS IN TETRAHEDRAL OXYANIONS

Figure 2 is a plot of BLDP *vs.* ELDP showing the boundaries within which all of the tetrahedra containing non-transition elements (solid line) and transition metals (dashed line) used in this study fall. (See Appendix B for a listing of structure studies from which tetrahedra were taken.) Tetrahedra were not used unless all four ligands were non-hydroxyl oxygen atoms; the criteria for precision of the data have already been stated. It appears that the extreme distortions (i.e., those that determine the boundary curves) observed in the tetrahedral oxyanions of non-transition elements are, as a population, different from those observed in transition metal tetrahedral oxyanions. Before proceeding with a detailed examination of the observed distortions, it must be understood that the maximum distortion boundaries in Figure 2 and figures below do not necessarily represent physical limits but serve only to outline the regions occupied by observed data points used in this study. Because of the precision and number of the data used, however, it is felt that there is a high probability that data for TO_4 groups from similarly well-refined crystal structures will plot within or near the curves for most species of tetrahedral oxyanions.

Tetrahedral oxyanions of non-transition elements

Figure 3 is a display of the BLDP *vs.* ELDP plots, by element and period, for tetrahedral oxyanions in which the central atom is a non-transition element. The solid line appearing on each is the empirically-determined line along which distortion parameters would plot if all of

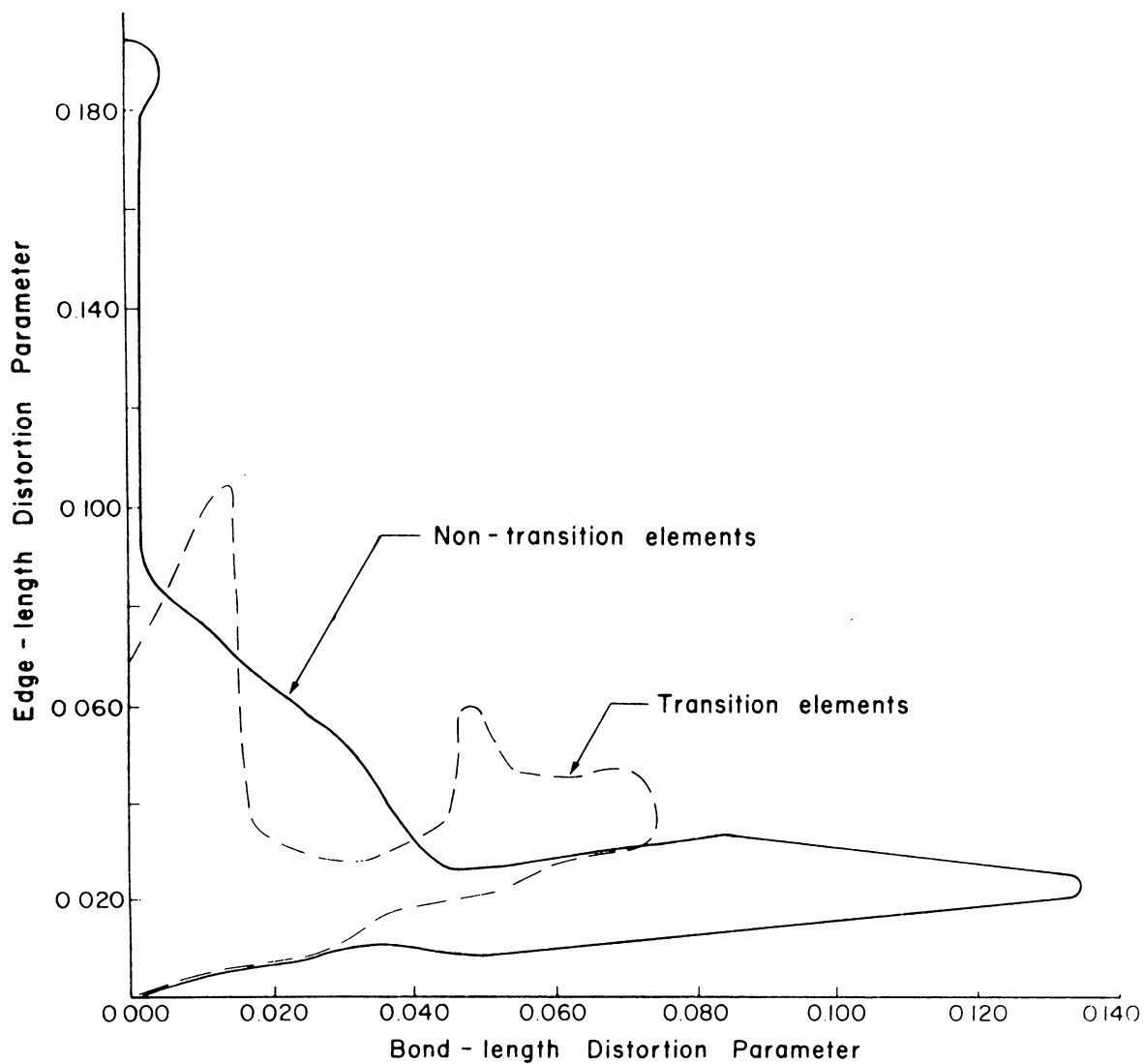


Figure 2: Plot of ELDP *vs.* BLDP for composite of all oxyanions of non-transition elements (solid boundary) and of transition metals (dashed boundary).

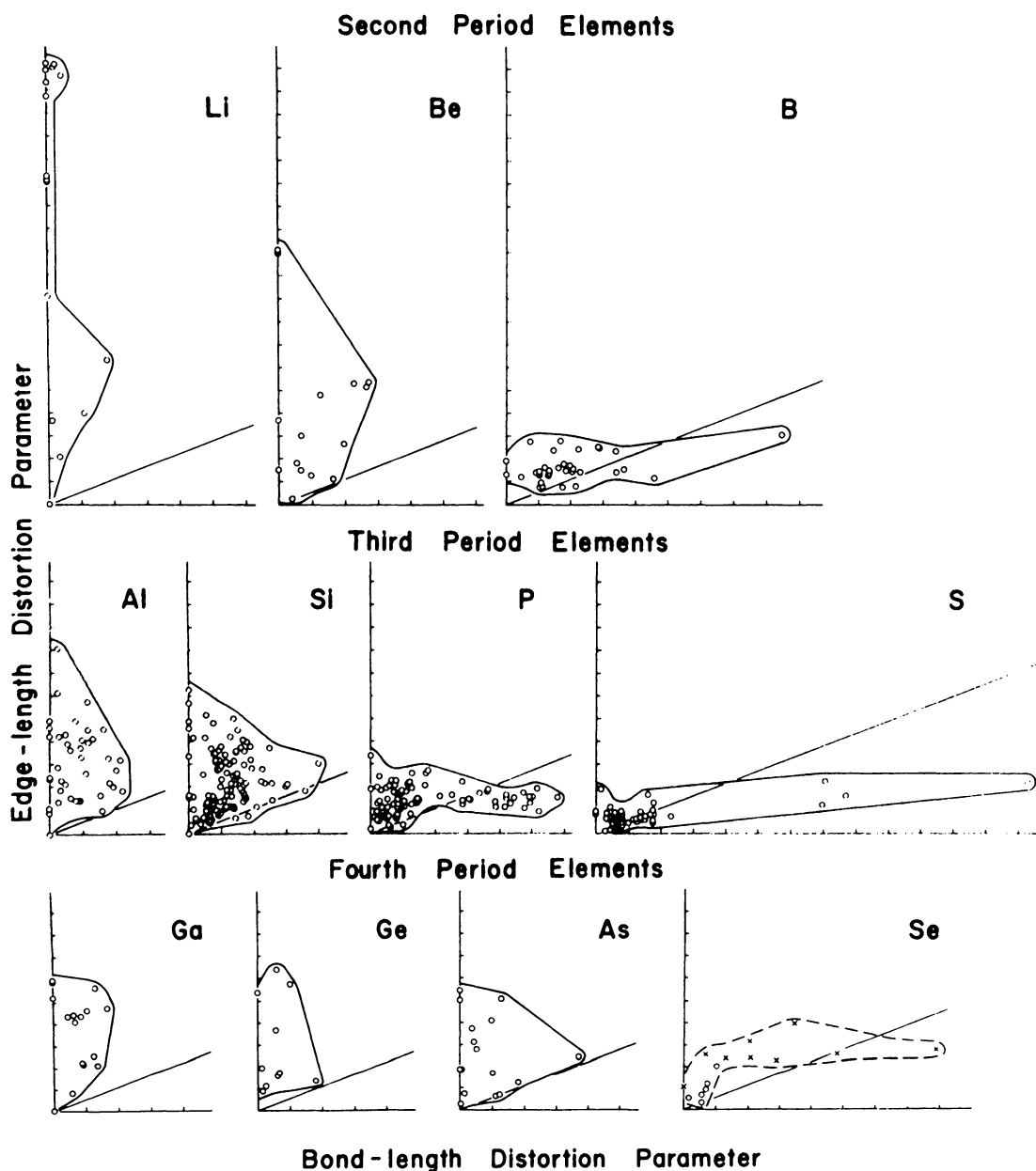


Figure 3: Plots of ELDP *vs.* BLDP for oxyanions of individual non-transition elements. Each circle represents a tetrahedron which meets the requirements for precision set forth in the text; "X" represents a tetrahedron which does not. Tic marks are at intervals of 0.01.

the O-T-O angles of a tetrahedron were ideal (109.47°). Perusal of Figure 3 will verify the following observations:

1. The only tetrahedra which exhibit 0.0 edge-length distortion also show 0.0 bond-length distortion. Alternatively stated, no data points fall on the BLDP axis except at the origin.
2. Large values of edge-length distortion are associated with small values of bond-length distortion; likewise, large values of BLDP are associated with tetrahedra whose ELDP values are small.
3. The range of edge-length distortions for oxyanions of each element decreases from left to right in each period.
4. The range of bond-length distortions for oxyanions of each element increases from left to right along a period.
5. The range in bond-length distortions decreases with increasing atomic number of the cation within a given group of the periodic table.
6. For third and fourth periods the shapes of the maximum distortion boundaries for oxyanions of elements diagonally related to each other (Al and Ge; Si and As; P and Se) are remarkably but inexplicably similar.

Insight into the first observation may be gained by examining

symmetry restrictions and by consideration of semi-empirical molecular orbital calculations. The equality of all six $O\cdots O$ distances in a tetrahedron implies that the forces acting between the ligands are equal. Such an anion arrangement is consistent with point symmetry 23 (or higher) at the tetrahedral site, requiring all oxygen atoms to be equivalent and all $T-O$ bonds to be equal. On the other hand if the $T-O$ bonds were not all equal, then all oxygen atoms would not be equivalent, $O\cdots O$ interactions would be different along different tetrahedral edges, and the edge lengths would consequently not all be alike. Of course the equivalence of ligands and equality of bond lengths do not necessarily imply equality of edge lengths (e.g., site symmetry $\bar{4}$). Hence it is to be expected that tetrahedra might plot along the ELDP axes in Figure 3, but not along the BLDP axes (except at the origin). This rationale is supported by extended Hückel molecular orbital calculations on the AsO_4^{3-} tetrahedron (Chiari and Gibbs, 1975) wherein the cation position was varied inside a rigid regular tetrahedron of anions. The results of this calculation showed that, as the cation was moved off the circumcenter along a $T-O$ bond, the $O\cdots O$ repulsions along the three tetrahedral edges adjacent to that bond increased while those along the remaining edges decreased.

Observations 2, 3 and 4 are related, though not equivalent, to the statements of Louisnathan and Gibbs (1972, p. 1282) that the ranges of tetrahedral edge lengths decrease from left to right in the third row, and that the "recorded bond length variations increase in range from left to right in the third row of the periodic table...whereas

the grand mean distances decrease."

The influence of shared edges and tetrahedral polymerization on the distribution of data within the maximum distortion boundaries is indicated by Figure 4. Within a given species of oxyanion, it appears that edge-length distortion is broadly controlled by the number of edges which a tetrahedron shares with other polyhedra, while bond-length distortion is related to the number of oxygen atoms shared with other *tetrahedra* (of any species). The effect of polyhedral edge-sharing in crystal structures is well known (Pauling, 1960) and its influence on ELDP is not surprising. The distribution of PO_4^{3-} and SO_4^{3-} data with respect to BLDP may be rationalized as a measure of the degree of similarity of the oxygen atoms in a tetrahedron. Baur (1974) has related variations in bond lengths in phosphate tetrahedra to Δp_o , the deviation from the mean (for a given tetrahedron) of the sum of the electrostatic bond strengths received by the oxygen atoms. In structures consisting of tetrahedral frameworks or containing isolated tetrahedra, the variation in Δp_o would be generally small, resulting in fairly uniform bond lengths and therefore low values of BLDP as observed in Figure 4. The sharing of one or two corners with other tetrahedra would generally result in greater variability of Δp_o among the anions of a given tetrahedron, leading to greater bond-length distortion (Figure 4).

The structural correlations illustrated in Figure 4 are not as obvious for oxyanions that exhibit both moderately large bond-length and edge-length distortions. Figures 5 and 6 show the number of shared

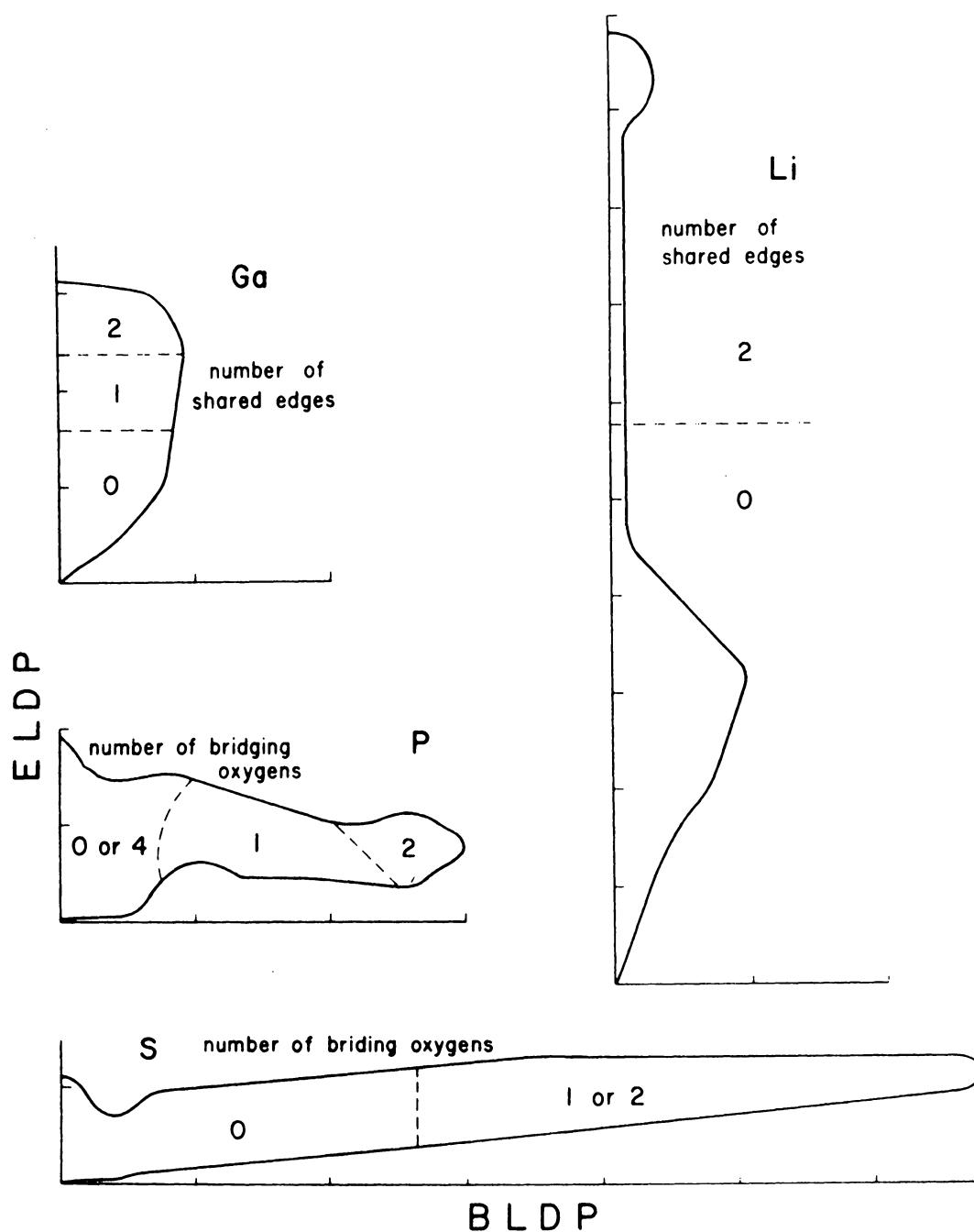


Figure 4: Variation in distortion parameters with the number of shared tetrahedral edges (Ga and Li oxyanions) and with tetrahedral polymerization (P and S oxyanions). Tic marks are at intervals of 0.02.

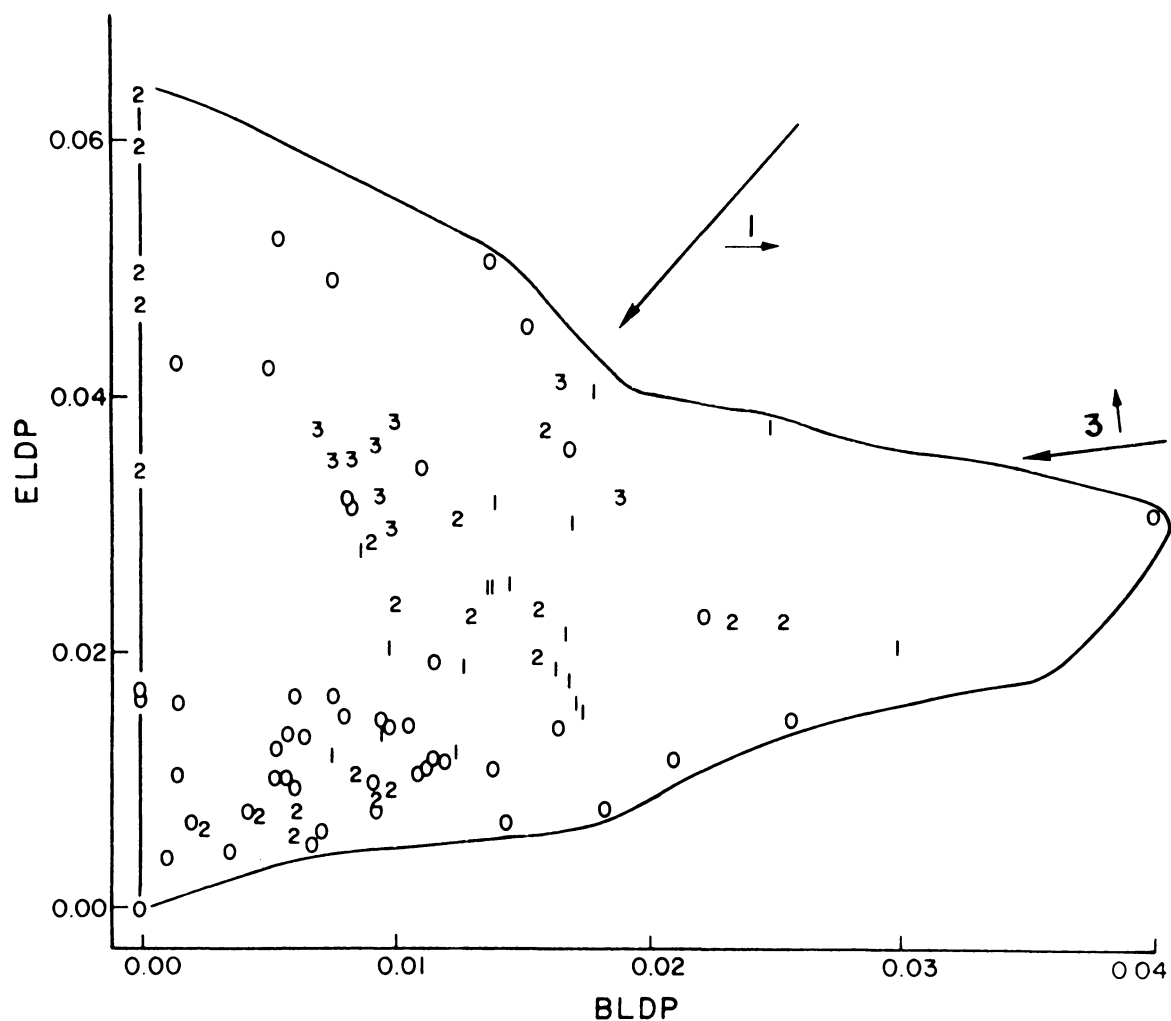


Figure 5: Distribution of data within the maximum distortion boundary for silicon oxyanions as a function of the number of shared edges. Arrows indicate the areas within the maximum distortion boundary where the distortions of tetrahedra that share one edge or three edges plot.

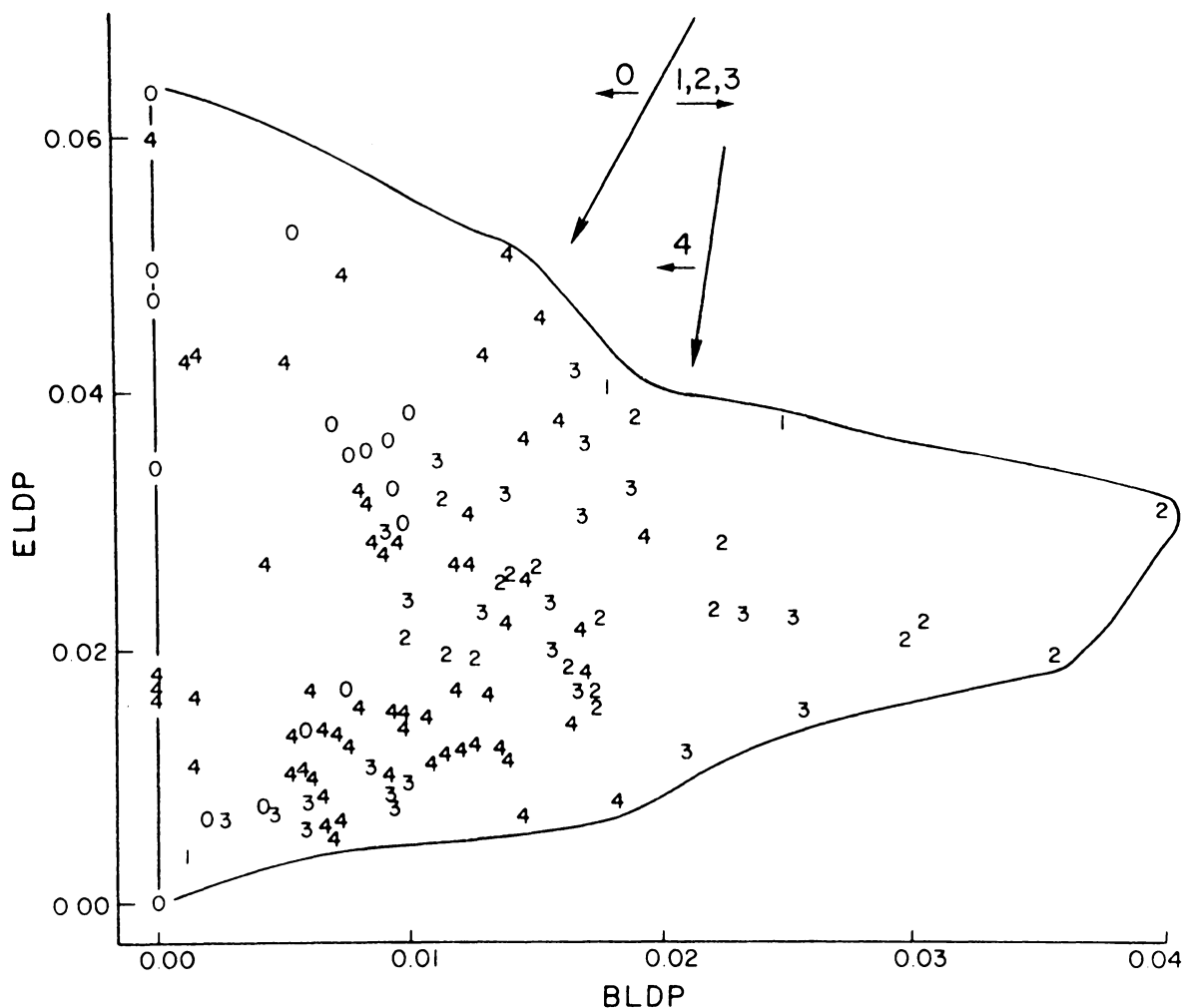


Figure 6: Distribution of data within the maximum distortion boundary for silicon oxyanions as a function of tetrahedral polymerization. Zones of demarcation (heavy arrows) separate distortions in tetrahedra that share 1, 2, or 3 corners with other tetrahedra from those that share none, and (right arrow) indicate observed limit in distortions for tetrahedra which share all four corners with other tetrahedra.

edges and bridging oxygens, respectively, for silicate tetrahedra. Not all of the tetrahedra used in Figure 3 are shown in these figures because of the difficulty in determining structural details from some of the descriptions in the literature. In Figure 5 one arrow indicates a zone to the right of which no tetrahedra sharing one edge are observed, and the other represents a zone above which all observed tetrahedra with three shared edges plot. There are two populations of tetrahedra which share two edges. One consists of tetrahedra which share two *opposite* edges, and these fall on the ELDP axis; the other comprises those which share two *adjacent* edges, and these plot in the same region as those with one shared edge. The distribution of distortions for tetrahedra with no shared edges does not seem to be very systematic, although the majority are concentrated below an ELDP of 0.02. Because all of the lithium and gallium oxyanions (Figure 4) have zero or four bridging oxygens, which is not true for the silicate tetrahedra, it appears that tetrahedral polymerization, as well as edge-sharing, may have an effect on edge-length distortion. The influence of tetrahedral polymerization on BLDP in silicates (Figure 6) is similar to that for phosphates and sulphates (Figure 4).

Relationships among bond lengths, edge lengths, and bond angles

As stated earlier, variations in O-T-O angles depend upon variations in T-O and O...O distances, and previous studies have treated the relative dependence of bond angle variations on the other two variables for third period oxyanions and BO_4^{5-} groups. Two equations, the first proposed by Baur (1970) and the second by Ribbe, Phillips

and Gibbs (1972) have been used in these studies:

$$\log[\sin(0-T-0/2)] = a + b[\log\langle T-0 \rangle], \text{ and} \quad (16)$$

$$\log[\sin(0-T-0/2)] = a + b[\log(0\cdots 0)]. \quad (17)$$

In equation (16) $\langle T-0 \rangle$ is the mean length of the two $T-0$ bonds which form the sides of the $0-T-0$ angle. These two equations correspond to the two extreme models for angular changes in tetrahedra. The first represents a change in angle caused by movement of the cation within a rigid framework of anions; the second represents angular change caused solely by changes in $0\cdots 0$ separations. The first model is the basis for Rule 5 of Baur's (1970) extended electrostatic valence rules. Baur (1970) found moderate to good correlations using equation (16) for borates, silicates, phosphates, and sulphates. In a comprehensive study of distortions in phosphate tetrahedra (Baur, 1974) he later determined that the orthophosphates obey equation (17) much more closely than equation (16), while most other phosphate populations require both models for adequate description.

Louisnathan and Gibbs (1972) showed that the correlation coefficient for equation (17) decreased for the third period sequence $T = \text{Al, Si, P, S}$ but increased again for Cl. They also found that the correlation coefficient for equation (16) increased from Al to Si to P, but decreased from P to S to Cl; a generally similar trend was observed in plots of $T-0$ vs. $\langle 0-T-0 \rangle_3$, where $\langle 0-T-0 \rangle_3$ is the average of the three angles common to a bond. They concluded that variations in $0-T-0$ angles are dependent on changes in both bond lengths and edge lengths for oxyanions of Si, P, S, and Cl, but almost entirely on changes in edge lengths for

oxyanions of Al. Ribbe *et al.* (1972) examined the applicability of equations (16) and (17) to the SiO_4 and AlO_4 tetrahedra of anorthite and found the latter to be a much better model.

Figures 7a, c, and e show plots and regression statistics corresponding to equation (16) for the oxyanions of non-transition elements considered in this study. Plots representing equation (17) are shown in Figures 7b, d, and f. In order to enhance the clarity of the figures, data points have been replaced by the curves which enclose them. The dashed curves enclose only one of 198 data for B, one of 732 for Si, and six of 306 for S. Figure 8 displays plots of $T-O$ vs. $\langle O-T-O \rangle_3$, which constitute an alternative test of equation (16). The regression statistics for this figure are listed in Table 1. With the exception of the germanium oxyanions, the correlation coefficients increase for equation (16) and decrease for equation (17) from left to right within each row of the periodic table. Bond length variation (equation (16)) makes essentially no contribution to angular variations in the tetrahedral oxyanions of Li, Be, Al, Ga, Ge, and As. In addition, most of the angular variation for BO_4^{5-} , Si_4^{4-} , PO_4^{3-} , and SeO_4^{2-} tetrahedra appears to be due to edge length changes, although bond length variations do make a significant contribution. Only for SO_4^{2-} groups does bond length variation appear to be the major factor influencing angular changes. Baur's (1974) observation that equation (16) is a much better model for condensed phosphates than for orthophosphates is readily explicable on the basis of Figure 4. The orthophosphates (and framework structures) show the least P-O variation (i.e., the lowest values of

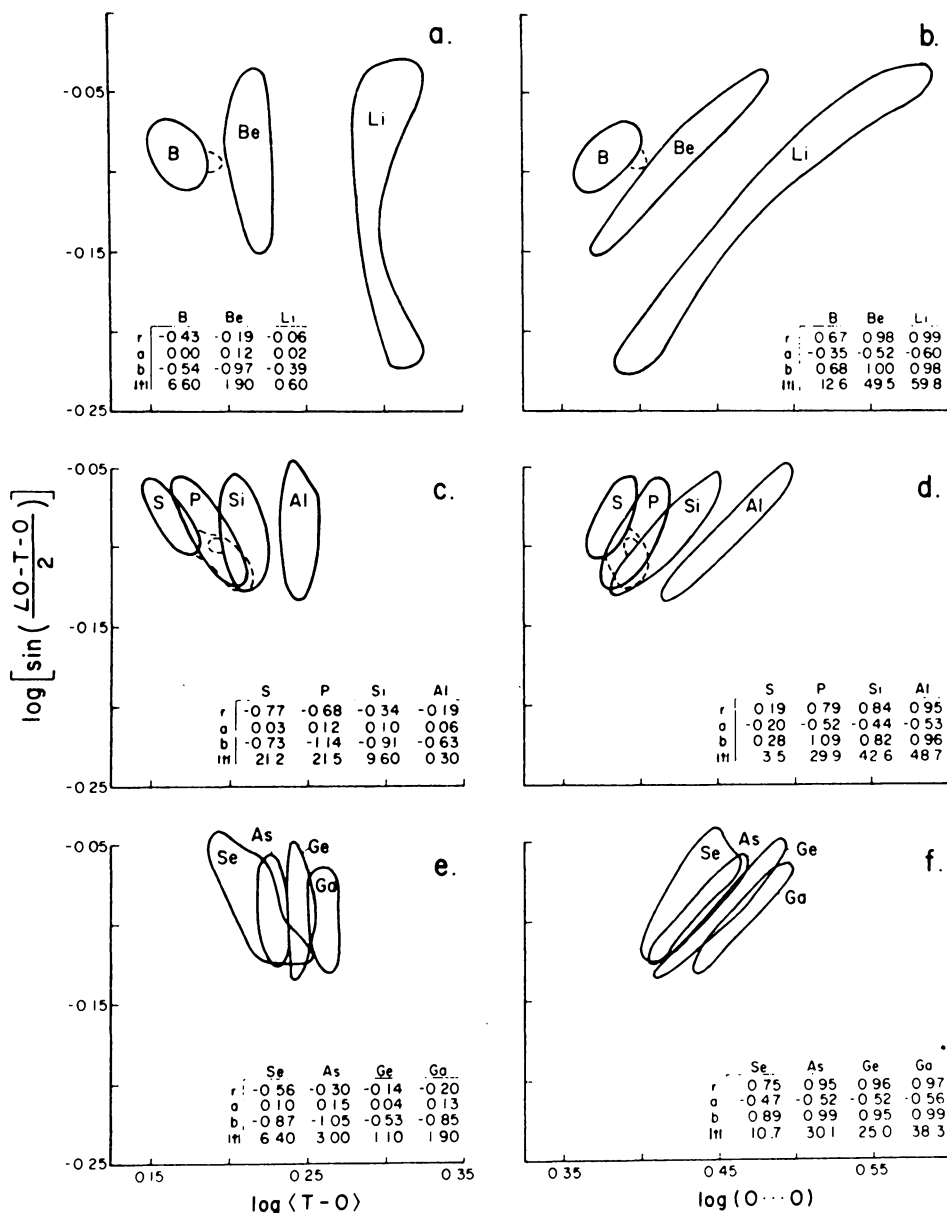


Figure 7: Tetrahedral bond angle as a function of the mean length of the two bonds forming the angle (a, c, e) and of the O...O distance subtended by the angle (b, d, f). Regression statistics given are: r, correlation coefficient; a, intercept; b, slope; |t|, statistic for test of zero regression. Data points are represented by enclosing boundaries. Dashed curves are explained in text.

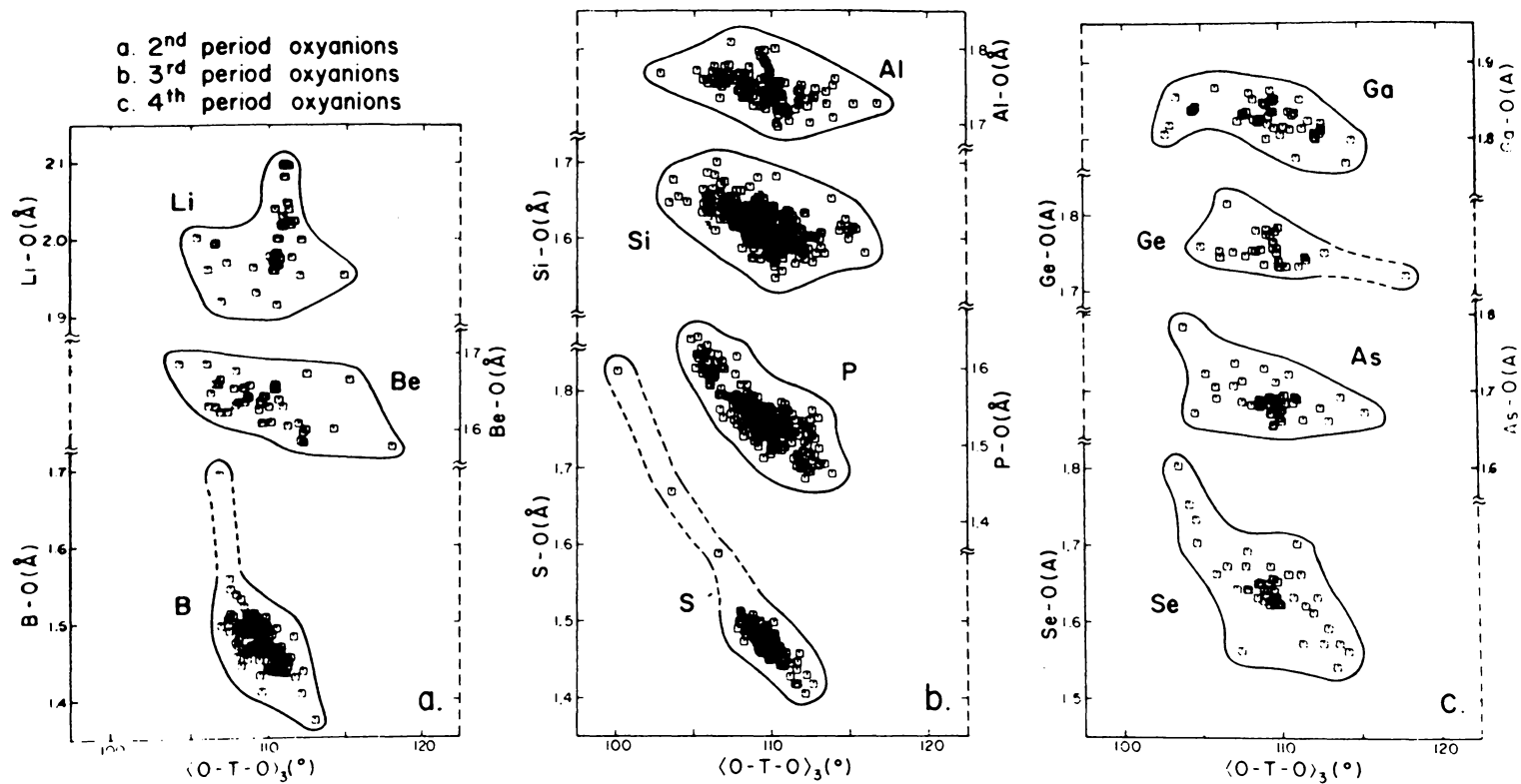


Figure 8: Bond length *vs.* $\langle O-T-O \rangle_3$ for oxyanions of non-transition elements, where $\langle O-T-O \rangle_3$ is the mean of the three angles in which a given bond is involved.

Table 1

Linear regression analyses for plots
of $T-0$ vs. $\langle 0-T-0 \rangle_3^*$

Cation	r	a	b	t
Li	0.30	0.925	0.010	2.6
Be	0.39	2.095	-0.004	3.4
B	0.60	3.382	-0.017	8.6
Al	0.32	2.154	-0.004	4.4
Si	0.38	2.266	-0.006	9.2
P	0.63	2.902	-0.012	15.1
S	0.81	4.143	-0.024	19.4
Ga	0.39	2.172	-0.003	3.2
Ge	0.37	2.132	-0.003	2.4
As	0.49	2.412	-0.005	4.4
Se	0.70	3.137	-0.014	7.5

* r = correlation coefficient

a = intercept

b = slope

|t| = statistic for test of
zero regression

BLDP). With increasing polymerization the variation in P-O distances increases, thus improving the relationship between bond lengths and bond angles. Baur's Table 7 shows that the correlation coefficient for equation (16) increases from orthophosphates (0.50) to pyrophosphates (0.83) to ring phosphates (0.92), thus confirming this explanation for phosphate tetrahedra. The same trends should occur for the other species of oxyanions as well.

Because a simple electrostatic model is sufficient for the characterization of many structural features in crystals, the general assumption among mineralogists has been that bonding in crystals is ionic. Pauling's (1948) electrostatic neutrality principle and recent experimental evidence (e.g., Cooper, Larsen, Coppens, and Giese, 1973) suggest, however, that the charges on atoms in crystals are much lower than those consistent with purely ionic bonding. In order to make inferences about bond type, the variations in bond lengths and bond angles in tetrahedral oxyanions have been correlated with Δp_o (e.g., Baur, 1970, 1971, and 1974) and with overlap population, $n(T-O)$, obtained from extended Hückel molecular orbital calculations (e.g., Louisnathan and Gibbs, 1972; Gibbs, Hamil, Louisnathan, Bartell, and Yow, 1972; and Lager and Gibbs, 1973). It has been pointed out (Lager and Gibbs, 1973; Chiari and Gibbs, 1975) that the correlation of p_o with bond length is better for more electronegative cations, and that there is a moderate correlation between p_o and $n(T-O)$, suggesting that p_o (and hence Δp_o) is a measure of a covalent bonding property. Thus it is perhaps unwise to base inferences about bond

type on correlations between bond length or bond angle variations and modelled parameters. It will be shown later in this study that limited implications on bond type may be suggested by considering the maximum tetrahedral distortions observed.

Tetrahedral oxyanions of transition metals

Plots of edge-length distortion *vs.* bond-length distortion for the transition metal tetrahedral oxyanions used in this study are presented in Figure 9. Because transition metals commonly exhibit more than one valence state, the formal valence is specified (except for the Mn plot, which contains data for tetrahedra containing Mn^{2+} , Mn^{6+} , and Mn^{7+}). It is at once obvious that, due to the amount of data available, the only useful plots are those for the oxyanions of V^{5+} , Cr^{6+} , Mo^{6+} , Fe^{3+} , and Zn^{2+} .

Of the following observations, the first was also made for oxyanions of non-transition elements:

1. No tetrahedra are observed to exhibit 0.0 ELDP unless they also exhibit 0.0 BLDP. The converse is not true.
2. In marked contrast to the maximum distortion boundaries for the oxyanions of the non-transition elements, those for oxyanions of V^{5+} , Cr^{6+} , and Mo^{6+} tend to follow the line along which ideal tetrahedral angles (109.47°) obtain.
3. The plots for Fe^{3+} and Zn^{2+} bear a much closer resemblance to some of the plots in Figure 3 than

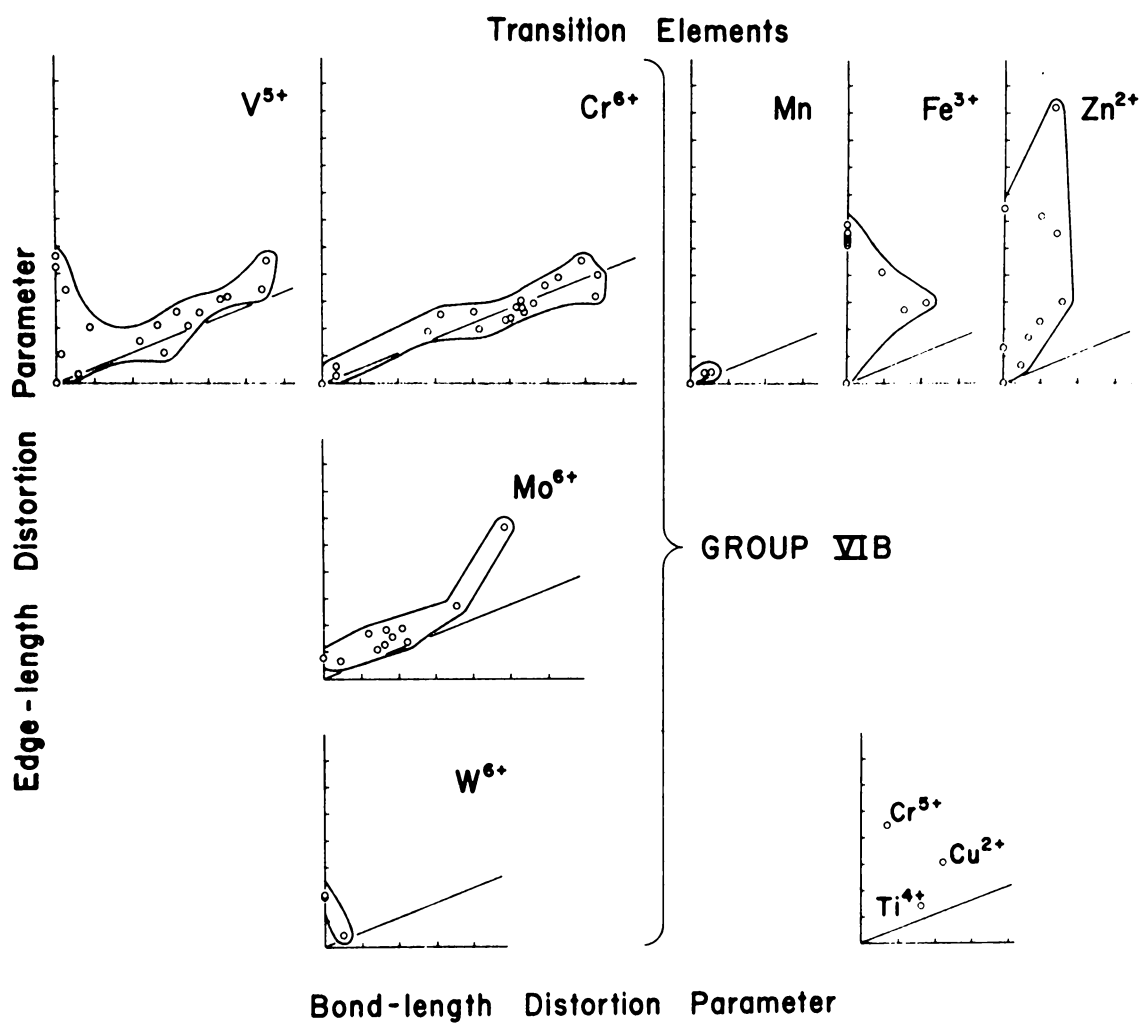


Figure 9: Plots of ELDP *vs.* BLDP for oxyanions of individual transition metals. Formal valences are indicated except for the Mn plot, which contains data for Mn^{2+} , Mn^{6+} , and Mn^{7+} oxyanions.

they do to those of V^{5+} , Cr^{6+} and Mo^{6+} oxyanions.

4. For oxyanions of Group VIB elements, maximum values of both edge-length distortion and bond length distortion decrease with increasing atomic number.

Stephens and Cruickshank (1970) observed that bond angles in chromate tetrahedra tend to be close to 109.47° . They ascribed this behavior to the "narrowness" of d^3s hybrid bonds as compared to sp^3 hybrid bonds, suggesting that small deviations from the ideal tetrahedral angle would cause a greater reduction in σ -bond overlap for chromate tetrahedra than would the same deviations in selenate or sulphate tetrahedra. Figure 9 indicates that a similar rationale may be applied to the tetrahedral oxyanions of molybdenum and vanadium, but not to those of ferric iron and zinc. No explanation for this difference is apparent, but the following points may be contributing factors: Iron and zinc ions are larger and bear lower formal charges than chromium, vanadium, and molybdenum ions; additionally, Zn^{2+} possesses a closed d -subshell, and Fe^{3+} possesses a half-filled d -subshell (if fully ionized).

Relationships among bond lengths, edge lengths, and bond angles

Table 2 shows the regression statistics for equations (16) and (17), and for $T-O$ vs. $\langle O-T-O \rangle_3$ plots, applied to the oxyanions of transition metals. For iron and zinc tetrahedra essentially all of the variation in bond angles can be attributed to edge length changes. For the three remaining species of oxyanions there is little variation

Table 2

Regression statistics for relations among $T-O$, $O\cdots O$, and $\angle O-T-O$ for oxyanions of five transition metals*

Cation	r	a	b	t
$\log[\sin(O-T-O/2)]$ vs. $\log\langle T-O \rangle$				
V	0.08	-0.112	0.099	0.8
Cr	0.21	-0.059	-0.133	2.3
Mo	0.33	-0.169	0.330	2.8
Fe	0.07	0.054	-0.526	0.6
Zn	0.12	0.038	-0.435	0.9
$\log[\sin(O-T-O/2)]$ vs. $\log(O\cdots O)$				
V	0.78	-0.342	0.567	12.4
Cr	0.39	-0.186	0.227	4.5
Mo	0.79	-0.305	0.472	10.3
Fe	0.99	-0.567	0.987	55.2
Zn	0.96	-0.567	0.946	23.5
$T-O$ vs. $\langle O-T-O \rangle_3$				
V	0.15	1.084	0.006	1.2
Cr	0.32	-0.026	4.536	2.9
Mo	0.51	0.019	-0.345	3.9
Fe	0.40	2.530	-0.006	3.0
Zn	0.21	2.277	-0.003	1.2
* symbols same as in Table 1.				

in bond angles. The variation which does exist for V and Mo oxyanions is correlated mostly with $O\cdots O$ variations. For the oxyanions of Cr, for which the distortion data plot closest to the line representing ideal tetrahedral angles (Figure 9), there is little correlation of angular variation with either bond length or edge length changes.

An interesting observation may be made regarding the molybdate tetrahedron which plots at $BLDP = 0.0483$, $ELDP = 0.0569$. It is one of three MoO_4^{2-} groups in $CuMoO_4$ (see Appendix B for reference). As expected from its position on the $ELDP$ - $BLDP$ plot (Figure 9) the O - Mo - O angles are not all close to 109.47° , but range from 104.5° to 120.1° . This tetrahedron shares the edge subtended by the 120.1° bond angle with a 5-coordinated Cu oxyanion; paradoxically, this edge is also the longest edge of the tetrahedron and the bonds adjacent to it are the longest Mo - O distances of the tetrahedron. It also subtends the largest O - Cu - O angle in the CuO_5 polyhedron. Although the Cu - Mo distance is not unusually short, the angular geometry and long shared edge suggest metal-metal bonding.

ANALYSIS OF DISTORTION RANGES OBSERVED FOR TETRAHEDRAL OXYANIONS

Tetrahedral oxyanions of non-transition elements

The consistency of the trends seen in Figure 3 and stated as observations 2 through 5 (p. 15) suggests that the *shapes* of the maximum distortion boundaries may be influenced significantly by some characteristic(s) of the respective cations, although it has already been shown that the distribution of data *within* the boundaries is largely controlled by the number of shared edges and degree of tetrahedral polymerization. These shapes, quantified in terms of mean values and ranges in the distortion parameters, will now be examined to determine whether they can provide insight concerning the phenomena which limit the maximum observed distortions in tetrahedra.

Observations 2 through 5 are graphically portrayed in Figures 10 and 11. Table 3 is a listing of the data from which these plots were constructed. To facilitate the recognition of trends, oxyanions of second period elements are represented by ellipses, those of the third period elements by triangles, and those of the fourth period elements by squares. Selenium oxyanions have been included as open squares to indicate the general lack of precision of the available data. Figure 10a shows that, within periods, the mean values of ELDP increase with the mean size of the tetrahedra, though the third and fourth period lines do not appear to be distinct. Separate trends for each period are clearly evident in Figure 10b, and it will be shown later that the overlapping of the third and fourth period trends in Figure 10a is probably fortuitous.

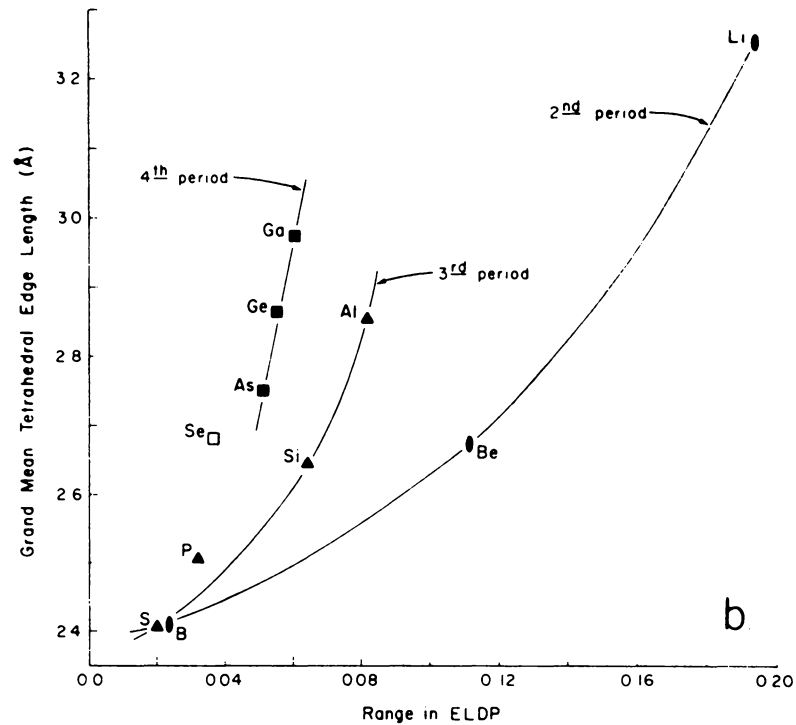
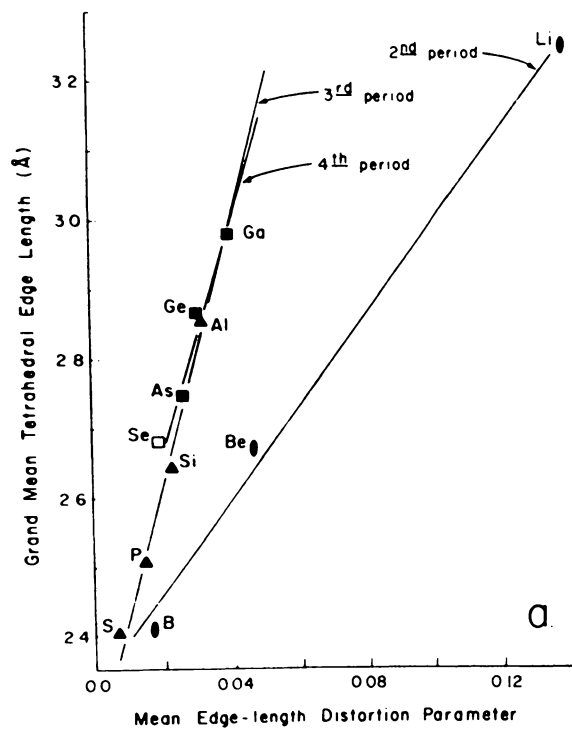


Figure 10: a. Relationship between grand mean tetrahedral edge length and mean ELDP for all tetrahedra of a given species. b. Grand mean tetrahedral edge length plotted against range in ELDP. The species of cation is indicated by chemical symbol.

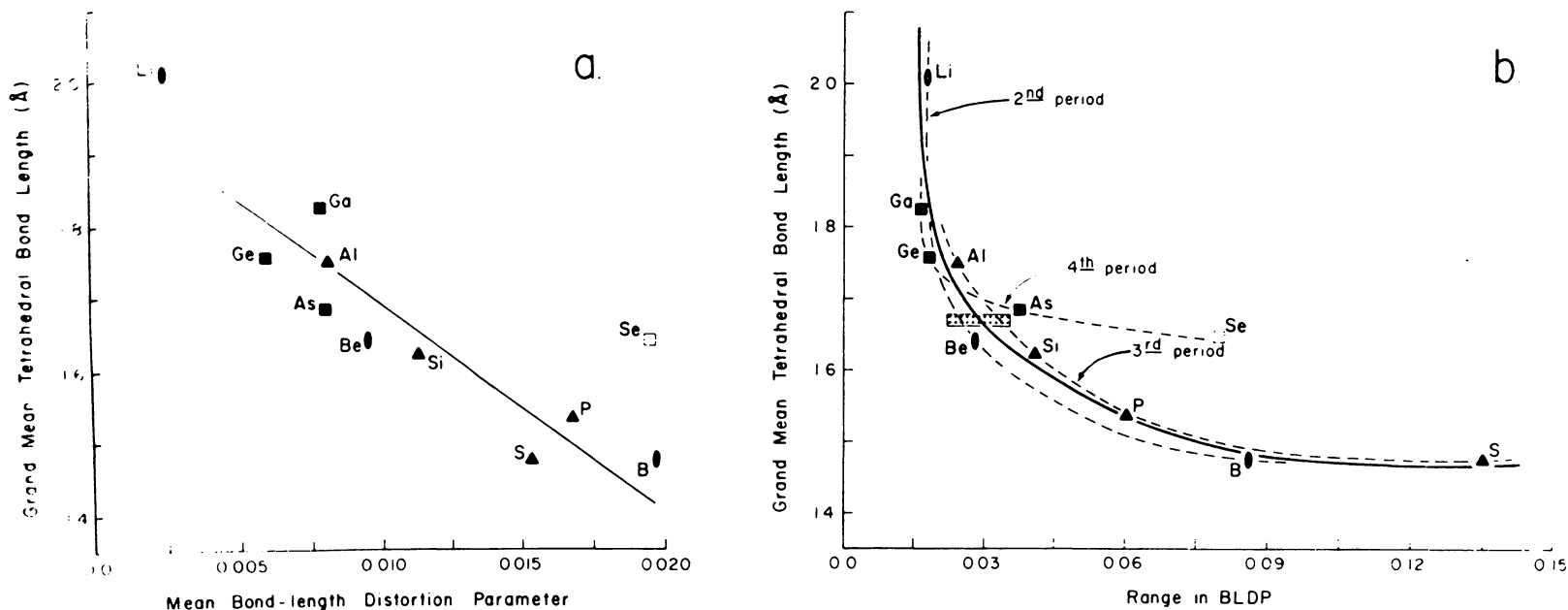


Figure 11. a. Relationship between grand mean tetrahedral bond length and mean BLDP for all tetrahedra of a given species. b. Grand mean tetrahedral bond length plotted against range in BLDP. Stippled bar represents the range of bond lengths corresponding to the "no-rattle limit" (see text). Cation species is indicated by chemical symbol.

Table 3

Grand mean interatomic distances, mean distortion
parameters, and ranges in distortion parameters
for sixteen oxyanions

Cation	$\langle\langle T-O \rangle\rangle$	$\langle\langle O \cdots O \rangle\rangle$	Mean BLDP	Mean ELDP	Range in BLDP	Range in ELDP
Li	2.009	3.249	0.0025	0.1365	0.0176	0.1923
Be	1.641	2.672	0.0095	0.0480	0.0276	0.1107
B	1.477	2.410	0.0197	0.0163	0.0859	0.0232
Al	1.750	2.854	0.0081	0.0316	0.0241	0.0808
Si	1.621	2.644	0.0112	0.0219	0.0405	0.0635
P	1.536	2.506	0.0168	0.0150	0.0600	0.0319
S	1.474	2.406	0.0153	0.0076	0.1340	0.0197
Ga	1.829	2.980	0.0078	0.0394	0.0162	0.0594
Ge	1.757	2.865	0.0059	0.0300	0.0180	0.0545
As	1.685	2.748	0.0080	0.0257	0.0372	0.0505
Se	1.643	2.679	0.0195	0.0192	0.0792	0.0365
V	1.716	2.802	0.0253	0.0261	0.0558	0.0456
Cr	1.654	2.701	0.0452	0.0276	0.0727	0.0449
Mo	1.759	2.873	0.0192	0.0189	0.0484	0.0496
Fe	1.871	3.051	0.0038	0.0488	0.0198	0.0585
Zn	1.963	3.199	0.0074	0.0372	0.0152	0.0604

Figure 11a displays the tendency of the tetrahedra occupied by larger atoms to exhibit, on the average, less bond-length distortion than those occupied by smaller ones. Because of the non-uniform distribution of data on the BLDP-ELDP plots, no systematically consistent trends related to chemical periodicity are observed. In Figure 11b, however, where the *ranges* of BLDP are plotted, the trends within periods (shown by dashed curves) are decidedly systematic. This suggests that there is no physical reason for a non-uniform distribution of BLDP values within the maximum distortion boundaries of Figure 3. The observed lack of uniformity for some types of oxyanions is simply a reflection of the fact that only a few structures with the appropriate degree of tetrahedral polymerization have been refined (e.g., compare S in Figures 3 and 4).

Among the traditionally useful concepts of crystal chemistry is the notion that the ratio of cation radius to anion radius governs the cation coordination number. The "no-rattle limit," which is 0.225 for a tetrahedron, is defined as the radius ratio which obtains when adjacent "hard-sphere" anions are in contact and the cation is just tangent to each (Bloss, 1971). In the "hard-sphere" model, cations yielding radius ratios smaller than this are permitted to "rattle" in the tetrahedral void. In terms of distortions this corresponds to an increased tendency toward bond-length distortion. The stippled bar in Figure 11b is located at the range of tetrahedral bond lengths corresponding to the "no-rattle limit" for tetrahedral oxyanions; for the radii of two- to four-coordinated oxygen atoms given by Shannon and Prewitt (1969) this represents a cation radius of $0.304\text{\AA}$ to $0.315\text{\AA}$. The placement of

the stippled bar depends, of course, on the choice of oxygen radius. Among the more recent estimates, Slater (1964) has given $0.60\text{\AA}$ as the atomic radius of oxygen, Fumi and Tosi (1964) have given a crystal radius of $1.21\text{--}1.28\text{\AA}$ (depending on coordination number and based on a radius for six-coordinated fluorine of $1.19\text{\AA}$), and Shannon and Prewitt (1969) have given an effective ionic radius of $1.35\text{--}1.42\text{\AA}$ (depending on coordination number and based on an assumed radius of $1.40\text{\AA}$ for six-coordinated oxygen). The effective ionic radii of Shannon and Prewitt (1969) have been used in this study for the following reasons:

- (1) They were empirically derived from bond lengths in oxide and fluoride structures rather than from alkali halides, theoretical calculations, or other methods. Thus they are specifically applicable to an investigation of oxy-anions.
- (2) Since they are empirical, they include the effects of variable bond type in crystalline oxides.
- (3) They reproduce observed lengths of $T\text{--}O$ bonds better than most other tables of radii.

The upper least-squares regression line of Figure 12 simply constitutes a test of the data, and shows that the grand mean $T\text{--}O$ and $O\cdots O$ distances obey the linear relationship required by tetrahedral geometry. The other line, grand mean $T\text{--}O$ distance *vs.* cation radius, demonstrates the need for revision of a few of the radii suggested by Shannon and Prewitt (1969). These revised radii, along with new tetrahedral radii for Cu^{2+} and Ti^{4+} , are listed in Table 4.

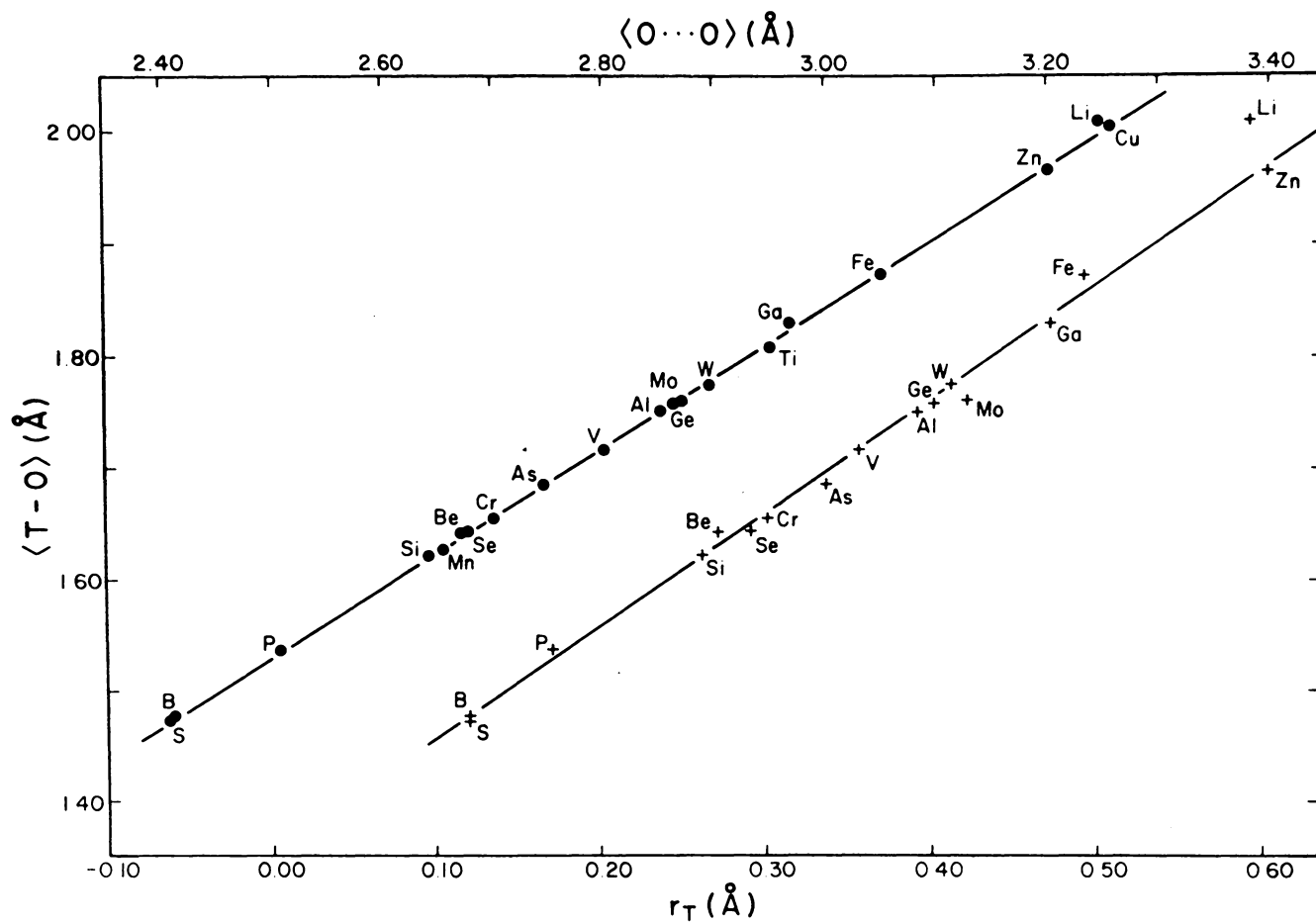


Figure 12: Grand mean bond lengths *vs.* grand mean edge lengths and ionic radii of Shannon and Prewitt (1969) for the twenty species of tetrahedral oxyanions used in this study.

Table 4

Revised effective ionic radii for
tetrahedral coordination

Ion	Radii of Shannon and Prewitt (1969)	Radii from this work
As ⁵⁺	0.335	0.325
Be ²⁺	0.27	0.28
Cu ²⁺	--	0.63
Fe ³⁺	0.49	0.50
Li ⁺	0.59	0.64
Mo ⁶⁺	0.42	0.40
Ti ⁴⁺	--	0.44

The "no-rattle limit" shown in Figure 11 evidently constitutes a zone of demarcation above which the range in BLDP increases slowly with decreasing grand mean bond length, and below which the same change occurs very rapidly. This is suggestive of cations "rattling" inside tetrahedra of "soft" (i.e., polarizable) anions. (The term "rattling" is, of course, not intended to convey the impression that the central atom of a given tetrahedron moves about within the tetrahedral void. Rather it simply denotes that, of all the tetrahedra, those having the smallest central atoms are also those which exhibit the relatively greatest ranges of displacement of the central atom from the circum-center.) It might be concluded, therefore, that the limiting factor in bond-length distortion is simply the size of the central atom relative to the size of the tetrahedral void. This view is substantiated by linear regression analyses wherein BLDP is the independent variable and the mean bond length of each tetrahedron is the dependent variable. For the most part the correlation coefficients are low and the $|t|$ -values for the tests of zero regression are not significant. For sulphur oxyanions, however, the correlation coefficient is 0.83 and $|t| = 10.24$, indicating that the SO_4^{2-} groups exhibiting the largest values of BLDP are also the largest sulphate tetrahedra. The borate and phosphate groups also show similar but less distinct trends, with $r = 0.35$ and 0.21 , and $|t| = 2.08$ and 2.00 , respectively.

Thus the solid curve in Figure 11b seems to indicate that the range in bond-length distortions is entirely a function of the effective size of the tetrahedrally-coordinated atom. The dashed curves suggest,

however, that within a given period the tetrahedral oxyanions in which bonding is more covalent experience greater bond-length variations. It has been demonstrated (Figure 4) that those tetrahedra which exhibit large values of BLDP tend to have one or two bridging oxygen atoms. Gillespie and Robinson (1964) have shown that bond orders calculated from force constants for the bridging bonds of T_2O_7 groups increase in the sequence $T = Cl, S, P, Si$. Concomitantly the bond orders of the $T-O(nbr)$ bonds show a general decrease, with the non-bridging and bridging bond orders of $Si_2O_7^{6-}$ being approximately equal. This suggests that the ranges in bond lengths for tetrahedral oxyanions containing bridging oxygen atoms should increase from left to right in the third period, as observed. This would result in a corresponding increase in bond-length distortions, consistent with Figure 3. Calculations of bond orders for second and fourth period T_2O_7 groups should show similar trends.

Turning now to a consideration of maximum edge-length distortions, the persistence of the second and third period trends in Figure 10b well below a mean edge length equal to twice the oxygen ionic radius (i.e., 2.7-2.8Å), and the continued decrease in mean bond length (Figure 11b) below the "no-rattle limit" both testify to the polarizability of oxygen atoms. Obviously there *is* some lower limit to the oxygen-oxygen non-bonded approach. The shortest observed O...O distances in crystals are $\sim 2.2\text{\AA}$ (Shannon and Prewitt, 1969); since this value is considerably in excess of twice the oxygen "covalent radius" of 0.74Å (Evans, 1966), it is to be concluded that the effects

of interactions between non-bonded oxygen atoms in arresting the ligand-ligand approach are important. These interactions have been considered to be of two kinds (Barrett, 1970; Bartell, 1968): (1) relatively long-range coulombic repulsions between two negatively-charged (though not necessarily fully-ionized) atoms, and (2) short-range repulsions arising from interactions between molecular orbitals (MOs) (i.e., resistance to the overlap of filled bonding MOs in accordance with the Pauli exclusion principle, and repulsion due to overlap of the antibonding orbitals orthogonal to bonding MOs). The factors which are important in determining the maximum extent of edge-length distortions also appear (Figure 10) to be of two kinds. Their recognition is facilitated by consideration of both the nature of the curves for individual periods and of the relationships among the three curves. From Figure 10b it is apparent that the range in ELDP is not entirely a function of tetrahedral size; if it were there would be only a single curve. Any explanation for the relationships shown in this figure must therefore incorporate more than cation size. It seems reasonable as a first approximation to assume that the range in ELDP is inversely proportional to the mean force of coulombic interaction between ligands. Figure 10b is suggestive of coulombic interactions in that the repulsive forces (expressed in terms of ranges in ELDP) increase with decreasing interatomic separations according to a non-linear relationship within each period. Repulsion between fully-ionized oxygen ions, however, would result not in the three separate curves observed, but in only one. An alternative, and more reasonable,

model is to consider the $T-O$ bonds as possessing "covalent character" commensurate with the electronegativity difference between atoms (Pauling, 1960), so that oxygen atoms bonded to lithium or beryllium, for example, would carry a greater negative residual charge than those bonded to silicon or phosphorus. Coulombic repulsion between such oxygen atoms would indeed result in three separate trends, but the order of curves, from left to right in Figure 10b, would be 2nd, 3rd, and 4th periods, rather than 4th, 3rd, and 2nd periods, as observed.

A third alternative is to invoke the variable covalency of the model just mentioned, but to consider repulsion between electrons concentrated (according to electronegativity) in bonding orbitals in regions between nuclei. As the chemical period of the cation increases, valence atomic orbitals contributing to bonding molecular orbitals become increasingly diffuse; for constant cation size, electronegativity increases with chemical period; for constant chemical period, electronegativity increases with diminishing cation size. All of these effects are consistent with this third interpretation of Figure 10b. The effective interactions which limit edge-length distortions may be coulombic interactions between electrons in different bonding orbitals, repulsions reflecting the efficacy of the exclusion principle, and repulsions between oxygen antibonding orbitals. The effects of the two latter short-range phenomena superimposed upon the coulombic repulsion may account for the crossing of curves at short mean edge lengths, resulting in "anomalously" low values of ELDP ranges for oxyanions of the smaller cations. Of course partial ionicity implies non-zero atomic

charges which would be expected to result in coulombic repulsion between oxygen atoms (as distinct from electron concentrations between nuclei). It appears that the coulombic repulsions between adjacent oxygen atoms of a tetrahedron are effectively counteracted by similar forces originating outside the tetrahedron.

Figures 10 and 11 can be recast in terms of electronegativity *vs.* distortion parameters (Figures 13 and 14). Because of the relationship (Figure 15) between electronegativities (Allred, 1961) and ionic radii (Shannon and Prewitt, 1969), no essentially new information results from this approach, but it is presented as an alternative point of view. It is to be noted that the overlapping third- and fourth period curves of Figure 10a are clearly separated in Figure 13a.

Tetrahedral oxyanions of transition metals

Figures 16 and 17 are analogous to Figures 10 and 11. The plotted values are listed in Table 3. Like Figure 11a, Figure 16a reflects the non-uniform distribution of data within the maximum distortion boundaries. The general tendency for smaller tetrahedra to exhibit smaller ranges in ELDP and larger ranges in BLDP is consistent with similar trends noted for oxyanions of non-transition elements. In detail, however, the shapes of corresponding curves are quite different.

The nature of the relationship shown in Figure 16b is complicated by several factors. First, molybdenum is not of the same chemical period as the other cations involved. In addition, it has been observed above that the distortions experienced by the tetrahedral oxyanions of molybdenum, chromium, and vanadium are of rather restricted

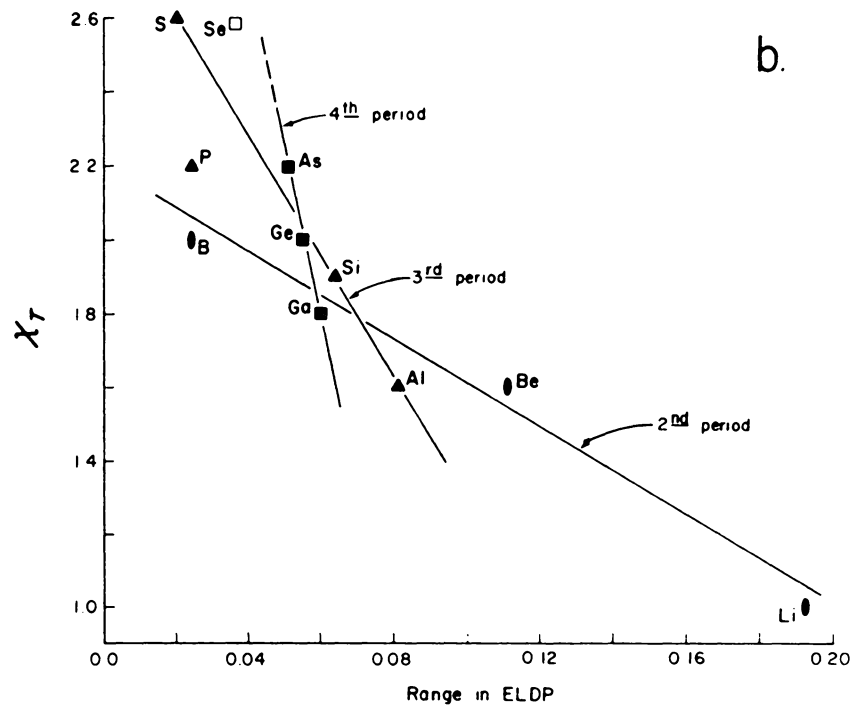
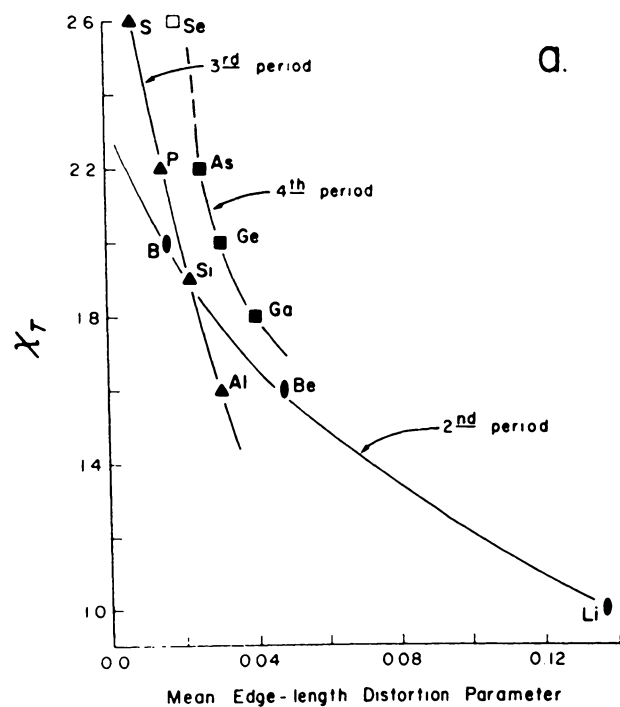


Figure 13: Electronegativity of cation *vs.* (a) mean ELDP and (b) range in ELDP for each species of non-transition oxyanion considered. Species of cation is indicated by chemical symbol.

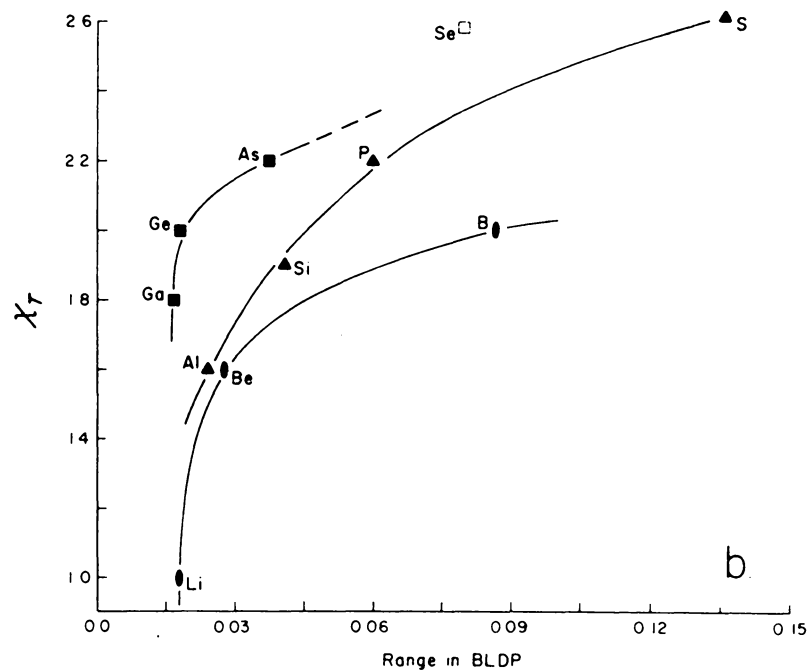
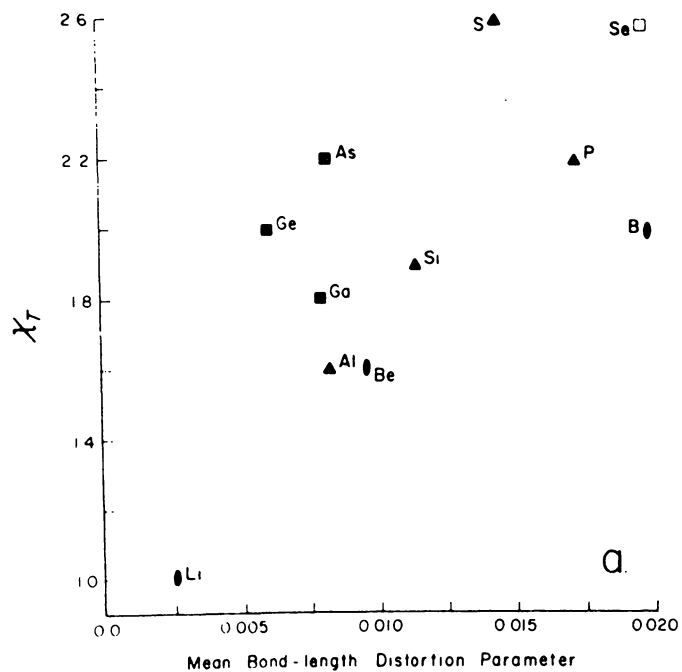


Figure 14: Electronegativity of cation *vs.* (a) mean BLDP and (b) range in BLDP for each species of non-transition oxyanion considered. Species of cation is indicated by chemical symbol.

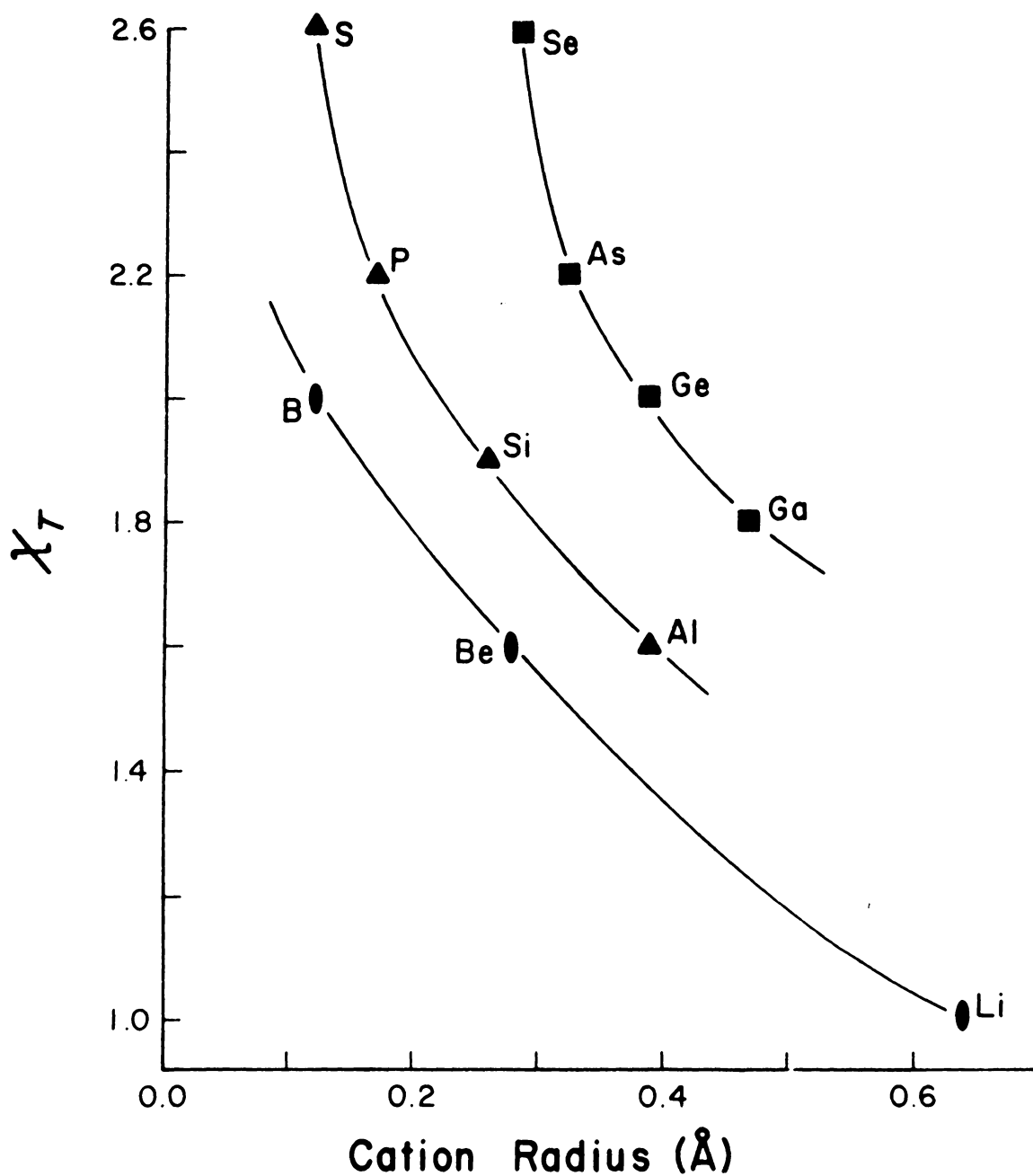


Figure 15: Electronegativity (Allred, 1961) as a function of effective ionic radius (Shannon and Prewitt, 1969; this study).

types. A further complication arises from the irregular correspondence between electronegativity and ionic sizes for transition elements. The fact that the ELDP ranges for V^{5+} , Cr^{6+} , and Mo^{6+} oxyanions are only slightly less than those for oxyanions of fourth period non-transition elements of nearly equal ionic size suggests that the same coulombic interactions between bonding electron concentrations may be effective in both cases.

Figure 17 reveals that "rattling," as defined previously, is not the limiting mechanism for bond-length distortions in oxyanions of transition metals. The range of tetrahedral bond lengths corresponding to the "no-rattle limit" is again indicated by the stippled bar. Comparison of this figure with Figure 11b shows that the BLDP ranges for oxyanions of Mo^{6+} , V^{5+} , and Cr^{6+} are all too large to be consistent with the "rattling" model developed for oxyanions of non-transition elements. This suggests the following possibilities: (1) Either the transition metal atoms are much more capable of penetrating the deformable oxygen atoms than are non-transition cations, or (2) the transition metal atoms themselves undergo greater polarization than non-transition cations. The results of these two alternatives would be the same in terms of maximum bond-length distortions. A third alternative yielding the same results is to postulate that the differences between bridging and non-bridging bond orders are larger for transition metal oxyanions than for those of non-transition cations of similar sizes. Even if bond order calculations supported this, the relationship between tetrahedral polymerization and bond-length distortion for the oxyanions of

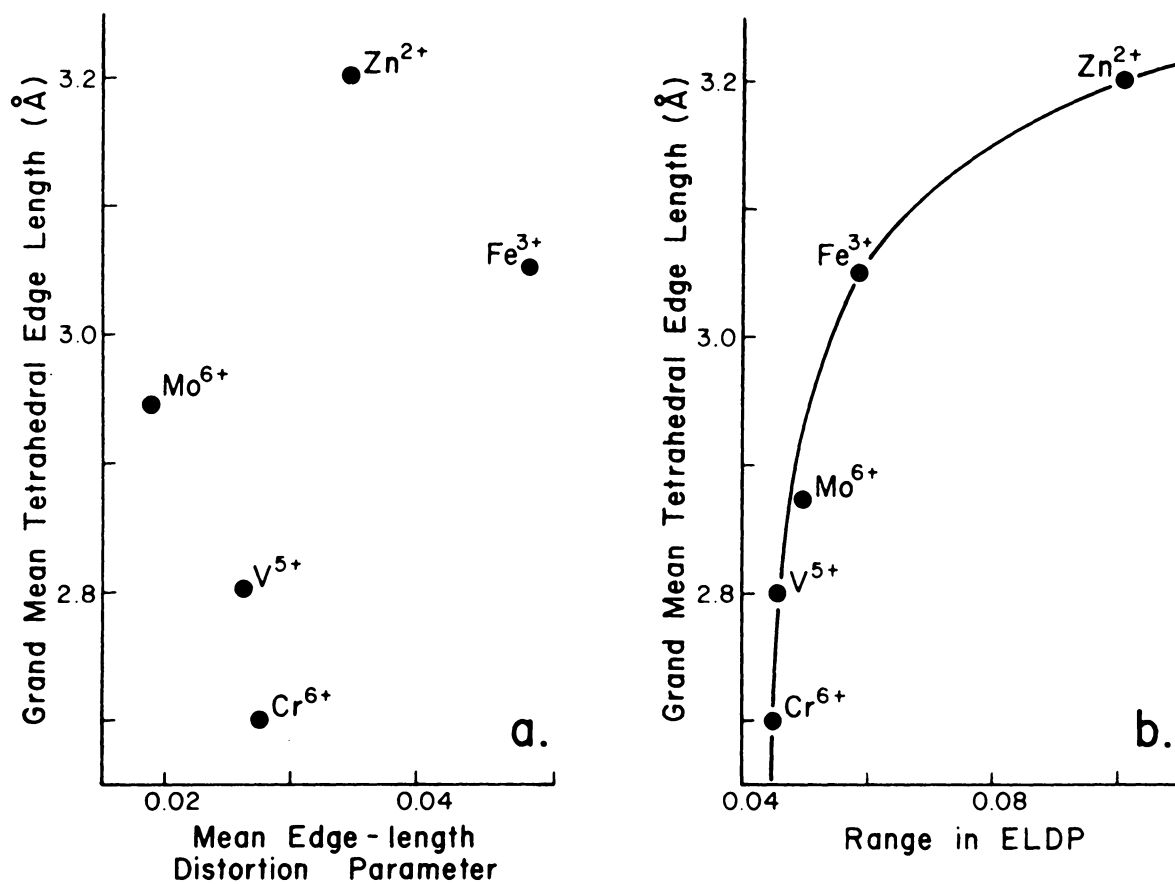


Figure 16: a. Grand mean tetrahedral edge lengths for five transition metal oxyanions *vs.* mean ELDP. b. Grand mean tetrahedral edge length *vs.* range in ELDP. Cation species is indicated by chemical symbol.

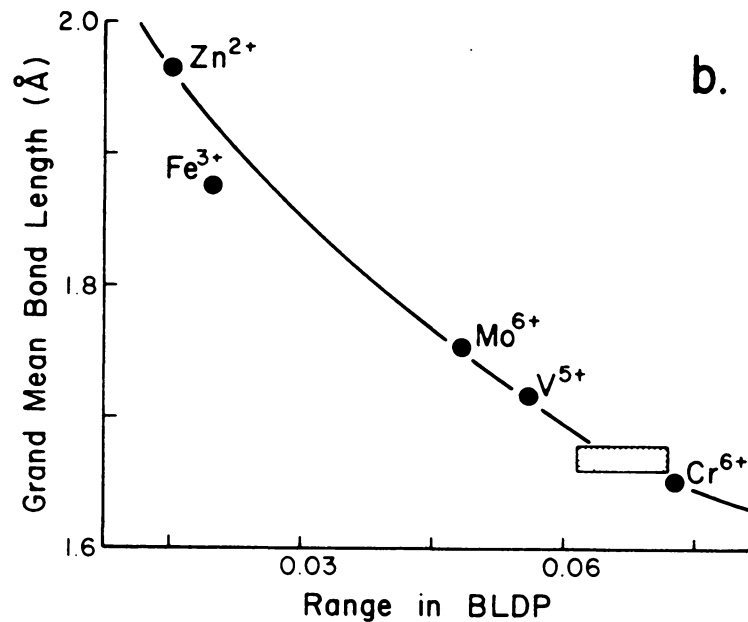
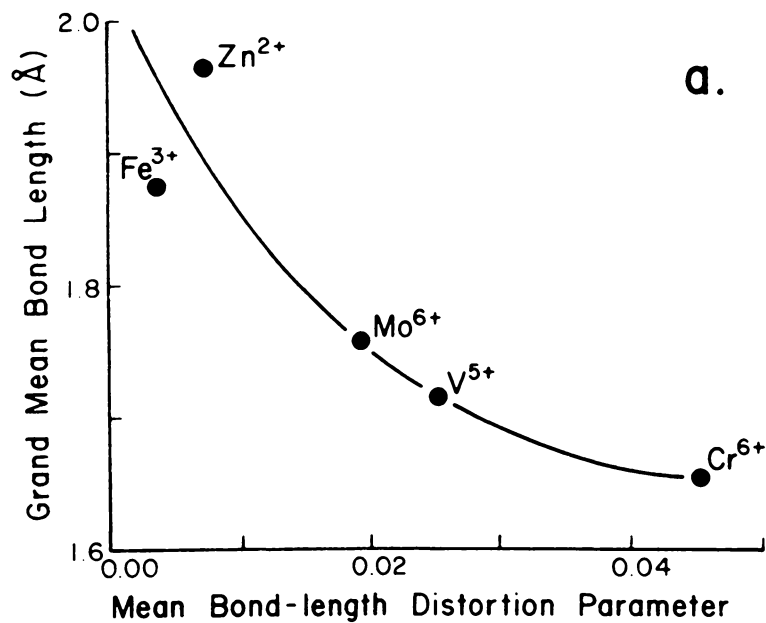


Figure 17: a. Grand mean tetrahedral bond length for five transition metal oxyanions *vs.* mean BLDP. b. Grand mean tetrahedral bond length *vs.* range in BLDP. Stippled bar represents the range of bond lengths corresponding to the "no-rattle limit" as defined in text. Cation species is indicated by chemical symbol.

transition elements does not appear to be strong.

CONCLUSION

The two distinct ways by which distortions in coordination polyhedra may be effected are (1) displacement of the central atom from a reference position within a polyhedron (*bond-length distortion*), and (2) displacement of the ligands from the apices of some reference polyhedron (*edge-length distortion*). It has been shown that, for tetrahedral coordination, the bond-length distortion parameter (BLDP) and edge-length distortion parameter (ELDP), respectively defined by equations (1) and (2), are linearly related to these two types of distortions. The several one-parameter methods which have been devised to characterize distortions are not sufficient to resolve the effects of both bond-length and edge-length distortions. The parameters used in this study of 489 tetrahedral oxyanions are similar to those of Baur (1974) but are designed to facilitate statistical testing.

For tetrahedral oxyanions of a given non-transition element the relative values of the distortion parameters depend upon the structural relationships between the tetrahedra and other coordination polyhedra. For tetrahedral oxyanions exhibiting little bond-length distortion (e.g., LiO_4^{7-} and GaO_4^{5-}), ELDP increases with the number of shared tetrahedral edges. For oxyanions which show little edge-length distortion (e.g., PO_4^{5-} and SO_4^{2-}), BLDP is related to the number of corners shared with other tetrahedra. Although the relationships for oxyanions such as SiO_4^{4-} , which exhibit fairly large ranges in both BLDP and ELDP, are not as straightforward, the same trends may be recognized. For the tetrahedral oxyanions of transition metals these structural trends

are not well-developed.

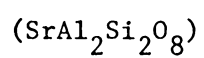
A detailed study of angular variations in the tetrahedral oxyanions of non-transition elements shows that the variations in bond angles are mainly a function of $T-O$ variations only for SO_4^{2-} tetrahedra. For the other types, $O-T-O$ angle variations are entirely or largely a function of $O\cdots O$ variations. With regard to transition metal oxyanions, those of V^{5+} , Cr^{6+} , and Mo^{6+} tend to have $O-T-O$ angles near 109.47° , while those of Fe^{3+} and Zn^{2+} behave much like oxyanions of non-transition elements. Baur's (1970) Rule 5 does not represent a generally adequate model for tetrahedral oxyanions.

An analysis of the maximum observed distortions has provided insight into the mechanisms by which these distortions are limited. For the oxyanions of non-transition elements, bond-length distortion appears to be limited by a phenomenon analogous to the "rattling" of the hard sphere model, although the data clearly indicate that the anions, at least, are not hard spheres. A rationale involving the relative bond orders of bridging and non-bridging bonds (Gillespie and Robinson, 1964) is also plausible, but relates more to the causes of bond-length distortion than to the factors which limit it. The maximum edge-length distortions appear to be limited chiefly by coulombic repulsions between bonding electron concentrations, with non-bonded (non-coulombic) repulsions becoming important at very small $O\cdots O$ separations. For transition metal oxyanions several complications render interpretations difficult. It appears that the same factors that limit edge-length distortions in the oxyanions of

non-transition elements may be effective here. The analysis of maximum bond-length distortions suggests that there is evidence for greater polarization of either the oxygen atoms or the cations (or both) in the oxyanions of transition metals than in those of the non-transition elements.

PART II

THE CRYSTAL STRUCTURE OF SLAWSONITE



INTRODUCTION

The structure of paracelsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$, $P2_1/a$), originally solved by Smith (1953), was refined by Craig, Louisnathan, and Gibbs (1973). Recently structures of several paracelsian analogs have been reported, in particular hurlbutite ($\text{CaBe}_2\text{P}_2\text{O}_8$; Lindbloom, Gibbs, and Ribbe, 1974) and synthetic $\text{SrGa}_2\text{Si}_2\text{O}_8$ ¹ and $\text{SrGa}_2\text{Ge}_2\text{O}_8$ (Phillips, Kroll, Pentinghaus, and Ribbe, 1975). Danburite ($\text{CaB}_2\text{Si}_2\text{O}_8$), which has paracelsian topology but a different T^{3+}/T^{4+} ordering scheme and space group ($Pnam$), was refined by Phillips, Gibbs, and Ribbe (1974). In addition, work is in progress on the paracelsian modifications of $\text{SrAl}_2\text{Ge}_2\text{O}_8$ (Kroll and Phillips, in preparation) and $\text{BaGa}_2\text{Ge}_2\text{O}_8$ (Calleri, pers. comm.). This study presents the structure of a new mineral, slawsonite ($\text{SrAl}_2\text{Si}_2\text{O}_8$), the Sr analog of paracelsian.

Barrer and Marshall (1964) synthesized pseudo-orthorhombic $\text{SrAl}_2\text{Si}_2\text{O}_8$ from gels in hydrothermal experiments. The lattice parameters determined by them are listed in Table 5. R.C. Erd, B.O. Nolf, and V.C. Smith (pers. comm.) have described natural slawsonite from metamorphosed limestones of the Triassic Martin Bridge Formation in Wallowa County, Oregon. Its cell dimensions and space group, $P2_1/a$, suggest that slawsonite is isomorphous with paracelsian (Table 5).

¹ $\text{SrGa}_2\text{Si}_2\text{O}_8$ has also been refined by Calleri and Gazzoni (Periodico di Mineralogia, XLIV, in press).

Table 5

Crystallographic data for slawsonite

	Barrer and Marshall (1964)	Erd, Nolf, and Smith (pers. comm.)	This study
a (Å)	8.91 ₀	8.895(1)*	8.888(2)
b (Å)	9.34 ₃	9.359(1)	9.344(2)
c (Å)	8.34 ₅	8.333(1)	8.326(3)
β (°)	~ 90	90.24(1)	90.33(2)
Vol. (Å ³)	-	693.7(1)	691.5

* e.s.d.'s, given in parentheses, refer

to last decimal place.

EXPERIMENTAL PROCEDURES

The crystal used for this structure refinement came from the type locality (Wallowa County, Oregon) and was provided by Dr. Richard C. Erd of the U.S. Geological Survey. It was a clear, flat triangular prism 62 μ m thick with sides measuring 140 $\times$ 217 $\times$ 155 μ m. The lattice parameters shown in Table 5 were determined by least-squares refinement of sixteen reflections measured with a fully-automated four-circle Picker diffractometer using Zr-filtered MoK α radiation. Electron microprobe analysis gave an Al:Si ratio of 1:1, within the limits of error. The only other cations detected in significant concentrations were Sr and Ca, accounting for 0.82 and 0.12 atoms, respectively, in the formula unit. Because of some uncertainty about the Sr-content of the "standard" used for microprobe analysis and because no substituents other than 0.04 weight percent Fe were detected, the values for Sr and Ca were scaled upward so that Sr + Ca = 1.0, giving an approximate formula of Sr_{0.87}Ca_{0.13}Al₂Si₂O₈.

Computer programs used during this study, as listed in the *World List of Crystallographic Computer Programs* (Third Edition), were DATALIB, DATASORT, OR XFLS3, and OR FFE3. For the refinement of the structure, 4168 symmetry-permitted intensities were collected from two equivalent quadrants. A θ -2 θ scanning rate of 1°/min was used and intensities were measured in the range $0.12 < \sin\theta/\lambda < 1.22$. Observed intensities were corrected for Lorentz-polarization effects and for absorption ($\mu_L = 93.4 \text{ cm}^{-1}$), and converted to F_{obs}^2 with the program DATALIB. These were weighted according to $1/\hat{\sigma}^2$, and the weighted values

for symmetry equivalent reflections were averaged using the program DATASORT, to give 1870 non-zero symmetry-independent observations.

The atomic coordinates of $\text{SrGa}_2\text{Si}_2\text{O}_8$ (Phillips *et al.*, 1975) were used as starting values in the least-squares refinement program OR XFLS3, and scattering factors for neutral atoms were employed (Doyle and Turner, 1968). Reflections for which $|F_{\text{obs}}|$ was less than $3\hat{\sigma}$ were omitted, and the remaining reflections were weighted according to $1/\hat{\sigma}^2$. An extinction correction was applied, and refinement with isotropic temperature factors yielded an unweighted residual of 0.050 ($wR = 0.055$) for 1617 reflections. With the introduction of anisotropic temperature factors the refinement converged to $R = 0.048$ ($wR = 0.053$). No significant correlations were noted among the parameters. The final fractional coordinates are shown in Table 6, while Table 7 gives the isotropic and anisotropic temperature factors. The important interatomic distances and bond angles (Table 8) were calculated with the computer program OR FFE3.

Table 6

Final atomic positional parameters

Atom	x	y	z
Sr	0.8902(1)*	0.4122(1)	0.2503(1)
T10	.2321(2)	.9249(2)	.9311(2)
T1m	.2405(2)	.9199(2)	.5605(2)
T20	.0595(2)	.2006(2)	.9440(2)
T2m	.0541(2)	.1944(2)	.5706(2)
O10	.1910(4)	.0934(4)	.0100(5)
O1m	.1875(4)	.0740(4)	.4937(5)
O20	.1192(4)	.3658(4)	.9458(5)
O2m	.1236(4)	.3699(4)	.5573(5)
O30	.9202(4)	.1919(4)	.0699(4)
O3m	.8979(4)	.1923(4)	.4399(5)
O4	.0092(5)	.1545(4)	.7662(5)
O5	.3139(4)	.9252(4)	.7407(5)

* e.s.d.'s, given in parentheses,

refer to last decimal place.

Table 7

Isotropic and anisotropic temperature factors

Atom	B ($\text{\AA}^2$)	Anisotropic temperature factors ($\times 10^4$)					
		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sr	0.66(1)*	30(1)	20(1)	29(1)	0(1)	0(1)	1(1)
T10	0.34(2)	9(2)	10(2)	12(2)	1(1)	0(1)	2(2)
T1m	0.31(2)	6(2)	9(1)	11(2)	0(1)	2(1)	0(1)
T20	0.27(2)	8(2)	6(1)	10(2)	-2(1)	0(1)	1(1)
T2m	0.30(2)	9(2)	7(2)	10(2)	-1(1)	1(1)	0(1)
O10	0.62(6)	21(4)	15(4)	22(5)	7(3)	3(4)	0(4)
O1m	0.67(6)	25(5)	10(4)	28(5)	8(4)	8(4)	5(4)
O20	0.48(6)	13(4)	7(4)	22(5)	-2(3)	-7(4)	3(3)
O2m	0.59(6)	17(5)	12(4)	20(5)	-1(3)	11(4)	-2(3)
O30	0.51(6)	13(4)	16(4)	15(5)	-2(3)	3(4)	-2(4)
O3m	0.63(6)	10(4)	16(4)	29(5)	0(3)	1(4)	4(4)
O4	0.89(6)	42(5)	27(4)	13(5)	-12(4)	0(4)	0(4)
O5	0.61(6)	12(4)	25(4)	17(5)	-6(4)	3(4)	2(4)

* e.s.d.'s, given in parentheses, refer to last

decimal place.

Table 8

Interatomic distances (Å) and angles (°)				
<i>T</i> -O		O•••O		O- <i>T</i> -O
<u>T10 tetrahedron</u>				
T10-O10	1.745(4)*	010-020	2.738(5)	102.8(2)
-020	1.757(4)	-030	2.922(5)	113.9(2)
-030	1.741(4)	-05	2.953(5)	115.4(2)
-05	1.749(4)	020-030	2.914(6)	112.8(2)
		-05	2.732(6)	102.4(2)
		030-05	<u>2.840(5)</u>	<u>108.9(2)</u>
Mean	1.748		2.850	109.4
<u>T1m tetrahedron</u>				
T1m-O1m	1.612(4)	01m-02m	2.579(5)	105.4(2)
-02m	1.629(4)	-03m	2.663(6)	111.1(2)
-03m	1.618(4)	-05	2.716(5)	113.6(2)
-05	1.633(4)	02m-03m	2.698(5)	112.4(2)
		-05	2.597(6)	105.5(2)
		03m-05	<u>2.642(5)</u>	<u>108.7(2)</u>
Mean	1.623		2.649	109.5
<u>T20 tetrahedron</u>				
T20-O10	1.634(4)	010-020	2.678(5)	110.2(2)
-020	1.631(4)	-030	2.628(5)	107.4(2)
-030	1.628(4)	-04	2.649(6)	109.9(2)
-04	1.602(4)	020-030	2.615(5)	106.8(2)
		-04	2.659(6)	110.6(2)
		030-04	<u>2.675(5)</u>	<u>111.8(2)</u>
Mean	1.624		2.651	109.5
<u>T2m tetrahedron</u>				
T2m-O1m	1.756(4)	01m-02m	2.871(5)	109.6(2)
-02m	1.757(4)	-03m	2.835(5)	107.5(2)
-03m	1.758(4)	-04	2.873(6)	111.4(2)
-04	1.720(4)	02m-03m	2.774(5)	104.2(2)
		-04	2.853(6)	110.2(2)
		03m-04	<u>2.909(6)</u>	<u>113.5(2)</u>
Mean	1.748		2.853	109.4

* e.s.d.'s, given in parentheses, refer to last decimal place.

Table 8, continued

<u>Sr-O distances</u>		<u>T-O-T angles</u>	
Sr-O10	2.662(4)	T10-O10-T20	125.2(2)
-O1m	2.723(4)	T1m-O1m-T2m	130.0(2)
-O20	2.641(4)	T10-O20-T20	123.1(2)
-O2m	2.594(4)	T1m-O2m-T2m	124.6(2)
-O30	2.562(4)	T10-O30-T20	128.5(2)
-O3m	2.591(4)	T1m-O3m-T2m	127.3(2)
-O5	2.635(4)	T20-O4-T2m	138.7(3)
		T10-O5-T1m	<u>131.9(2)</u>
Mean	2.630		128.7

DISCUSSION

Lattice parameters

The lattice parameters for five paracelsian analogs and danburite are listed in Table 9. The latter is topologically identical to paracelsian, but topochemically different: whereas paracelsian contains $T^{3+}-O-T^{4+}$ linkages but no $T^{3+}-O-T^{3+}$ or $T^{4+}-O-T^{4+}$ linkages, all three types occur in danburite. Figures 18 and 19 show the variations in lattice parameters with chemistry for these compounds, and as expected, they vary directly with both the mean $M-O$ and grand mean $T-O$ distances. It is obvious, however, that the sizes of the tetrahedra in the framework are more highly correlated with cell dimensions than are the effective sizes of the M cations. In fact, $SrGa_2Ge_2O_8$, with the largest framework, has larger cell dimensions than $BaAl_2Si_2O_8$, which contains the largest M cation.

It appears from Figure 18 that variations in lattice parameters with $\langle M-O \rangle$ may be better described by a non-linear relationship, although linearity has been assumed in computing the regression lines. This suggests that the ability of the paracelsian structure to adjust to accommodate the M cation diminishes with increasing cation size. The addition to Figure 18 of the forthcoming data for $BaGa_2Ge_2O_8$ (Calleri, pers. comm.) should help in determining whether these relationships are truly non-linear.

The Sr site

As in the other paracelsian structures and danburite, the strontium

Table 9

Crystallographic data for five paracelsian analogs and danburite

	Paracelsian $\text{BaAl}_2\text{Si}_2\text{O}_8$	Slawsonite $\text{SrAl}_2\text{Si}_2\text{O}_8$	(Synthetic) $\text{SrGa}_2\text{Si}_2\text{O}_9$	(Synthetic) $\text{SrGa}_2\text{Ge}_2\text{O}_8$	Hurlbutite $\text{CaBe}_2\text{P}_2\text{O}_8$	Danburite $\text{CaB}_2\text{Si}_2\text{O}_8$
a (Å)	9.065(3)*	8.888(2)	9.001(1)	9.206(1)	8.299(1)	8.038(3)
b (Å)	9.568(1)	9.344(2)	9.484(1)	9.660(1)	8.782(2)	8.752(5)
c (Å)	8.574(5)	8.326(3)	8.399(1)	8.581(1)	7.798(3)	7.730(3)
β (°)	90.00(1)	90.33(2)	90.68(1)	90.43(1)	90.5	90.0
$\langle M^{\text{VII}}-\text{O} \rangle$ (Å)	2.801	2.630	2.626	2.630	2.469	2.461
$\langle T^{3+}-\text{O} \rangle$ (Å)	1.747	1.748	1.823	1.825	---	1.474
$\langle T^{4+}-\text{O} \rangle$ (Å)	1.619	1.624	1.628	1.748	---	1.617
$\langle \langle T-\text{O} \rangle \rangle$ (Å)	1.683	1.686	1.726	1.786	1.577	1.546
Symbol	BASP	SASP	SGSP	SGGP	CBePP	CBSD

* e.s.d.'s, given in parentheses, refer to last decimal place.

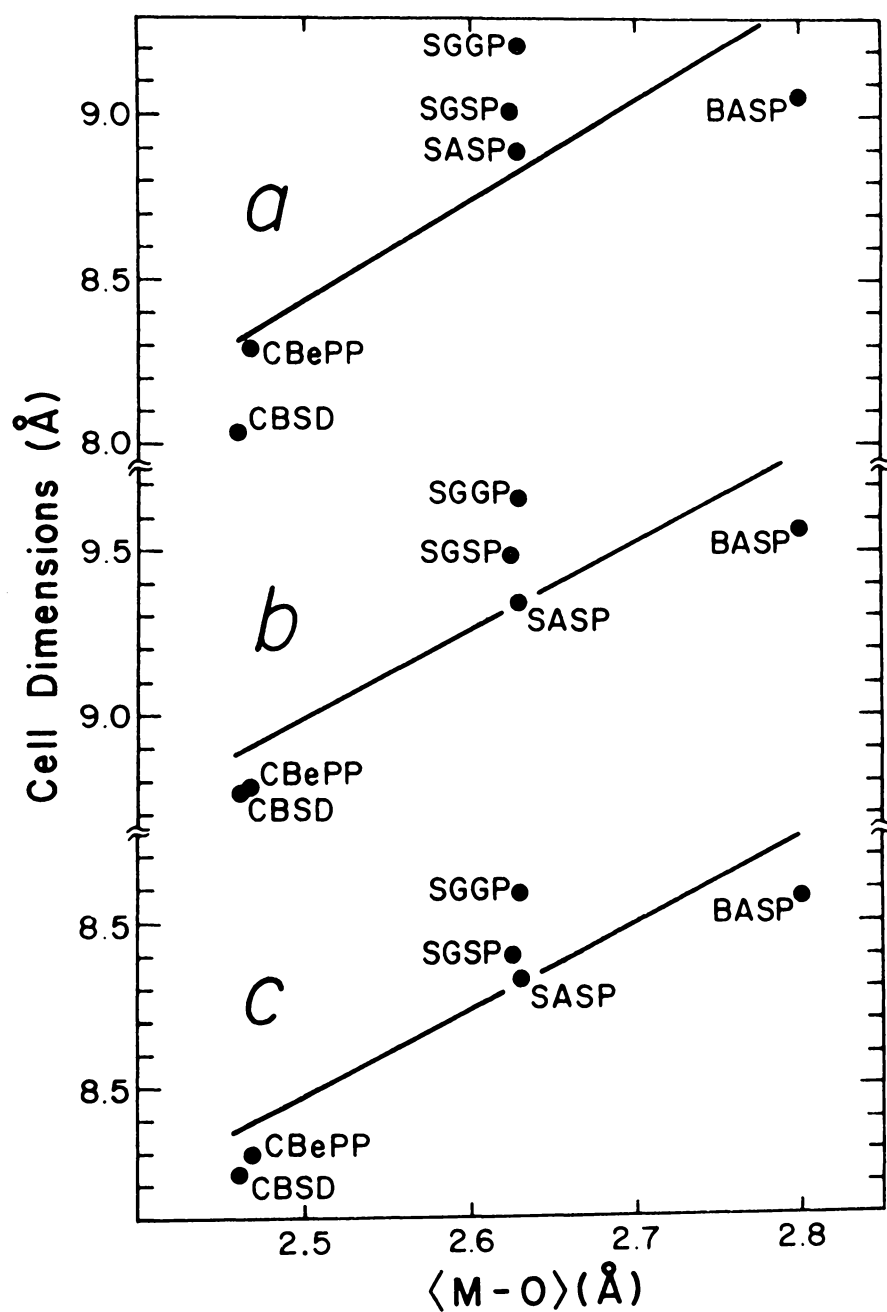


Figure 18: Variations in cell dimensions as a function of the mean $M-O$ bond lengths for paracelsian analogs and danburite. Structures to which symbols refer are listed in Table 9.

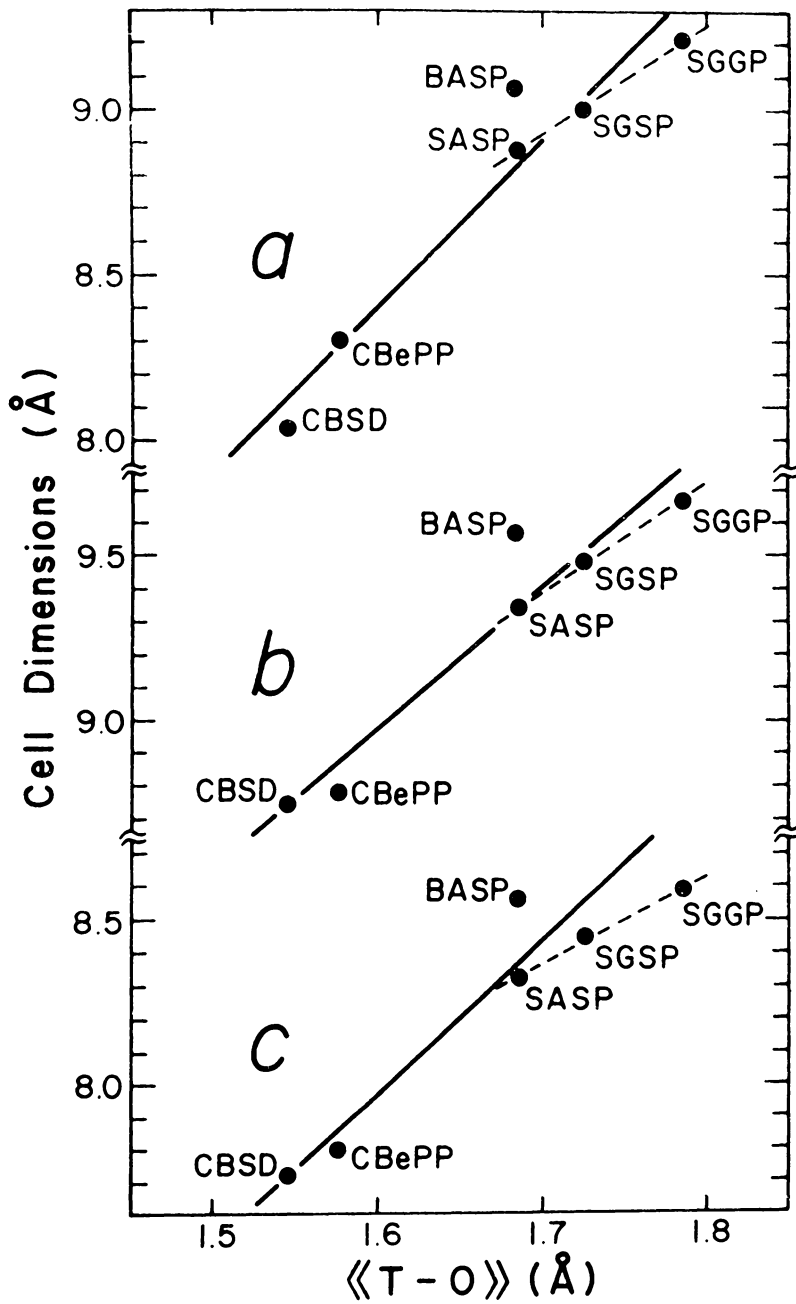


Figure 19: Cell dimensions *vs.* grand mean tetrahedral bond lengths for paracelsian analogs and danburite. Dashed lines connect data for strontium paracelsian analogs. Structures to which symbols refer are listed in Table 9.

atom in slawsonite may be considered seven-coordinated. Phillips *et al.* (1975) have established the sympathetic relationship between mean $T-O-T$ angles and $\langle M-O \rangle / \langle \langle T-O \rangle \rangle$ for paracelsian analogs and danburite (see Figure 20). By examining changes in individual $T-O-T$ angles Phillips and Kroll (in preparation) have shown that the tetrahedral framework collapses (i.e., individual $T-O-T$ angles decrease) with decreasing $\langle M-O \rangle$ and with increasing $\langle \langle T-O \rangle \rangle$, thus providing a physical interpretation for the parameter $\langle M-O \rangle / \langle \langle T-O \rangle \rangle$. In light of this it is interesting to note that the *mean* Sr-O distances for the three Sr paracelsian analogs are statistically identical despite the increase in framework size in the order $\text{SrAl}_2\text{Si}_2\text{O}_8 < \text{SrGa}_2\text{Si}_2\text{O}_8 < \text{SrGa}_2\text{Ge}_2\text{O}_8$. The *range* in individual Sr-O distances, however, increases in the same order, suggesting that the collapse of the framework about the Sr-site causes some Sr-O distances to increase while others decrease, leaving the mean essentially unchanged. The same is true for the Ca-O distances in danburite and hurlbutite, where the framework size increases from $\text{CaB}_2\text{Si}_2\text{O}_8$ to $\text{CaBe}_2\text{P}_2\text{O}_8$.

The tetrahedral framework

The mean Si-O and Al-O distances in fully-ordered anorthite have been generally used as standards for the estimation of order in framework aluminosilicates. The mean Al-O distances in slawsonite, paracelsian and anorthite are statistically identical (1.748Å, 1.747Å, and 1.747Å, respectively), whereas the mean Si-O distances are 1.624Å, 1.619Å, and 1.614Å, respectively. Phillips *et al.* (1975) found a mean Si-O distance of 1.628Å in $\text{SrGa}_2\text{Si}_2\text{O}_8$ and they attributed this increase

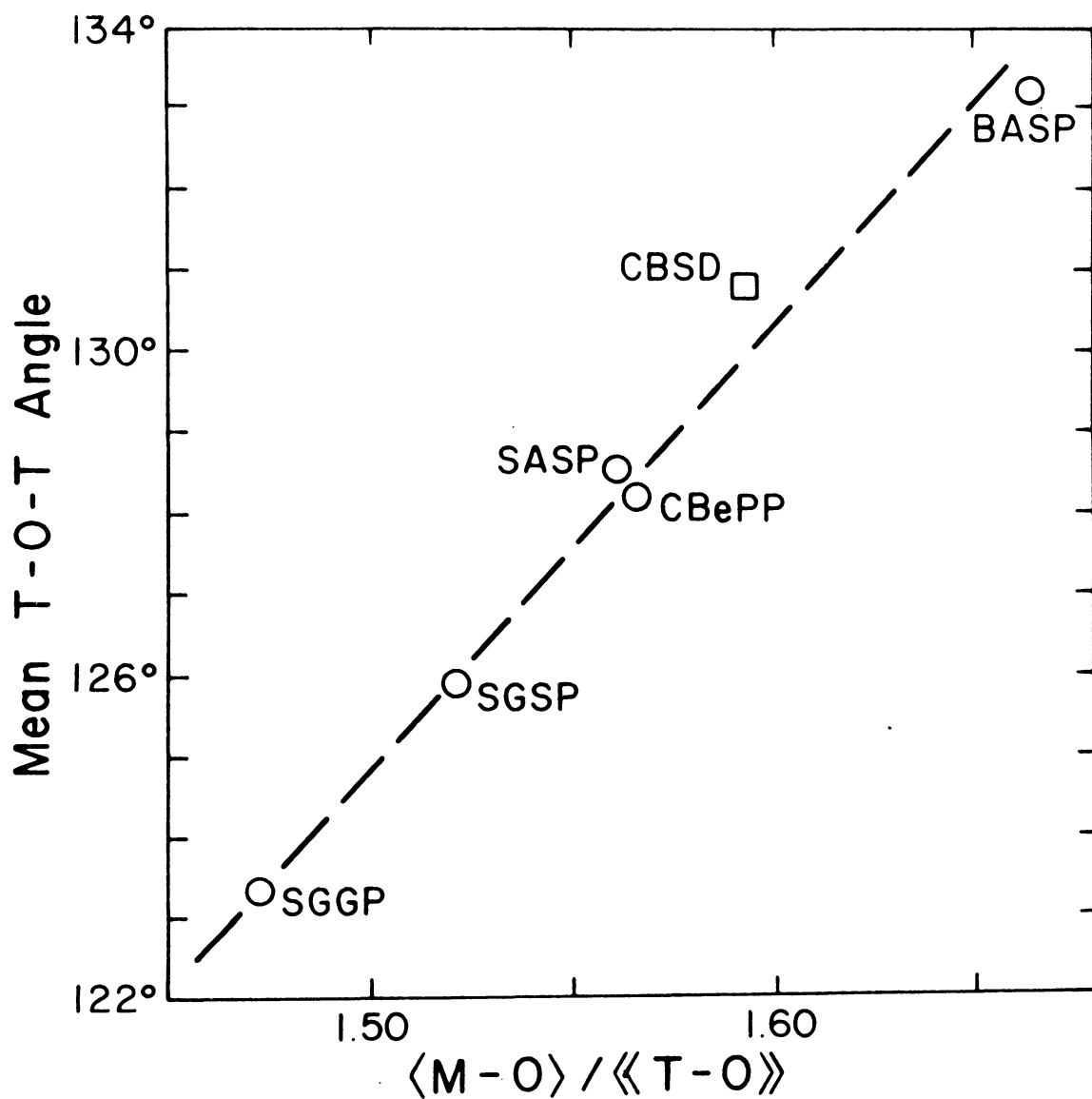


Figure 20: Mean $T-O-T$ angle as a function of mean $M-O$ and grand mean $T-O$ bond lengths for paracelsians and danburite. Symbols are listed in Table 9.

over $\langle \text{Si-O} \rangle$ in $\text{BaAl}_2\text{Si}_2\text{O}_8$ to inductive effects of the much larger Ga atoms. Because silicon and gallium possess quite different x-ray scattering characteristics, they were able to determine by site refinement techniques that $\text{SrGa}_2\text{Si}_2\text{O}_8$ is completely ordered. Since the mean Si-O distance in this paracelsian analog is $0.004\text{\AA}$ larger than that in slawsonite, it may be concluded with some confidence that slawsonite is also fully-ordered. Thus the significantly larger mean Si-O bond length in $\text{SrAl}_2\text{Si}_2\text{O}_8$ relative to $\text{BaAl}_2\text{Si}_2\text{O}_8$ suggests that the M cation may also be influential in determining the sizes of the tetrahedral sites. Certainly if "standard" mean T -O distances are to be useful for the estimation of order, they must be determined separately for each framework structure type and each combination of cations.

PART III

REFINEMENT OF THE CRYSTAL STRUCTURE OF CELSIAN

INTRODUCTION

The first x-ray study of celsian ($\text{BaAl}_2\text{Si}_2\text{O}_8$, symbol: Cn) by Taylor, Darbyshire, and Strunz (1934) showed it to be approximately isomorphous with the monoclinic K-feldspar orthoclase. Subsequently Gay (1956) found that single crystal photographs of celsian showed a set of very weak diffraction maxima with $h+k$ odd, l odd, indicating that celsian is body-centered and that the c -dimension of its unit cell is $\sim 14.4\text{\AA}$, approximately twice that of the $C2/m$ orthoclase. The choice of the unconventional space group $I2/c$ (cf. Figure 1, Chiari *et al.*, 1975) was made by Newnham and Megaw (1960) in order to preserve the axial orientation of celsian relative to orthoclase and other feldspars, some of which also have been given unconventional space groups (albite and microcline, $C\bar{1}$; bytownite, $I\bar{1}$).

Newnham and Megaw (1960) solved the structure of a celsian (approximate formula $\text{Ba}_{0.84}\text{K}_{0.18}\text{Al}_{1.90}\text{Si}_{2.11}\text{O}_8$) from Broken Hill, N.S.W., using intensities from five zero-layer Weissenberg photographs taken about the zones $[100]$, $[010]$, $[001]$, $[110]$, and $[111]$. They first determined the "average" structure, using only the strong 'a'-type reflections ($h+k$ even, l even) and refining in space group $C2/m$ with $c = 7.2\text{\AA}$, the Ba atom and one oxygen (O_A2) on the mirror plane, one oxygen (O_A1) on the two-fold axis through the origin, and the two tetrahedrally coordinated Al, Si "average" atoms (T_1 and T_2) and the other oxygens O_B , O_C , O_D in general positions. They continued the refinement in space group $I2/c$ by including the weak 'b' reflections ($h+k$ odd,

ℓ odd) and doubling the *c* cell edge. The Ba, O_A¹, and O_A² atoms were shifted slightly from special to general positions. The tetrahedral and oxygen sites were "split" and given a notation which has since been simplified to T₁O, T₁z, T₂O, T₂z; O_BO, O_Bz; O_CO, O_Cz; O_DO, O_Dz to indicate that they are related by a pseudo-*c*/2 translation in the doubled cell.¹

Newnham and Megaw found that the mean T-O bond lengths at T₁O and T₂z (1.639 and 1.635Å) and at T₂O and T₁z (1.712 and 1.717Å) indicated a highly ordered Al/Si distribution in celsian. In fact, since the Ba atom remained on the glide plane at *y* = 0.0000, it was evident that the weak 'b' reflections and the doubling of the *c* cell dimension resulted only from this ordering.

A recent refinement of a synthetic *I*2/*c* strontium feldspar (SrAl₂Si₂O₈, symbol: Srf) by Chiari, Calleri, Bruno, and Ribbe (1975) indicated that the smaller Sr cation was significantly shifted off the *c*-glide (*y* = 0.0020[1]). The mean T-O bond lengths (T₁O = 1.626; T₂z = 1.630; T₂O = 1.735; T₁z = 1.732Å), when compared to the grand mean Si-O bond length of 1.614Å and Al-O bond length of 1.747Å in ordered anorthite (Wainwright and Starkey, 1971) suggest ~10 percent Si in the Al-rich and ~10 percent Al in the Si-rich sites in Srf. By analogy there is ~25 percent Si in the Al-rich and ~17 percent Al in the Si-rich sites in the Broken Hill celsian, consistent with its

¹ This notation is modified somewhat and simplified from that suggested by Megaw (1956). It corresponds to that used by Chiari *et al.* (1975).

$\text{Cn}_{\sim 84}\text{Or}_{\sim 18}$ composition.

It is the purpose of this refinement to provide precise structural data for a nearly pure celsian, for comparison with other aluminosilicate feldspar-type compounds ($I2/c$ Srf and ordered $P\bar{1}$ anorthite) and with synthetic $\text{SrGa}_2\text{Si}_2\text{O}_8$ and $\text{BaGa}_2\text{Si}_2\text{O}_8$, both of which crystallize in space group $I2/c$ and have similar highly ordered framework structures (Calleri and Gazzoni, 1975). Table 10 contains the crystal data for these compounds.

Table 10

Crystal data for $M^{2+}T_2^{3+}T_2^{4+}O_8$ feldspar-type compounds

	Celsian ($Cn_{95}Or_{95}$)	Celsian ($Cn_{84}Or_{18}$)	$SrAl_2Si_2O_8$	$CaAl_2Si_2O_8$	$SrGa_2Si_2O_8$	$BaGa_2Si_2O_8$
Source, reference*	(1)	(2)	(3)	(4)	(5)	(6)
Space group	$I2/c$	$I2/c$	$I2/c$	$P/\bar{1}$	$I2/c$	$I2/c$
<i>a</i>	8.622(4)**	8.627	8.388(3)	8.173(1)	8.481(2)	8.727(5)
<i>b</i>	13.078(6)	13.045	12.974(4)	12.869(1)	13.142(2)	13.240(6)
<i>c</i>	14.411(8)	14.408	14.263(6)	14.165(1)	14.444(3)	14.608(6)
α	90	90	90	93.11(1)	90	90
β	115.09(2)	115.2	115.2(1)	115.91(1)	115.48(4)	115.00(6)
γ	90	90	90	91.26(1)	90	90
Volume	1471.6	1467.0	1404.4	1337.7	1453.3	1530.0

* (1) Jakobsberg, Sweden, this work; (2) Broken Hill, N.S.W., Newnham and Megaw (1960) -- standard errors not determined; (3) synthetic, Chiari *et al.* (1975); (4) Val Paseda, Italy, Wainwright and Starkey (1971); (5) synthetic, Calleri and Gazzoni (1975).

** e.s.d.'s, given in parentheses, refer to last decimal place.

EXPERIMENTAL METHODS

The crystal used in this study was a clear cleavage fragment ($60 \times 60 \times 70 \mu\text{m}$) from Jakobsberg, Sweden. It was provided by Mr. Timothy Grove from specimen #10062 of the Harvard Mineralogical Museum. Electron microprobe analysis indicated the approximate formula to be $\text{Ba}_{0.95}\text{K}_{0.05}\text{Al}_{1.95}\text{Si}_{2.05}\text{O}_8 (\text{Cn}_{.95}\text{Or}_{.5})$, which is similar to that of other celsians from the same locality studied by Gay and Roy (1968). The lattice parameters, listed in Table 10 with those of previously refined $M^{2+}_2T^{3+}_2T^{4+}_2\text{O}_8$ feldspar-type structures, were determined by least-squares refinement using 24 reflections measured on a fully-automated Picker four-circle diffractometer. They are within the range of those determined by Gay and Roy for other Jakobsberg celsians.

The computer programs used in this study, as listed in the *World List of Crystallographic Computer Programs* (Third Edition) were DATALIB, OR XFLS3, and OR FFE3. A total of 1054 intensities (557 'a' and 497 'b' reflections) were measured using Zr-filtered $\text{MoK}\alpha$ radiation in the range $0.1 < \sin\theta/\lambda < 1.2$ for 'a' reflections and $0.1 < \sin\theta/\lambda < 1.0$ for 'b' reflections; 'a' reflections were scanned at $1.0^\circ 2\theta/\text{min}$, and the weaker 'b' reflections at $0.25^\circ 2\theta/\text{min}$. In order to place the 'a' and 'b' reflections on the same scale, 20 weak 'a' reflections were measured at $0.25^\circ 2\theta/\text{min}$ and 20 strong 'b' reflections were measured at $1^\circ 2\theta/\text{min}$. The best-fit conversion factor for scaling the raw 'b' intensities to a $1^\circ 2\theta/\text{min}$ scan rate was then determined, and the 'b' F_{obs} were later multiplied by it during the refinement. Lorentz-

polarization and absorption corrections ($\mu_L = 61.3 \text{ cm}^{-1}$) were applied using the data reduction program DATLIB. Of the measured intensities 538 'a' and 331 'b' reflections had non-zero values of $|F_{\text{obs}}|$; of these, 528 and 272, respectively, were greater than $1\hat{\sigma}$ and were thus included in the refinement.

Refinement of the structure was carried out in space group $I2/c$ with the full-matrix least-squares computer program OR XFLS3. The final atomic coordinates of Newnham and Megaw (1960) were used as starting parameters. A test for extinction showed that no extinction correction was necessary. The $|F_{\text{obs}}|$ were weighted proportionally to $1/\hat{\sigma}^2$.

Using isotropic temperature factors for all atoms the refinement converged to an unweighted residual of 0.049 ($wR = 0.052$). Upon attempting a full anisotropic refinement, the R-factor dropped to 0.037, but the thermal parameters for O_A became non-positive definite. Careful examination of the data disclosed a single obviously erroneous 'b' reflection (077; $|F_{\text{obs}}| = 42$, $F_{\text{calc}} = 3$). Removal of this reflection permitted full anisotropic refinement. The final unweighted residual for reflections with $|F_{\text{obs}}| > 1\hat{\sigma}$ was 0.034 ($wR = 0.037$). The inclusion of all 869 non-zero intensities yielded $R = 0.037$ ($wR = 0.045$).

Atomic coordinates, temperature factors, and r.m.s. components of thermal displacement with thermal ellipsoid orientations are listed in Tables 11 and 12. Table 13 contains the important interatomic distances and angles calculated using the crystallographic function and error

program OR FFE3. It is worth noting that the removal of the erroneous 'b' reflection mentioned above had a marked effect on the calculated interatomic distances. The calculated $\langle \text{Si-O} \rangle$ increased and $\langle \text{Al-O} \rangle$ decreased by $0.013\text{\AA}$, while the e.s.d.'s of all distances decreased by approximately 30 percent.

Table 11

Fractional coordinates

Atom	x	y	z
Ba	0.2827(1)*	0.0000(1)	0.0653(0)
T ₁ O	.0096(3)	.1820(2)	.1103(2)
T ₁ z	.0076(3)	.1830(2)	.6148(2)
T ₂ O	.7054(4)	.1214(2)	.1730(2)
T ₂ z	.7019(3)	.1163(2)	.6743(2)
O _A 1	.0005(9)	.1377(4)	-.0002(5)
O _A 2	.6206(7)	-.0003(5)	.1438(4)
O _B 0	.8349(8)	.1368(5)	.1119(5)
O _B z	.8198(8)	.1370(5)	.6136(5)
O _C 0	.0220(8)	.3062(5)	.1210(5)
O _C z	.0293(8)	.3120(5)	.6312(5)
O _D 0	.1836(8)	.1296(5)	.1958(5)
O _D z	.1900(8)	.1231(5)	.7017(5)

* e.s.d.'s, given in parentheses,

refer to last decimal place.

Table 12

Isotropic and anisotropic temperature factors

Atom	B(Å)	Anisotropic temperature factors ($\times 10^4$)					
		β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	0.99(1)*	28(1)	14(1)	19(1)	-1(1)	7(1)	-1(1)
T ₁ O	0.70(5)	28(5)	9(2)	12(2)	-1(3)	8(2)	-1(2)
T ₁ z	0.49(5)	13(5)	7(2)	8(2)	-4(3)	2(3)	0(2)
T ₂ O	0.51(5)	22(5)	4(2)	9(2)	3(3)	5(3)	1(2)
T ₂ z	0.54(5)	16(4)	7(2)	10(2)	-1(3)	4(2)	1(2)
O _A 1	0.70(10)	47(9)	5(3)	8(3)	-5(7)	6(5)	0(4)
O _A 2	0.84(10)	31(9)	2(3)	22(4)	8(6)	5(5)	4(4)
O _B 0	1.40(13)	64(14)	15(4)	27(5)	-11(6)	22(7)	-2(4)
O _B z	1.04(12)	39(12)	9(4)	16(4)	4(6)	4(6)	-1(3)
O _C 0	1.21(13)	55(13)	9(4)	22(5)	-3(6)	12(7)	1(4)
O _C z	1.08(12)	24(12)	19(4)	22(4)	-1(6)	16(6)	4(4)
O _D 0	1.13(12)	38(12)	19(4)	17(4)	-2(6)	6(6)	-3(4)
O _D z	1.14(12)	41(12)	22(5)	16(5)	8(6)	12(6)	3(4)

r.m.s. components of thermal displacement along principal axes (r) and thermal ellipsoid orientation for Ba

r	r.m.s. displacement	Angle (°) with respect to		
		a	b	c
1	0.093(2)	27(3)	84(5)	89(2)
2	0.109(2)	81(4)	169(4)	99(4)
3	0.133(1)	115(2)	99(4)	9(4)

* e.s.d.'s, given in parentheses, refer to last decimal place.

Table 13

Interatomic distances (Å) and angles (°)				
<i>T</i> -O distances			O-O distances	O- <i>T</i> -O angles
<u>T₁O tetrahedron</u>				
T ₁ O-O _A 1	1.664(6)*	O _A 1-O _B O	2.570(8)	102.7(3)
-O _B O	1.628(7)	-O _C O	2.768(8)	114.4(3)
-O _C O	1.630(7)	-O _D O	2.589(9)	103.4(3)
-O _D O	1.634(7)	O _B O-O _C O	2.710(8)	112.6(3)
		-O _D O	2.725(9)	113.3(4)
		O _C O-O _D O	2.676(9)	110.1(4)
Mean	1.639		2.673	109.4
<u>T₁z tetrahedron</u>				
T ₁ z-O _A 1	1.727(6)	O _A 1-O _B z	2.686(8)	102.4(3)
-O _B z	1.721(7)	-O _C z	2.900(8)	115.5(3)
-O _C z	1.701(7)	-O _D z	2.669(9)	101.1(3)
-O _D z	1.728(7)	O _B z-O _C z	2.859(8)	113.3(3)
		-O _D z	2.898(8)	114.3(3)
		O _C z-O _D z	2.804(9)	109.6(3)
Mean	1.719		2.803	109.4
<u>T₂O tetrahedron</u>				
T ₂ O-O _A 2	1.728(7)	O _A 2-O _B O	2.749(9)	106.5(3)
-O _B O	1.702(6)	-O _C O	2.654(8)	100.7(3)
-O _C O	1.719(7)	-O _D O	2.788(9)	107.8(3)
-O _D O	1.722(7)	O _B O-O _C O	2.856(8)	113.2(3)
		-O _D O	2.843(8)	112.3(3)
		O _C O-O _D O	2.904(9)	115.1(3)
Mean	1.718		2.799	109.3

* e.s.d.'s, given in parentheses, refer to last decimal place.

Table 13: continued

<i>T</i> -O distances		O-O distances		O- <i>T</i> -O angles
<u>T₂z tetrahedron</u>				
T ₂ ^z -O _A ²	1.650(7)	O _A ² -O _B ^z	2.639(9)	107.6(3)
-O _B ^z	1.621(6)	-O _C ^z	2.561(8)	102.1(3)
-O _C ^z	1.643(7)	-O _D ^z	2.668(9)	108.9(3)
-O _D ^z	1.630(7)	O _B ^z -O _C ^z	2.707(7)	112.0(3)
		-O _D ^z	2.706(8)	112.6(3)
		O _C ^z -O _D ^z	2.727(9)	112.8(3)
Mean	1.636		2.668	109.3
<u>Ba polyhedron</u>		<u>T-O-T angles</u>		
Ba-O _A ²	2.641(5)	T ₁ O-O _A ¹ -T ₁ ^z	139.6(3)	
-O _A ¹	2.847(6)	T ₂ O-O _A ² -T ₂ ^z	133.9(3)	
-O _A ¹	2.854(6)	T ₁ O-O _B ⁰ -T ₂ ⁰	149.9(5)	
-O _D ^z	2.903(6)	T ₁ ^z -O _B ^z -T ₂ ^z	148.9(4)	
-O _B ⁰	2.916(6)	T ₁ O-O _C ⁰ -T ₂ ⁰	127.0(4)	
-O _D ⁰	2.924(7)	T ₁ ^z -O _C ^z -T ₂ ^z	130.3(4)	
-O _B ^z	2.949(6)	T ₁ O-O _D ⁰ -T ₂ ⁰	139.4(4)	
-O _C ^z	3.124(6)	T ₁ ^z -O _D ^z -T ₂ ^z	137.8(4)	
-O _C ⁰	3.150(7)			
Mean	2.862 (CN=7)		138.4	
	2.923 (CN=9)			

DISCUSSION

The results of this structure refinement are surprisingly similar to those obtained for $\text{Cn}_{\sim 84}\text{Or}_{\sim 18}$ by Newnham and Megaw (1960), particularly with regard to the tetrahedral $\text{O}\cdots\text{O}$ distances, $\text{O}-T-\text{O}$ angles, and mean $T-\text{O}$ and $\text{Ba},\text{K}-\text{O}$ bond lengths. Only for $T_2\text{O}$ do the corresponding $\langle T-\text{O} \rangle$ distances in the two structures differ by more than $0.002\text{\AA}$. Despite the difference in chemical composition the mean $\text{Ba},\text{K}-\text{O}$ distances are also statistically identical, whether the M -site is considered 7- or 9-coordinated. As in $\text{Cn}_{\sim 84}\text{Or}_{\sim 18}$ the Ba,K and O_2 atoms lie statistically on the c -glide and O_1 is on the pseudo-diad axis. Thus the intensities of the 'b' reflections are due entirely to tetrahedral ordering.

Ordering in the tetrahedral sites

In anorthite, which has served as a standard for the determination of ordering in aluminosilicate feldspars, the $\text{Al}:\text{Si}$ ratio is 1:1 and every oxygen atom forms a bridge between an AlO_4 and an SiO_4 tetrahedron. The ordering scheme in celsian does not appear to be as straightforward. In both $\text{Cn}_{\sim 84}\text{Or}_{\sim 18}$ and $\text{Cn}_{\sim 95}\text{Or}_{\sim 5}$ some degree of disorder is inevitable since the $\text{Al}:\text{Si}$ ratios are 1.84:2.16 and 1.95:2.05, respectively. Even after the silicon atoms in excess of 2.00 in the formula are assigned to the Al sites, the mean $T-\text{O}$ bond lengths, when compared to those in anorthite (Wainwright and Starkey, 1971), indicate the presence of an additional ~ 0.35 silicon atoms in the Al sites and the same amount of Al in the Si sites of both structures. There appears to be no obvious reason to expect Al/Si disorder beyond that due to the Or

content, and it is particularly surprising that the amount of this "excess" disorder is the same in two such chemically different celsians.

Two synthetic compounds containing Ga and Si in a 1:1 ratio have been refined by Calleri and Gazzoni (1975), and one of them, $\text{SrGa}_2\text{Si}_2\text{O}_8$, has mean Si-O and Ga-O distances of 1.614 and 1.821 Å, respectively, clearly indicating complete order in the tetrahedral framework. By contrast the mean Si-O and Ga-O distances in $\text{BaGa}_2\text{Si}_2\text{O}_8$ are 1.634 Å and 1.805 Å, respectively, strongly suggesting partial Ga/Si disorder. In 1962 Megaw, Kempster, and Radoslovich pointed out that it is statistically invalid to base conclusions about ordering on mean bond length differences which are of the same order of magnitude as the r.m.s. deviations of individual bond lengths from those means. Because the differences between corresponding mean bond lengths in the two gallosilicates are approximately equal to the r.m.s. values for bond length deviations (~ 0.02 Å), and because the temperature factors of the tetrahedral atoms are smaller than those in anorthite (Wainwright and Starkey, 1971) and similar to each other, Calleri and Gazzoni have concluded that the postulate of disorder in their $\text{BaGa}_2\text{Si}_2\text{O}_8$ is unnecessary. At least three circumstances mitigate against their conclusion. First, with one exception the temperature factors for the T-atoms of $\text{Cn}_{95}\text{Or}_{5}$, which must necessarily be partially disordered due to its composition, are also lower than any of those for tetrahedral sites in anorthite and are similar to each other; that of T_1O is slightly higher than those in anorthite. Second, $\langle\text{Si-O}\rangle$ increases from $\text{SrGa}_2\text{Si}_2\text{O}_8$ to $\text{BaGa}_2\text{Si}_2\text{O}_8$ by about the same amount that $\langle\text{Ga-O}\rangle$

decreases, a highly fortuitous circumstance if $\text{BaGa}_2\text{Si}_2\text{O}_8$ is not partially disordered. Third, Phillips and Kroll (pers. comm.) have completed the refinement of another synthetic $\text{BaGa}_2\text{Si}_2\text{O}_8$ in which the $\langle\text{Si-O}\rangle$ distances are shorter and the $\langle\text{Ga-O}\rangle$ distances are longer than in the specimen of Calleri and Gazzoni. Statistical theory notwithstanding, it would seem reasonable to postulate ~ 10 percent disorder in this structure. A similar degree of disorder was observed in one synthetic $\text{SrAl}_2\text{Si}_2\text{O}_8$ (Chiari *et al.*, 1975), but another synthesized by Pentinghaus and investigated by Kroll and Phillips (pers. comm.) shows weak 'c' ($h+k$ even, l odd) and 'd' ($h+k$ odd, l even) reflections indicative of a primitive space group and (possibly) complete Al/Si order. This specimen would be analogous to anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$, which has always proven to be completely ordered (Megaw *et al.*, 1962; Wainwright and Starkey, 1971; J.R. Smyth, pers. comm.).

Unless an anti-phase domain structure similar to that postulated for bytownite and transitional anorthite occurs in the $\text{SrAl}_2\text{Si}_2\text{O}_8$ of Chiari *et al.* (1975) or these two celsian structures, there is no obvious rationalization of their partial disorder. Lacking any direct crystallographic evidence for a domain texture, it must be concluded that the nearly sacrosanct Al-avoidance principle so clearly applicable to plagioclase feldspars is not operative in these compounds, or by extension, in $\text{BaGa}_2\text{Si}_2\text{O}_8$.

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APPENDIX A

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** ** ** ** ** ** ** 
*
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* *
* * DISTORT * *
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DISTORT IS A FORTRAN PROGRAM WRITTEN BY CANA T. GRIFFEN. IT PROVIDES A COMPLETE DISTORTION ANALYSIS FOR EACH TETRAHEDRON FOR WHICH INPUT DATA IS SUPPLIED, AS WELL AS A STATISTICAL ANALYSIS OF THE DATA AND PLOTS ON THE CALCOMP PLOTTER. DESCRIPTIONS OF EACH SUBROUTINE ARE FOUND IN THE RESPECTIVE SUBPROGRAMS THEMSELVES.

THE REQUIRED INPUT CARDS ARE PREPARED AS FOLLOWS:

CARD ONE - INTEGER VALUES FOR CCDE, NOPRNT, M, LIST, AND MORPLT,
RIGHT-JUSTIFIED IN COLUMNS 1-3, 4-6, 7-9, 10-12, AND
13-15.

THE VALUE OF CGDE DETERMINES THE TYPES OF PLOTS
OBTAINED, AS FOLLOWS:

CCODE 0 - NO PLOTS DESIRED

CCODE 1 - PLOT 1 = BOND LENGTH DIST. VS DIST. FROM CENT.

CCDE 2 - PLOT 2 = EDGE LENGTH DIST. VS AVG. OXY. DISP.

CCDE 3 - PLOT 3 = BOND LENGTH DIST. VS EDGE LENGTH DIS.

CODE 4 - PLOT 1 AND PLOT 2

C CODE 5 - PLOT 1 AND PLOT 3
C CCDE 6 - PLOT 2 AND PLOT 3
C CCDE 7 - PLOT 1, PLOT 2, AND PLOT 3
C

C NOPRNT IS A PRINT SUPPRESSION PARAMETER. IF NOPRNT = 0
C THE COMPLETE DISTORTION ANALYSIS IS PRINTED, REQUIRING
C ONE SHEET OF OUTPUT PER TETRAHEDRON. IF NOPRNT = 1,
C THE DISTORTION ANALYSIS FOR EACH TETRAHEDRON IS OMIT-
C TED. IF NOPRNT = 2, AN ABBREVIATED DISTORTION ANALYSIS
C IS PRINTED FOR EACH TETRAHEDRON. REGARDLESS OF THE
C VALUE OF NOPRNT, THE STATISTICAL ANALYSIS OF THE DATA
C IS PRINTED (AS LONG AS THE INPUT DATA CONSISTS OF AT
C LEAST THREE TETRAHEDRA), AND PLOTS MAY BE MADE AS
C DESIRED.
C

C THE VALUE OF M DETERMINES THE NUMBER OF SEPARATE PLOTS
C OF TYPE 3 WHICH WILL BE MADE, ONE FOR EACH DIFFERENT
C SPECIES OF TETRAHEDRAL ATOM SPECIFIED ON CARD 2; IF
C M = 0 AND A PLOT OF TYPE 3 IS SPECIFIED, THEN A SINGLE
C PLOT 3 WILL BE MADE WITH ALL TETRAHEDRA INCLUDED.
C

C IF A SEQUENTIAL LISTING OF THE TITLE INFORMATION AND
C ASSOCIATED CATION FOR EACH TETRAHEDRON IS DESIRED,
C LIST MUST EQUAL 1. OTHERWISE, NO SUCH LISTING WILL BE
C PRINTED.
C

C IF MORPLT IS NON-ZERO, PLOTS OF BLDP VS. MEAN BOND
C LENGTH AND ELDP VS. MEAN EDGE LENGTH WILL BE MADE FOR
C EACH SPECIES OF TETRAHEDRALLY-COORDINATED ATOM.
C

C CARD TWO - USED ONLY IF M ON CARD ONE IS GIVEN A NON-ZERO VALUE.
C THIS CARD CONTAINS THE CHEMICAL ELEMENT SYMBOLS FOR THE

C M DIFFERENT TETRAHEDRALLY-COORDINATED ATOMIC SPECIES
 C WHICH THE USER DESIRES TO PLOT ON M SEPARATE PLOTS OF
 C TYPE THREE. THE FORMAT IS 20A4; I.E., THE ELEMENT
 C SYMBOLS ARE PUNCHED IN COLUMNS 1-4, 5-8, 9-12, ETC.,
 C BEGINNING IN THE LEFT-MOST COLUMN IN EACH BLOCK. UP TO
 C TWENTY DIFFERENT TYPE 3 PLOTS MAY BE MADE IF SUFFICIENT
 C PLOTTER TIME IS SPECIFIED IN THE JCL. IF M = 0, THIS
 C CARD MUST BE OMITTED ALTOGETHER.

C CARD THREE - THIS CARD CONTAINS ANY IDENTIFYING ALPHANUMERIC
 C INFORMATION WHICH THE USER DESIRES IN COLUMNS 1 THROUGH
 C 48. COLUMNS 50 AND 51 CONTAIN THE CHEMICAL SYMBOL FOR
 C THE TETRAHEDRALLY COORDINATED ATOM. (IF THE SYMBOL
 C CONSISTS OF ONLY ONE LETTER, IT IS PUNCHED IN COLUMN
 C 50.) THE CHEMICAL SYMBOLS PERMITTED BY THE PROGRAM ARE
 C AL, AS, B, BE, CR, CU, FE, GA, GE, LI, MN, MO, P, S,
 C SE, SI, TI, V, W, AND ZN.

C CARD FOUR - THIS CARD CONTAINS THE BOND LENGTHS AND ANGLES FOR A
 C TETRAHEDRON. THESE MUST BE PUNCHED IN THE FOLLOWING
 C SEQUENCE:

C T-C(1) BOND LENGTH
 C T-C(2) BOND LENGTH
 C T-O(3) BOND LENGTH
 C T-O(4) BOND LENGTH
 C C(1)-T-O(2) ANGLE
 C C(1)-T-O(3) ANGLE
 C C(1)-T-O(4) ANGLE
 C C(2)-T-C(3) ANGLE
 C C(2)-T-C(4) ANGLE

C
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C
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C
C
C

THE FORMAT IS 9(F6.4); I.E., THE DATA IS PUNCHED IN
COLUMNS 1-6, 7-12, . . . ,49-54. NUMBERING OF THE
OXYGEN ATOMS WITHIN A GIVEN TETRAHEDRON IS ARBITRARY.

CARDS THREE AND FOUR ARE REPEATED ONCE FOR EACH TETRAHEDRON.
THE PROGRAM IS PRESENTLY DIMENSIONED TO ACCOMMODATE UP TO SIX
HUNDRED TETRAHEDRA.

```

REAL SIGTO(600),DFGC(600),SIGLIG(600),DISPID(600)
REAL ST(600),DF(600),SL(600),DI(600)
REAL BLN(600),EGL(600),SIT(600),SIL(600)
REAL CATCN(600),TYPE(600),NAME(600,12),TITLE(12)
REAL CHRS(20)
REAL BL(600),EG(600),BOND(600),EDGE(600)
INTEGER CODE
REAL SUMTO(20),SUMOO(20),SUMSIG(20),SUMSGO(20),MEANTO(20),
1  MEANOC(20),MEANSO(20),MEANSL(20)
REAL TJ(20)
INTEGER JJ(20)
COMMON/PASS/CO12,OO13,OO14,OO23,OO24,OO34,AVTO,AVOO
COMMON/TEST/CORCO,CODET,SSREG,SSE,MSE,TZERO,SLOPE,YNTRCP
COMMON/PRINT/NOPRNT,ATOM,TITLE
DATA CHRS/'LI ','BE ','B ','AL ','SI ','P ','S ','GA ','
1'GE ','AS ','SE ','TI ','V ','CR ','MN ','FE ','CU ','ZN
2  ','MO ','W ' /
1 FORMAT(5I3)
2 FORMAT('1','LEAST SQUARES REGRESSION AND STATISTICAL ANALYSES',
1/,'+',',',
2' ','FOR A REGRESSION EQUATION OF THE FORM:',//,' ',
315X, '(DISTANCE OF THE TETRAHEDRAL CATION FROM THE CIRCUMCENT
4ER) = A + B*(BOND-LENGTH DISTORTION PARAMETER)',//,' ',15X,'THE SL

```

```

      SOPE IS ',F5.3, ', AND THE INTERCEPT IS ',F6.3,///,' ', 'THE COEFF
      6ICIENT OF DETERMINATION IS ', F5.3,///,' ', 'THE CORRELATION COEFFIC
      7IENT IS ',F5.3)
3  FCRMAT('0','REGRESSION SUM OF SQUARES = ',F11.8,///,' ', 'RESIDUAL
  1SUM OF SQUARES = ',F11.8,///,' ', 'MEAN SQUARE ERROR = ',F11.8,///,
  2' ', 'FOR THE TEST OF THE NULL HYPCTHESIS THAT THE SLOPE IS ZERO, |
  3T| = ',F7.3)
4  FCRMAT('1')
5  FCRMAT('0',////////,' ', 'FOR A REGRESSION EQUATION OF THE FORM:',//,
  1' ',15X,'(AVERAGE DISPLACEMENT OF OXYGENS FROM IDEAL ARRAY) = A +
  2B*(EDGE-LENGTH DISTORTION PARAMETER)',//,' ',15X,'THE SLOPE IS',F6
  3.3,' ', AND THE INTERCEPT IS ',F6.3,///,' ', 'THE COEFFICIENT OF DET
  4ERMINATION IS ',F5.3,///,' ', 'THE CORRELATION COEFFICIENT IS ',F5.3
  5)
6  FORMAT('0','REGRESSION SUM OF SQUARES = ',F11.8,///,' ', 'RESIDUAL S
  1UM OF SQUARES = ',F11.8,///,' ', 'MEAN SQUARE ERROR = ',F11.8,///,' '
  2,'FOR THE TEST OF THE NULL HYPCTHESIS THAT THE SLOPE IS ZERO, |T|
  3= ',F7.3)
7  FORMAT('0','THE NUMBER OF DEGREES OF FREEDOM IS ',13)
8  FORMAT(20A4)
9  FORMAT('1','A SEQUENTIAL LIST OF MINERALS/COMPOUNDS USED IN THIS C
  1ALCULATION FOLLOWS:',///)
10 FCRMAT(' ',5X,12A4,10X,1A4)
850 FORMAT('1',12X,'MEAN BOND LENGTH',10X,'MEAN EDGE LENGTH',14X,
  1 'MEAN BLDP',14X,'MEAN ELDP',//)
851 FCRMAT('0',A4,13X,F5.3,21X,F5.3,22X,F6.4,18X,F6.4)
852 FORMAT('0',A4,13X,'NONE FOUND IN INPUT DATA')

```

C

```

      READ(5,1) CCDE,NOPRNT,M,LIST,MORPLT
      IF(M.EQ.0) GO TO 15
      READ(5,8) (TYPE(I),I=1,M)
15  DO 725 I=1,20

```

```

MEANTO(I)=0.
MEANOO(I)=0.
MEANSG(I)=C.
MEANSL(I)=0.
JJ(I)=0
SUMTO(I)=0.0
SUMCO(I)=0.0
SUMSIG(I)=0.0
725 SUMSGO(I)=0.0

```

C
C
C
C
C
C
C

```

CALL SUBROUTINE READY TO DETERMINE THE LOCATION OF THE CIRCUM-
CENTER OF THE TETRAHEDRON, THE DISTANCE OF THE TETRAHEDRALLY
COORDINATED ATCM FROM THE CIRCUMCENTER, AND THE BOND-LENGTH
DISTORTION PARAMETER. READY CALLS SUBROUTINE TETFIT, WHICH DOES
THE CALCULATIONS RELATIVE TO THE EDGE-LENGTH DISTORTIONS.

```

```

DC 20 I=1,600
CALL READY(SIG,DIST,SIGC,DISP,CEASE,I)
IF(CEASE.GT.0.0) GO TO 21
SIGTO(I)=SIG
DFGC(I)=DIST
SIGLIG(I)=SIGC
DISPID(I)=DISP
CATION(I)=ATCM
BCND(I)=AVTO
EDGE(I)=AVCO
NAME(I,1)=TITLE(1)
NAME(I,2)=TITLE(2)
NAME(I,3)=TITLE(3)
NAME(I,4)=TITLE(4)
NAME(I,5)=TITLE(5)
NAME(I,6)=TITLE(6)

```

```

NAME(I,7)=TITLE(7)
NAME(I,8)=TITLE(8)
NAME(I,9)=TITLE(9)
NAME(I,10)=TITLE(10)
NAME(I,11)=TITLE(11)
NAME(I,12)=TITLE(12)
IF(ATOM.EQ.CHRS(1)) N=1
IF(ATOM.EQ.CHRS(2)) N=2
IF(ATOM.EQ.CHRS(3)) N=3
IF(ATOM.EQ.CHRS(4)) N=4
IF(ATOM.EQ.CHRS(5)) N=5
IF(ATOM.EQ.CHRS(6)) N=6
IF(ATOM.EQ.CHRS(7)) N=7
IF(ATOM.EQ.CHRS(8)) N=8
IF(ATOM.EQ.CHRS(9)) N=9
IF(ATOM.EQ.CHRS(10)) N=10
IF(ATOM.EQ.CHRS(11)) N=11
IF(ATOM.EQ.CHRS(12)) N=12
IF(ATOM.EQ.CHRS(13)) N=13
IF(ATOM.EQ.CHRS(14)) N=14
IF(ATOM.EQ.CHRS(15)) N=15
IF(ATOM.EQ.CHRS(16)) N=16
IF(ATOM.EQ.CHRS(17)) N=17
IF(ATOM.EQ.CHRS(18)) N=18
IF(ATOM.EQ.CHRS(19)) N=19
IF(ATOM.EQ.CHRS(20)) N=20
JJ(N)=JJ(N)+1
SUMTO(N)=SUMTO(N)+AVTO
SUMOO(N)=SUMCO(N)+AVCO
SUMSIG(N)=SUMSIG(N)+SIG
SUMSGO(N)=SUMSGO(N)+SIGO

```

20 L=I

```

21 CONTINUE
DO 63 I=1,20
IF(SUMTO(I).EQ.0.) GO TO 63
TJ(I)=FLCAT(JJ(I))
MEANTO(I)=SUMTC(I)/TJ(I)
MEANOQ(I)=SUMOO(I)/TJ(I)
MEANSQ(I)=SUMSIG(I)/TJ(I)
MEANSL(I)=SUMSGO(I)/TJ(I)
63 CONTINUE
IF(L.LT.3) GO TO 16

```

C
C
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C

CALL SUBROUTINE STAT TO DETERMINE THE LEAST SQUARES REGRESSION
LINE WITH DISTANCE OF THE TETRAHEDRALLY-COORDINATED ATOM FROM THE
CIRCUMCENTER AS THE DEPENDENT VARIABLE AND THE BOND-LENGTH
DISTORTION PARAMETER AS THE INDEPENDENT VARIABLE, AS WELL AS THE
T-STATISTIC FOR THE TEST OF ZERO REGRESSION.

```

CALL STAT(SIGTO,DFGC,L)
NDF=L-2
WRITE(6,2) SLOPE,YNTRCP,CODET,CCRCD
WRITE(6,3) SSREG,SSE,MSE,TZERO
WRITE(6,7) NDF

```

C
C
C
C
C
C
C

CALL SUBROUTINE STAT TO DETERMINE THE LEAST SQUARES REGRESSION
LINE WITH AVERAGE DISPLACEMENT OF THE OXYGEN ATOMS FROM AN IDEAL
TETRAHEDRAL ARRAY AS THE DEPENDENT VARIABLE AND THE EDGE-LENGTH
DISTORTION PARAMETER AS THE INDEPENDENT VARIABLE, AS WELL AS THE
T-STATISTIC FOR THE TEST OF ZERO REGRESSION.

```

CALL STAT(SIGLIG,DISPID,L)
WRITE(6,5) SLOPE,YNTRCP,CODET,CORCO
WRITE(6,6) SSREG,SSE,MSE,TZERO

```

```

        WRITE(6,7) NDF
        WRITE(6,850)
        DC 855 I=1,20
        IF(MEANTO(I).EQ.0.) GO TO 854
        WRITE(6,851) CHRS(I),MEANTO(I),MEANOC(I),MEANSG(I),MEANSL(I)
        GO TO 855
854 WRITE(6,852) CHRS(I)
855 CCNTINUE
    16 IF(LIST.NE.1) GO TO 22
        WRITE(6,9)
        DC 17 I=1,L
    17 WRITE(6,10) (NAME(I,J),J=1,12),CATION(I)
    22 WRITE(6,4)
C
C      CALL SUBROUTINE PLOT TO OBTAIN DESIRED PLOTS AS SPECIFIED BY CODE
C
        IF(CCDE.EQ.C.AND.MORPLT.EQ.0) GO TO 60
        IF(CODE.EQ.0.AND.MORPLT.NE.0) GO TO 85
        GO TO (27,28,30,27,27,28,27),CODE
27 DC 26 I=1,L
        ST(I)=SIGTO(I)
26 DF(I)=DFGC(I)
        CALL AXIS(0.5,0.7,'BCND-LENGTH DISTORTION PARAMETER',32,-10.,0.,
1.000,.01401)
        CALL AXIS(0.5,0.7,'DISTANCE FROM CIRCUMCENTER',-26,-10.,90.,.000,
1.03201)
        DC 25 I=1,L
        XPLT=(ST(I)/.014) + 0.5
        YPLT=(DF(I)/.032) + 0.7
        CAT=CATION(I)
        CALL SYMBCL(XPLT,YPLT,.1,0,0.,-1)
25 CCNTINUE

```

```

      CALL PLOT(13.,0.,-3)
      IF(CODE.EQ.4) GO TO 28
      IF(CODE.EQ.5) GO TO 30
      IF(CODE.EQ.7) GO TO 28
      GO TO 50
28  DC 24 I=1,L
      SL(I)=SIGLIG(I)
24  DI(I)=DISPID(I)
      CALL AXIS(0.5,0.7,'EDGE-LENGTH DISTORTION PARAMETER',32,-10.,0.,
1.000,.02001)
      CALL AXIS(0.5,0.7,'AVERAGE OXYGEN DISPLACEMENT',-27,-10.,90.,.000,
1.07401)
      DC 41 I=1,L
      EXPT=(SL(I)/.020) + 0.5
      WYPT=(DI(I)/.074) + 0.7
      CAT=CATION(I)
      CALL SYMBOL(EXPT,WYPT,.1,0,0.,-1)
41  CCNTINUE
      CALL PLOT(13.,0.,-3)
      IF(CODE.EQ.4.OR.CODE.EQ.2) GO TO 50
30  IF(M.EQ.0) MM=M+1
      IF(M.NE.0) MM=M
      DC 45 J=1,MM
29  DC 23 I=1,L
      ST(I)=SIGTO(I)
23  SL(I)=SIGLIG(I)
      CALL AXIS(0.5,0.7,'BCND-LENGTH DISTORTION PARAMETER',32,-10.,0.,
1.000,.01401)
      CALL AXIS(0.5,0.7,'EDGE-LENGTH DISTORTION PARAMETER',-32,-10.,90.,
1.0,.02001)
      DC 43 I=1,L
      IF(M.EQ.0) GO TO 44

```

```

      IF(CATION(I).NE.TYPE(J)) GO TO 43
44  XPLT=(ST(I)/.014) + 0.5
      EXPT=(SL(I)/.020) + 0.7
      CAT=CATION(I)
      CALL SYMBOL(XPLT,EXPT,.1,0,0.,-1)
43  CONTINUE
      IF(M.EQ.0) GO TO 45
      CALL SYMBOL(7.5,7.5,1.5,CAT,0.,2)
      CALL PLOT(13.,0.,-3)
45  CCNTINUE

```

C
C
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```

      IF MORPLT IS NON-ZERO, MAKE PLOTS OF BLDP VS. MEAN BCND LENGTH AND
      ELDP VS. MEAN EDGE LENGTH.

85  IF(MORPLT.EQ.0) GO TO 50
      DO 80 I=1,20
      IF(MEANTO(I).EQ.0.) GO TO 80
      JCOUNT=0
      DO 81 J=1,L
      BL(J)=BCND(J)
      EG(J)=EDGE(J)
      ST(J)=SIGTO(J)
      SL(J)=SIGLIG(J)
      IF(CATION(J).NE.CHRS(I)) GO TO 81
      JCOUNT=JCOUNT+1
      BLN(JCOUNT)=BL(J)
      EGL(JCOUNT)=EG(J)
      SIT(JCOUNT)=ST(J)
      SIL(JCOUNT)=SL(J)
81  CCNTINUE
      CALL SCALE(SIT,JCOUNT,10.,SITMIN,DSIT,1)
      CALL AXIS(0.5,0.6,'BOND-LENGTH DISTORTION PARAMETER',32,-10.,0.,

```

```

1SITMIN,DSIT)
  CALL SCALE(BLN,JCOUNT,10.,XMIN,DX,1)
  DX=DX+.00001
  CALL AXIS(0.5,0.6,'MEAN BOND LENGTH',-16,-10.,90.,XMIN,DX)
  K=0
  DC 82 J=1,L
  IF(CATION(J).NE.CHRS(I)) GO TO 82
  K=K+1
  TETCAT=CHRS(I)
  BLDPAR=SIT(K) + 0.5
  BONDL=BLN(K) + 0.6
  CALL SYMBOL(BLDPAR,BONDL,.1,0,0.,-1)
82 CCNTINUE
  CALL SYMBOL(7.5,7.5,1.5,TETCAT,0.,2)
  CALL PLOT(13.,0.,-3)
  CALL SCALE(SIL,JCOUNT,10.,SILMIN,DSIL,1)
  CALL AXIS(0.5,0.6,'EDGE-LENGTH DISTORTION PARAMETER',32,-10.,0.,
1SILMIN,DSIL)
  CALL SCALE(EGL,JCOUNT,10.,XMN,D,1)
  D=D+0.00001
  CALL AXIS(0.5,0.6,'MEAN EDGE LENGTH',-16,-10.,90.,XMN,D)
  K=0
  DC 83 J=1,L
  IF(CATION(J).NE.CHRS(I)) GO TO 83
  K=K+1
  ELDPAR=SIL(K) + 0.5
  EDGEL=EGL(K) + 0.6
  CALL SYMBOL(ELDPAR,EDGEL,.1,0,0.,-1)
83 CCNTINUE
  CALL SYMBOL(7.5,7.5,1.5,TETCAT,0.,2)
  CALL PLOT(13.,0.,-3)
  DC 84 NN=1,JCOUNT

```

```
      BLN(NN)=0.  
      EGL(NN)=0.  
      SIT(NN)=0.  
84    SIL(NN)=0.  
80    CCNTINUE  
50    CALL PLOT(0.,0.,-4)  
60    RETURN  
      END
```

```

      SUBROUTINE CENT(X,Y,Z)
C
C      SUBROUTINE CENT IS CALLED BY SUBROUTINE TETFIT, AND DETERMINES THE
C      CENTROID OF THE TETRAHEDRON.  CENT IS ADAPTED FROM DOLLASE'S POLFT
C      (SEE COMMENTS IN SUBROUTINE TETFIT).
C
      DIMENSION X(4,3),Y(3),Z(3)
      DO 10 J=1,3
10    Z(J)=0.0
      N=0
      DO 20 I=1,4
      DO 20 J=1,3
      N=N+1
20    Z(J)=Z(J)+X(I,J)
      DO 30 J=1,3
30    Z(J)=Z(J)/Y(J)
      RETURN
      END

```

```

SUBROUTINE LLS
C
C SUBROUTINE LLS IS CALLED BY SUBROUTINE TETFIT. IT DETERMINES
C THE PARAMETER P IN ORDER TO TEST FOR LEAST SQUARES CONVERGENCE.
C THE TEST IS MADE IN SUBROUTINE TETFIT. LLS IS ADAPTED FROM
C UCLLASE'S PCLFT (SEE COMMENTS IN SUBROUTINE TETFIT).
C
COMMON/DCLL/P(3),C(12,3),S(12),W(12),NP,NG
DIMENSION A(9),B(3,3),T(3),AO(3,3)
REAL*8 A,B,AO,T,P,ER,ERM
N=0
DO 44 I=1,NP
DO44 J=I,NP
A=N+1
A(N)=0.
DO 4 K=1,NG
4 A(N)=A(N)+C(K,I)*C(K,J)*W(K)
AC(J,I)=A(N)
44 AO(I,J)=A(N)
CALL SMI(A,NP,IND)
M=0
DO 65 I=1,NP
DO 65 J=I,NP
M=M+1
B(J,I)=A(M)
65 B(I,J)=A(M)
ERM=0.
DO 68 I=1,NP
DO 68 J=1,NP
ER=0.
DO 67 K=1,NP
67 ER=ER+AO(I,K)*B(K,J)

```

```

        IF(I.EQ.J) ER=ER-1.
68      ERM=DMAX1(ERM,ER)
        DC 7 I=1,NP
          T(I)=0.
          DC 7 J=1,NO
7        T(I)=T(I)+C(J,I)*S(J)*W(J)
          DC 9 I=1,NP
            P(I)=0.
            DC 9 J=1,NP
9          P(I)=P(I)+B(I,J)*T(J)
        RETURN
      END

```

SUBROUTINE READY(SIGMA,DFC,SIGOX,DISPL,QUIT,ICOUNT)

SUBROUTINE READY READS THE INPUT DATA FOR EACH TETRAHEDRON,
COMPUTES THE CARTESIAN COORDINATES FOR THE OXYGEN ATOMS (ORIENTED
AS DESCRIBED IN COMMENT CARDS BELOW), SOLVES THREE SIMULTANEOUS
EQUATIONS FOR THE COORDINATES OF THE CIRCUMCENTER OF THE
TETRAHEDRON, COMPUTES THE BOND LENGTH DISTORTION PARAMETER AND THE
DISTANCE OF THE CATION FROM THE CIRCUMCENTER, AND CALLS SUBROUTINE
TETFIT.

REAL TITLE(12),ELNAME(3),CHAR(68)

CCMPCN/PASS/0012,0013,0014,0023,0024,0034,AVTC,AVOO

CCMPCN/COORD/X01,X02,X03,X04,Y01,Y02,Y03,Y04,Z01,Z02,Z03,Z04

CCMPCN/PRINT/NOPTNT,ATCM,TITLE

DATA CHAR/'AL ','ALUM','INUM','AS ','ARSE','NIC ','B ',

1'BORO','N ','BE ','BERY','LLIU','M ','CR ','CHRO','MIUM',

2'GA ','GALL','IUM ','GE ','GERM','ANIU','M ','FE ','IRON',

3'LI ','LITH','IUM ','MG ','MAGN','ESIU','M ','MN ','MANG',

4'ANES','E ','MO ','MOLY','BDEN','UM ','P ','PHOS','PHOR',

5'US ','S ','SULP','HUR ','SE ','SELE','NIUM','SI ','SILI',

6'CGN ','V ','VANA','DIUM','ZN ','ZINC',' ','TI ','TITA',

7'NIUM','CU ','COPP','ER ','W ','TUNG','STEN'/

1 FORMAT(9F6.4)

2 FORMAT(12A4,1X,A4)

3 FORMAT('O','INPUT DATA IS AS FOLLOWS: T-O = ',F5.3,10X,'ANGLES =

1',F6.2,/,',',33X,F5.3,19X,F6.2,/,',',33X,F5.3,19X,F6.2,/,',',33X,

2F5.3,19X,F6.2,/,',',57X,F6.2,//)

4 FORMAT(' ',12A4, '//',' ','THE TETRAHEDRALLY COORDINATED ATOM IS '

1,3A4)

5 FORMAT(' ','COORDINATES OF THE CIRCUMCENTER OF THE TETRAHEDR

1CN ARE: X ',F8.5/62X,'Y ',F8.5/62X,'Z ',F8.5,//)

6 FORMAT('O', 21X,'THE DISTANCE OF THE CENTRAL ATCM FROM THE CIRCUM

```

1CENTER IS ',F5.3,' ANGSTROMS')
7 FORMAT('O',//,' ',10X,'*** THE BOND-LENGTH DISTORTION PARAMETER
1IS ',F6.4)
8 FORMAT('1','TETRAHEDRON NUMBER ',I3,' :',//,' ', 'THE ATOMIC SPECIE
1S CONTAINED IN THIS TETRAHEDRON IS NOT ONE',/, ' ', 'OF THOSE INITIA
2LIZED IN THE ARRAY NAMED CHAR BY THE DATA',/, ' ', 'STATEMENT. CHEC
3K TO INSURE THAT THE ELEMENT SYMBOL HAS NOT BEEN',/, ' ', 'MISPUNCHE
4D ON THE TITLE CARD. IF NOT, THEN A NEW TYPE OF',/, ' ', 'TETRAHEDR
5AL ATOM HAS BEEN ADDED, AND THIS MUST BE ADDED TO',/, ' ', 'THE ARRA
6Y CHAR, AND THE DIMENSION OF CHAR INCREASED ACCORDINGLY.')
9 FORMAT('O',10X,'*** THE EDGE-LENGTH DISTORTION PARAMETER IS ',
1F6.4)
10 FORMAT('O',21X,'THE AVERAGE DISPLACEMENT OF THE OXYGEN ATOMS FROM
1AN IDEAL TETRAHEDRAL ARRAY IS ',F5.3,' ANGSTROMS')
11 FORMAT(' ', 'CARTESIAN COORDINATES FOR THE OXYGEN ATOMS ARE:',//,
1' ',21X,'O(1)',23X,'O(2)',23X,'O(3)',23X,'O(4)',//,' ',4(14X,'X',
24X,F8.5),/, ' ',4(14X,'Y',4X,F8.5),/, ' ',4(14X,'Z',4X,F8.5),//,' ',
2/, ' ', 'O...O SEPA
3RATIONS (IN ANGSTROMS) BASED ON THESE COORDINATES ARE: O(1)..
4.O(2)',4X,F5.3,10X,'O(2)...O(3)',4X,F5.3,/, ' ',70X,'O(1)...O(3)',
54X,F5.3,10X,'O(2)...O(3)',4X,F5.3,/, ' ',70X,'O(1)...O(4)',4X,F5.3,
610X,'O(3)...O(4)',4X,F5.3,/)
12 FORMAT(' ',//)
13 FORMAT('1')
14 FORMAT('O','AVERAGE BOND LENGTH = ',F5.3,' ANGSTROMS.',20X,
1 'AVERAGE EDGE LENGTH = ',F5.3,' ANGSTROMS.',//)
QUIT=0.0
READ(5,2,END=68) (TITLE(I), I=1,12),ATCM
READ(5,1) R1,R2,R3,R4,A12,A13,A14,A23,A24
RAD=3.14159/180.
A12=A12*RAD
A13=A13*RAD

```

```
A14=A14*RAD
A23=A23*RAD
A24=A24*RAD
```

C
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C

```
COMPUTE CARTESIAN COORDINATES FOR OXYGEN ATOMS (O1 ON Z-AXIS, O2
IN YZ PLANE, O3 IN +X HEMISPHERE, CATION AT THE ORIGIN.)
```

```
XC1=0.0
Y01=0.0
ZC1=R1
X02=0.0
Y02=R2*SIN(A12)
Z02=R2*CCS(A12)
XC3=R3*(SQRT(1.-((COS(A23)-(COS(A12)*CCS(A13)))/SIN(A12))* ((COS(A
123)-(COS(A12)*COS(A13)))/SIN(A12))-(COS(A13))*COS(A13)))
YC3=R3*((COS(A23)-(COS(A12)*COS(A13)))/SIN(A12))
Z03=R3*CCS(A13)
XC4=R4*(SQRT(1.-((COS(A24)-(COS(A12)*COS(A14)))/SIN(A12))* ((COS(A
124)-(COS(A12)*COS(A14)))/SIN(A12))-(COS(A14))*COS(A14)))*(-1.0)
Y04=R4*((COS(A24)-(COS(A12)*COS(A14)))/SIN(A12))
ZC4=R4*CCS(A14)
```

C
C
C
C

```
COMPUTE BOND LENGTHS AND OXYGEN-OXYGEN SEPARATIONS FROM CARTESIAN
COORDINATES.
```

```
CR1=SQRT(Z01*ZC1)
CR2=SQRT((Y02*Y02) + (ZC2*Z02))
CR3=SQRT((X03*X03)+(Y03*Y03)+(Z03*Z03))
CR4=SQRT((X04*X04)+(Y04*Y04)+(ZC4*Z04))
OO12=SQRT((Y02*Y02)+((Z01-Z02)*(Z01-Z02)))
OO13=SQRT((XC3*X03)+(Y03*Y03)+((ZC1-Z03)*(Z01-Z03)))
OO14=SQRT((X04*X04)+(Y04*Y04)+((ZC1-Z04)*(Z01-Z04)))
```

```

0023=SQRT(((XC3*X03)+((Y02-Y03)*(Y02-Y03))+((Z02-Z03)*(Z02-Z03)))
0024=SQRT(((XC4*X04)+((Y02-Y04)*(Y02-Y04))+((Z02-Z04)*(Z02-Z04)))
0034=SQRT(((XC3-X04)*(XC3-X04))+((Y03-Y04)*(Y03-Y04))+((Z03-Z04)*
1ZC3-Z04)))
AVTC=(R1+R2+R3+R4)/4.
AV00=(0012+0013+0014+0023+0024+0034)/6.

```

C
C
C

```
CCMPUTE ANGLE O(3)-T-O(4)
```

```

A34=ARCOS((0034*0034-R3*R3-R4*R4)/(-2.*R3*R4))
A12=A12/RAD
A13=A13/RAD
A14=A14/RAD
A23=A23/RAD
A24=A24/RAD
A34=A34/RAD
IF(ATOM.NE.CHAR(1)) GO TO 20
ELNAME(1)=CHAR(2)
ELNAME(2)=CHAR(3)
ELNAME(3)=CHAR(59)
GO TO 40
20 IF(ATOM.NE.CHAR(4)) GO TO 21
ELNAME(1)=CHAR(5)
ELNAME(2)=CHAR(6)
ELNAME(3)=CHAR(59)
GO TO 40
21 IF(ATOM.NE.CHAR(7)) GO TO 22
ELNAME(1)=CHAR(8)
ELNAME(2)=CHAR(9)
ELNAME(3)=CHAR(59)
GO TO 40
22 IF(ATOM.NE.CHAR(10)) GO TO 23

```

```
    ELNAME(1)=CHAR(11)
    ELNAME(2)=CHAR(12)
    ELNAME(3)=CHAR(13)
    GC TO 40
23  IF(ATOM.NE.CHAR(14)) GC TO 24
    ELNAME(1)=CHAR(15)
    ELNAME(2)=CHAR(16)
    ELNAME(3)=CHAR(59)
    GC TO 40
24  IF(ATOM.NE.CHAR(17)) GC TO 25
    ELNAME(1)=CHAR(18)
    ELNAME(2)=CHAR(19)
    ELNAME(3)=CHAR(59)
    GC TO 40
25  IF(ATOM.NE.CHAR(20)) GC TO 26
    ELNAME(1)=CHAR(21)
    ELNAME(2)=CHAR(22)
    ELNAME(3)=CHAR(23)
    GC TO 40
26  IF(ATOM.NE.CHAR(24)) GC TO 27
    ELNAME(1)=CHAR(25)
    ELNAME(2)=CHAR(59)
    ELNAME(3)=CHAR(59)
    GC TO 40
27  IF(ATOM.NE.CHAR(26)) GC TO 28
    ELNAME(1)=CHAR(27)
    ELNAME(2)=CHAR(28)
    ELNAME(3)=CHAR(59)
    GC TO 40
28  IF(ATOM.NE.CHAR(29)) GC TO 29
    ELNAME(1)=CHAR(30)
    ELNAME(2)=CHAR(31)
```

```
      ELNAME(3)=CHAR(32)
      GC TO 40
29  IF(ATOM.NE.CHAR(33)) GC TO 30
      ELNAME(1)=CHAR(34)
      ELNAME(2)=CHAR(35)
      ELNAME(3)=CHAR(36)
      GC TO 40
30  IF(ATOM.NE.CHAR(37)) GC TO 31
      ELNAME(1)=CHAR(38)
      ELNAME(2)=CHAR(39)
      ELNAME(3)=CHAR(40)
      GC TO 40
31  IF(ATOM.NE.CHAR(41)) GC TO 32
      ELNAME(1)=CHAR(42)
      ELNAME(2)=CHAR(43)
      ELNAME(3)=CHAR(44)
      GC TO 40
32  IF(ATOM.NE.CHAR(45)) GC TO 33
      ELNAME(1)=CHAR(46)
      ELNAME(2)=CHAR(47)
      ELNAME(3)=CHAR(59)
      GC TO 40
33  IF(ATOM.NE.CHAR(48)) GC TO 34
      ELNAME(1)=CHAR(49)
      ELNAME(2)=CHAR(50)
      ELNAME(3)=CHAR(59)
      GC TO 40
34  IF(ATOM.NE.CHAR(51)) GC TO 35
      ELNAME(1)=CHAR(52)
      ELNAME(2)=CHAR(53)
      ELNAME(3)=CHAR(59)
      GC TO 40
```

```

35 IF(ATOM.NE.CHAR(54)) GO TO 36
   ELNAME(1)=CHAR(55)
   ELNAME(2)=CHAR(56)
   ELNAME(3)=CHAR(59)
   GO TO 40
36 IF(ATOM.NE.CHAR(57)) GO TO 37
   ELNAME(1)=CHAR(58)
   ELNAME(2)=CHAR(59)
   ELNAME(3)=CHAR(59)
   GO TO 40
37 IF(ATOM.NE.CHAR(60)) GO TO 38
   ELNAME(1)=CHAR(61)
   ELNAME(2)=CHAR(62)
   ELNAME(3)=CHAR(59)
   GO TO 40
38 IF(ATOM.NE.CHAR(63)) GO TO 39
   ELNAME(1)=CHAR(64)
   ELNAME(2)=CHAR(65)
   ELNAME(3)=CHAR(59)
   GO TO 40
39 IF(ATOM.NE.CHAR(66)) GO TO 50
   ELNAME(1)=CHAR(67)
   ELNAME(2)=CHAR(68)
   ELNAME(3)=CHAR(59)
   GO TO 40
50 WRITE(6,8) ICCUNT
40 IF (NOPRNT.EQ.1) GO TO 42
   IF(NOPRNT.EQ.2) GO TO 41
   WRITE(6,13)
41 WRITE(6,4) (TITLE(I),I=1,12),(ELNAME(I),I=1,3)
   WRITE(6,3)R1,A12,R2,A13,R3,A14,R4,A23,A24
   IF(NOPRNT.EQ.2) GO TO 42

```

```

WRITE(6,14) AVTG,AVOO
WRITE(6,11) X01,X02,X03,X04,Y01,Y02,Y03,Y04,Z01,Z02,Z03,Z04,
10012,0013,0014,0023,0024,0034
42 CCNTINUE

```

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```

SET UP D-MATRIX IN EQUATION DX=Y, WHERE X IS THE MATRIX OF
COORDINATES FOR THE CIRCUMCENTER OF THE TETRAHEDRON.

```

```

D11=0.0
D12=0.-Y02
D13=Z01-Z02
D21=0.-X03
D22=Y02-Y03
D23=Z02-Z03
D31=X03-X04
D32=Y03-Y04
D33=Z03-Z04

```

C
C
C

```

SET UP Y-MATRIX

```

```

YA=0.5*(XC1*X01-X02*X02+Y01*Y01-YC2*Y02+ZC1*Z01-Z02*Z02)
YB=0.5*(XC2*X02-X03*X03+Y02*Y02-Y03*Y03+ZC2*Z02-Z03*Z03)
YC=0.5*(X03*X03-X04*X04+Y03*Y03-Y04*Y04+ZC3*Z03-Z04*Z04)

```

C
C
C

```

INVERT D-MATRIX

```

```

DADJ11=(D22*D33)-(D32*D23)
DADJ12=((D12*D33)-(D32*D13))*(-1.)
DADJ13=(D12*D23)-(D22*D13)
DADJ21=((D21*D33)-(D31*D23))*(-1.)
DADJ22=(D11*D33)-(D31*D13)
DADJ23=((D11*D23)-(D21*D13))*(-1.)

```

```

DADJ31=(D21*C32)-(D31*D22)
DADJ32=((C11*D32)-(D31*D12))*(-1.)
DADJ33=(C11*D22)-(D21*C12)
DET=(D11*D22*D33)+(D12*D23*D31)+(D13*D21*C32)-(D31*D22*D13)-
1(D32*D23*D11)-(D33*D21*D12)
DINV11=DADJ11/DET
DINV12=DADJ12/DET
CINV13=DADJ13/DET
DINV21=DADJ21/DET
DINV22=DADJ22/DET
DINV23=DADJ23/DET
DINV31=DADJ31/DET
DINV32=DADJ32/DET
DINV33=DADJ33/DET

```

C
C
C

DETERMINE COORDINATES OF CIRCUMCENTER

```

X1=(DINV11*YA)+(DINV12*YB)+(DINV13*YC)
Y1=(DINV21*YA)+(DINV22*YB)+(DINV23*YC)
Z1=(DINV31*YA)+(DINV32*YB)+(DINV33*YC)

```

C
C
C

COMPUTE BCND-LENGTH DISTORTION PARAMETER

```

VARTC=((R1-AVTC)*(R1-AVTO)+(R2-AVTC)*(R2-AVTO)+(R3-AVTO)*(R3-AVTO)
1+(R4-AVTC)*(R4-AVTO))/3.
SIGMA=(SQRT(VARTC))/AVTC

```

C
C
C

COMPUTE THE DISTANCE OF THE CENTRAL ATOM FROM THE CIRCUMCENTER

```

DFC=SQRT(X1*X1+Y1*Y1+Z1*Z1)
IF(NOPRNT.EQ.1.OR.NOPRNT.EQ.2) GO TO 44
WRITE(6,5) X1,Y1,Z1

```

44 CCNTINUE

C
C CALL SUBRCUTINE TETFIT TO DETERMINE THE EDGE-LENGTH DISTORTION
C PARAMETER, AND CALCULATE THE OXYGEN DISPLACEMENTS NECESSARY FOR
C THE OXYGEN ATOMS TO LIE AT THE CORNERS OF A REGULAR TETRAHEDRON.
C

CALL TETFIT(SIGOX,DISPL)
IF (NOPRNT.EQ.1) GO TO 46
WRITE(6,7) SIGMA
WRITE(6,6) DFC
WRITE(6,9)SIGCX
WRITE(6,10) DISPL
IF(NOPRNT.EQ.2) WRITE(6,12)

46 CCNTINUE

C
C AT THIS POINT ALL BOND LENGTHS, EDGE LENGTHS, O-T-O ANGLES,
C DISTORTION VALUES, AND DISTORTION PARAMETERS ARE KNOWN. THIS IS
C THEREFOR A CONVENIENT LOCATION AT WHICH TO INSERT WRITE STATE-
C MENTS IN ORDER TO OBTAIN ANY OF THESE QUANTITIES ON PUNCHED CARDS.
C BOND LENGTHS ARE R1,R2,R3,AND R4; EDGE LENGTHS ARE OO12,OO13,...,
C OO34; O-T-O ANGLES ARE A12,A13,...,A34; DISTORTIONS ARE DFC AND
C DISPL; AND DISTORTION PARAMETERS ARE SIGMA AND SIGCX. FUNCTIONS
C (LOG, SINE, ETC.) OF THESE QUANTITIES MAY ALSO BE OBTAINED BY
C INSERTING APPROPRIATE FORTRAN STATEMENTS PRIOR TO THE WRITE STATE-
C MENTS. NOTE, HOWEVER, THAT THE ANGLES ARE IN DEGREES AND MUST BE
C CONVERTED TO RADIANS BEFORE TRIGONOMETRIC FUNCTIONS MAY BE USED.
C

GC TO 70
68 QUIT=1.0
70 RETURN
END

```

      SUBROUTINE SMI(A,NY,NR)
C
C      SUBROUTINE SMI IS CALLED BY SUBROUTINE LLS.  IT IS ADAPTED FROM
C      DOLLASE'S POLFT (SEE COMMENTS IN SUBROUTINE TETFIT).
C
      DIMENSION R(3),A(9)
      REAL*8 R,A,BIGJ,Y,Q
      NN=NY
      DO 16 I=1,NN
16      R(I)=1.
      DO 1 I=1,NN
      BIGJ=0.
      J=-NN
      KJ=NN+1
      DO 3 K=1,NN
      J=J+KJ
      KJ=KJ-1
      IF(R(K)) 3,4,4
4      Y=DABS(A(J))
17      BIGJ=Y
      KK=K
      KL=J
3      CCNTINUE
5      R(KK)=-1.
      Q=1./A(KL)
      J=-NN+KK
      NJ=NN+1
      K=0
      IK=KK-1
      JK=KK+1
      IF(IK) 103,103,100
100      DO 102 N=1,IK

```

```

      NJ=NJ-1
      J=J+NJ
      Y=A(J)*Q
      NI=J
      MJ=NJ
      DO 19 M=N,IK
      K=K+1
      A(K)=A(K)-Y*R(M)*A(J)
      MJ=MJ-1
19    J=J+MJ
      J=NI
      A(J)=Y
      K=K+1
      L=KL
      IF(JK-NN) 101,101,102
101   DO 18 M=JK,NN
      L=L+1
      K=K+1
18    A(K)=A(K)-Y*A(L)
102   CCNTINUE
103   K=KL+NN-KK
      J=KL
      IF(JK-NN) 104,104,105
104   DO 20 N=JK,NN
      J=J+1
      Y=R(N)*A(J)*Q
      NI=J
      DO 26 M=N,NN
      K=K+1
      A(K)=A(K)-Y*A(J)
26    J=J+1
20    J=NI

```

```
105  K=KL  
      A(K)=Q  
      IF(JK-NN) 106,106,1  
106  DC 21 M=JK,NN  
      K=K+1  
21   A(K)=-A(K)*Q  
1    CCNTINUE  
      NR=0  
      RETURN  
      END
```

```

SUBROUTINE STAT(EX,WYE,L)
C
C SUBROUTINE STAT COMPUTES THE SIMPLE LEAST SQUARES REGRESSION LINE
C BETWEEN TWO VARIABLES, THE RELEVANT SUMS OF SQUARES, THE MEAN
C SQUARE ERROR, AND THE T-STATISTIC FOR THE TEST OF ZERO REGRESSION
C
REAL EX(600),WYE(600),CFCHAT(600),MSE
COMMON/TEST/CORCO,CODET,SSREG,SSE,MSE,TZERO,SLOPE,YNTRCP
21 SUMX=0.0
SUMYX=0.0
SUMY=0.0
SUMX2=0.0
DO 24 I=1,L
SUMYX=SUMYX+EX(I)*WYE(I)
SUMX=SUMX + EX(I)
SUMY=SUMY + WYE(I)
24 SUMX2=SUMX2+(EX(I)*EX(I))
SXY=SUMYX - ((SUMY*SUMX)/L)
SXX=SUMX2 - ((SUMX**2.)/L)
SLOPE=SXY/SXX
YNTRCP=(SUMY/L) - (SLOPE*(SUMX/L))
SYY=0.0
C
C COMPUTE R AND R-SQUARED
C
DO 26 I=1,L
26 SYY=SYY+(WYE(I)-(SUMY/L))*(WYE(I)-(SUMY/L))
CODET=(SXY*SXY)/(SYY*SXX)
CORCO=SQRT(CODET)
SSREG=0.0
SSE=0.0
C

```

```

C      COMPUTE |T| VALUE FOR TEST OF ZERO SLOPE
C
      DO 22 I=1,L
      DFCHAT(I)=YNTRCP+SLOPE*EX(I)
      SSE=SSE+(WYE(I)-DFCHAT(I))*(WYE(I)-DFCHAT(I))
22  SSREG=SSREG+(DFCHAT(I)-(SUMY/L))*(DFCHAT(I)-(SUMY/L))
      MSE=SSE/(L-2.)
      TZERO=SLOPE/(SQRT(MSE/SXX))
      RETURN
      END

```

SUBROUTINE TETFIT(SIGOO,AVDISP)

SUBROUTINE TETFIT IS AN ADAPTATION OF WAYNE DOLLASE'S PROGRAM POLFT. SEE WAYNE A. DOLLASE (1974) ACTA CRYSTALLOGR., A30, 513-517. POLFT DETERMINES A DISTORTION INDEX BASED ON THE CLOSEST LEAST SQUARES FIT, THROUGH ROTATION AND DILATION, OF THE REAL POLYHEDRON TO SOME POLYHEDRON OF SPECIFIED SYMMETRY. THIS PROGRAM HAS BEEN EXTENSIVELY MODIFIED HERE. SUBROUTINE TETFIT COMPUTES THE CLOSEST LEAST SQUARES FIT, THROUGH ROTATION ALONE, BETWEEN THE REAL TETRAHEDRON (OMITTING THE CENTRAL ATOM) AND AN IDEAL TETRAHEDRON WHOSE EDGE LENGTH IS THE AVERAGE EDGE LENGTH OF THE REAL TETRAHEDRON. THE AVERAGE SEPARATION BETWEEN THE RESPECTIVE OXYGEN ATOMS OF THE REAL AND IDEAL TETRAHEDRA IS TAKEN AS THE EDGE-LENGTH DISTORTION. SUBROUTINE TETFIT CALLS SUBROUTINES CENT, LLS, AND SMI, EACH OF WHICH HAS BEEN MODIFIED TO A GREATER OR LESSER EXTENT FROM POLFT. DOLLASE'S SUBROUTINE DIST HAS BEEN ELIMINATED.

```

CCMMCN/DCLL/P(3),A(12,3),S(12),W(12),NP,NO
CCMMCN/PASS/CG12,OO13,CC14,OO23,OC24,OO34,AVTC,AVOO
CCMMCN/CCGRD/XC1,XO2,XO3,XO4,YC1,YO2,YC3,YO4,ZO1,ZO2,ZO3,ZO4
CCMMCN/PRINT/NCPRNT,ATOM,TITLE
DIMENSION T(3,3),R(3,3),F(4,3),H(3),V(4,3),CELL(6),
1E(4,3),B(3),G(3),JA(12),WO(3),OT(3),OR(3),DC(1),
2FR(3,3),RR(3,3),SU(3),KA(4),LP(3),L(5),DISP(4),SOELS(4)
REAL*8 P
9 FORMAT('O','COORDINATES FOR OXYGENS DISPLACED SO AS TO LIE AT THE
1CCRNERS OF AN IDEAL TETRAHEDRON ARE',//,' ',22X,'O(1)',24X,'O(2)',
224X,'O(3)',24X,'O(4)',//,' ',4(15X,'X',4X,F8.5),/, ' ',
34(15X,'Y',4X,F8.5),/, ' ',4(15X,'Z',4X,F8.5),/)
11 FORMAT('O','OXYGEN DISPLACEMENTS (IN ANGSTROMS):      O(1)',
12X,F6.4,5X,'O(2)',2X,

```

```

2F6.4,5X,'O(3)',2X,F6.4,5X,'O(4)',2X,F6.4)
C
C   CALCULATE EDGE LENGTH DISTORTION PARAMETER
C
   VARCC=((CC12-AVCC)*(0012-AVCC)+(CC13-AVCC)*(0013-AVCC)+(0014-AVCC)
1*(0014-AVCC)+(0023-AVCC)*(0023-AVCC)+(0024-AVCC)*(0024-AVCC)+
2(CC34-AVCC)*(0034-AVCC))/5.
1 SIGCC=(SQRT(VARCC))/AVCC
   RAD=3.14159265/180.
   S3=SQRT(3.)
   NC=12
   N=0
   NI=0
   NSF=0
   NPP=3
   LP(1)=0
   DC(1)=1.0
   DO 10 I=1,3
10  SU(I)=0.0
   LP(2)=LP(1)
   LP(3)=LP(1)
   DC 25 I=1,4
   NI=NI+1
   KA(NI)=1
   DC 25 J=1,3
   N=N+1
25 JA(N)=LP(J)
C
C   DETERMINE THE CARTESIAN COORDINATES FOR THE IDEAL TETRAHEDRON.
C
   TANG=(109.471/2.)*RAD
   TOID=(AVCC/2.)/(SQRT(2./3.))

```

```

V(1,1)=-1.*TCID*SIN(TANG)
V(1,2)=0.0
V(1,3)=TCID*CCS(TANG)
V(2,1)=TCID*SIN(TANG)
V(2,2)=0.0
V(2,3)=TCID*COS(TANG)
V(3,1)=0.0
V(3,2)=-1.*TCID*SIN(TANG)
V(3,3)=-1.*TCID*COS(TANG)
V(4,1)=0.0
V(4,2)=TCID*SIN(TANG)
V(4,3)=-1.*TCID*COS(TANG)
CELL(1)=1.0
CELL(2)=1.0
CELL(3)=1.0
CELL(4)=90.
CELL(5)=90.
CELL(6)=90.
35 CA=COS(RAD*CELL(4))
CB=COS(RAD*CELL(5))
CG=COS(RAD*CELL(6))
SNB=SIN(RAD*CELL(5))
SNG=SIN(RAD*CELL(6))
ONE=(CA-CB*CG)/SNG
T(1,1)=CELL(1)
T(1,2)=CELL(2)*CG
T(1,3)=CELL(3)*CB
T(2,1)=0.0
T(2,2)=CELL(2)*SNG
T(2,3)=CELL(3)*ONE
T(3,1)=0.0
T(3,2)=0.0

```

```

      T(3,3)=CELL(3)*SQRT(SNB**2-GNE**2)
99      N=0
      DO 110 I=1,4
        IF(I.EQ.1) H(1)=X01
        IF(I.EQ.1) H(2)=Y01
        IF(I.EQ.1) H(3)=Z01
        IF(I.EQ.2) H(1)=X02
        IF(I.EQ.2) H(2)=Y02
        IF(I.EQ.2) H(3)=Z02
        IF(I.EQ.3) H(1)=X03
        IF(I.EQ.3) H(2)=Y03
        IF(I.EQ.3) H(3)=Z03
        IF(I.EQ.4) H(1)=X04
        IF(I.EQ.4) H(2)=Y04
        IF(I.EQ.4) H(3)=Z04
        WC(1)=1.0
        WC(2)=1.0
        WC(3)=1.0
101     DO 110 J=1,3
        N=N+1
        E(I,J)=0.0
        DO 102 K=1,3
102     E(I,J)=E(I,J)+T(J,K)*H(K)
108     W(N)=1.0
109     SU(J)=SU(J)+W(N)
110     CCNTINUE
120     CCNTINUE
        CALL CENT(E,SU,OT)
        CALL CENT(V,SU,H)
        DO 130 I=1,3
130     OT(I)=OT(I)-H(I)
        N=0

```

```

      DO 150 I=1,4
      DO 150 J=1,3
      E(I,J)=E(I,J)-OT(J)
150   F(I,J)=V(I,J)
      DO 152 I=1,3
      DO 151 J=1,3
151   RR(I,J)=0.0
152   RR(I,I)=1.0
      NSTOP=1
      NCY=0
C
C      TEST FOR LEAST SQUARES CONVERGENCE OR TOO MANY CYCLES (>15).
C
200   IF((NCY.GE.15).OR.(NSTCP.EQ.0)) GO TO 275
      NCY=NCY+1
      NSTCP=0
      NP=3
      N=0
      DO 250 I=1,4
      DO 250 J=1,3
      N=N+1
      S(N)=E(I,J)-F(I,J)
205   IF(J-2)206,207,208
206   A(N,1)=0.
      A(N,2)=F(I,3)
      A(N,3)=-F(I,2)
      GO TO 250
207   A(N,1)=-F(I,3)
      A(N,2)=0.0
      A(N,3)=F(I,1)
      GO TO 250
208   A(N,1)=F(I,2)

```

```

      A(N,2)=-F(I,1)
      A(N,3)=0.0
250  CCNTINUE
      CALL LLS
      TH=DSQRT(P(1)**2+P(2)**2+P(3)**2)
      IF(TH.GE..00005)          NSTOP=1
      DL=P(1)/TH
      DM=P(2)/TH
      DN=P(3)/TH
      STH=SIN(TH)
      CTH=COS(TH)
      AC=1.-CTH
      R(1,1)=DL**2+CTH*(1.-DL**2)
      R(1,2)=AC*DL*DM-STH*DN
      R(1,3)=AC*DL*DN+STH*DM
      R(2,1)=AC*DL*DM+STH*DN
      R(2,2)=DM**2+CTH*(1.-DM**2)
      R(2,3)=AC*DM*DN-STH*DL
      R(3,1)=AC*DL*DN-STH*DM
      R(3,2)=AC*DM*DN+STH*DL
      R(3,3)=DN**2+CTH*(1.-DN**2)
      DO 252 I=1,3
      DO 252 J=1,3
      FR(I,J)=0.0
      DO 252 K=1,3
252  FR(I,J)=FR(I,J)+R(I,K)*RR(K,J)
      DO 253 I=1,3
      DO 253 J=1,3
253  RR(I,J)=FR(I,J)
      P(1)=1.0
273  DO 274 I=1,4
      DO 274 J=1,3

```

```

      F(I,J)=0.0
      DC 274 K=1,3
274  F(I,J)=F(I,J)+RR(J,K)*V(I,K)
      GO TO 200
275  CCNTINUE
      DC 276 I=1,4
276  SDELS(I)=0.0
C
C      CALCULATE THE DISPLACEMENTS (DISP(I)) BETWEEN RESPECTIVE LIGANDS
C      AND THE MEAN DISPLACEMENT (AVDISP).
C
      DO 290 I=1,4
      DO 290 J=1,3
      CEL=E(I,J)-F(I,J)
      DELS=DEL*DEL
      SDELS(I)=SDELS(I)+DELS
290  CCNTINUE
      DO 291 I=1,4
291  DISP(I)=SQRT(SDELS(I))
      AVDISP=(DISP(1)+DISP(2)+DISP(3)+DISP(4))/4.
      IF(NOPRNT.EQ.1.OK.NOPRNT.EQ.2) GO TO 24
      2  WRITE(6,9) ((F(I,J),I=1,4),J=1,3)
      WRITE(6,11) (DISP(I), I=1,4)
24  CCNTINUE
      RETURN
      END

```

APPENDIX B

APPENDIX B

CRYSTAL STRUCTURE STUDIES USED IN THIS WORK

YEAR	PUBLICATION	VOL.	PAGE	CHEMICAL FORMULA	MINERAL NAME
ALUMINUM					
54	JCPSA	22	1597	NI AL2 O3	SILLIMANITE
62	ZEKGA	118	127	AL2 SI O5	
65	ACCRA	19	396	GAMMA LI AL O2	
65	ACCRA	19	971	LU3 AL2 AL3 O12	
65	ACCRA	19	971	YB3 AL2 AL3 O12	
65	ACCRA	19	971	Y2 AL2 AL3 O12	BAVENITE
65	ACCRA	19	971	GD3 AL2 AL3 O12	
66	ACCRA	20	301	CA4 (BE O H)2 AL2 SI9 O26	CORDIERITE
66	AMMIA	51	1068	AL3 MG2 SI5 AL O18 . N(H2 O)	
66	ZEKGA	123	161	AL P O4	SODALITE
67	ACCRA	23	434	NA8 SI6 AL6 O24 CL2	
69	ACBCA	325	1503	NA AL SI3 O8	LOW ALBITE
69	AMMIA	54	31	MG3.5 AL9.0 SI1.5 O20	SAPPHIRINE
70	ZEKGA	121	314	CA NA AL SI2 O7	SODA MELILITE
71	ADCSA	101	250	CA AL2 SI2 O8 . 4(H2 O)	GISMONDITE
71	CAMIA	10	822	CA2 AL (AL,SI)2 O7	GEHLENITE
71	ZEKGA	133	75	CA AL2 SI2 O8	ANORTHITE
72	AMMIA	57	1089	AL13 SI5 F4 (O H)14 O20 CL	ZUNYITE
72	ZEKGA	135	175	LI AL SI O4	BETA EUCRYPTITE
73	ACBCA	329	1550	11(CA O) . 7(AL2 O3) . CA F2	NATROLITE
73	AMMIA	58	676	NA2 AL2 SI3 O10 . 2(H2 O)	
73	AMMIA	58	676	NA2 AL2 SI3 O10 . 2(H2 O)	NATROLITE, 88 DEGREES
73	AMMIA	58	676	NA2 AL2 SI3 O10 . 2(H2 O)	NATROLITE, 146 DEGREES
73	AMMIA	58	676	NA2 AL2 SI3 O10 . 2(H2 O)	NATROLITE, 198 DEGREES
73	AMMIA	58	681	LI AL SI O4	BETA EUCRYPTITE
73	AMMIA	58	681	LI AL SI O4	BETA EUCRYPTITE, 200 DEGREES
73	AMMIA	58	681	LI AL SI O4	BETA EUCRYPTITE, 335 DEGREES
73	AMMIA	58	681	LI AL SI O4	BETA EUCRYPTITE, 400 DEGREES
75	ACBCA	831	1169	CA8.5 NA AL6 O18	

ARSENIC

66	ACCRA	21	808	3(AS2 O5) . 5(H2 O)	
70	ACSA	24	3711	LI MO O2 AS O4	
70	CJCHA	48	881	CG3 (AS O4)2	
70	CJCHA	48	890	MG2 AS2 O7	
70	INOCA	9	2259	CA2 AS O4 CL	
71	ACBCA	827	2124	NA3 AS O4 . (NA O H)O.2 . 12(H*	
72	ACBCA	828	3056	CA K AS O4 . 8(H2 C)	
72	BUFCA	95	33	CA5 (H AS O4)2 (AS O4)2 . 4(H2*	SAINFELDITE
72	CJCHA	51	2082	NA4 AS2 O7	
73	ACBCA	829	141	LU AS O4	
73	ACBCA	829	2611	MG3 AS2 O8	
73	ACBCA	829	2721	N H4 H2 AS O4	
73	AMMIA	58	1634	CA4 MG AS2 B12 O22 (C H)12 . 14*	TERRUGITE
73	JSSCB	6	80	MG8.5 AS3 O16	

BORON

65	ACCRA	19	297	BA O . 2(B2 O3)	
66	JCPSA	44	3348	LI B O2	
67	ACCRA	22	815	NA2 O . 4(B2 O3)	
67	ZEKGA	125	423	CS BE4 B12 AL4 J28	RHODIZITE
68	ACBCA	824	869	B2 O3 (III)	
69	ACBCA	825	955	CA B2 O4 (III)	
69	ACBCA	825	965	CA B2 O4 (IV)	
69	ACBCA	825	1787	K2 B5 O8 (C H) . 2(H2 O)	
70	ZEKGA	132	241	CA B3 O5 (C H)	FABIANITE
72	ACBCA	828	1571	BETA NA2 O . 3(B2 O3)	
72	ACBCA	828	3089	K2 O . 3(B2 O3)	
73	AMMIA	58	691	MG3 CL B7 O13	CUBIC BORACITE
74	ACBCA	830	578	NA2 O . 2(B2 O3)	
74	ACBCA	830	1178	CS2 O . 3(B2 O3)	
74	ACBCA	830	1827	5(K2 O) . 19(B2 O3)	

BERYLLIUM

59	ACCRA	12	623	BE4 O (C H3 C O2)6	
63	AMMIA	48	804	AL2 BE O4	CHRYSOBERYL
64	JESCA	111	78	BE O	BROMELLITE
68	ACBCA	824	672	LA2 BE2 O5	
68	LITHA	1	275	AL2 BE3 Si6 O18	BERYL
68	LITHA	1	275	AL2 BE3 Si6 O18 . N(H2 O)	HYDROUS BERYL
68	LITHA	1	275	AL1.9 CR0.1 BE3 Si5 O18	EMERALD
68	LITHA	1	275	AL1.9 CR0.1 BE3 Si5 O18 . N(H2*	HYDROUS EMERALD

69	ACBCA	825	304	BE S O4 . 4(H2 O)
69	ACBCA	825	1647	SR BE3 O4
70	AMMIA	55	1541	H NA BE S13 O8
72	ACBCA	828	114	MN4 (BE SI O4)3 S
72	AMMIA	57	1345	NA2 BE2 S16 O15 . H2 O
72	KRISA	16	1167	BE2 SI O4
74	AMMIA	59	1267	CA BE2 P2 O8

EPIDIDYMIT
HELVITE
EUDIDYMIT
PHENACITE
HURLBUTITE

CHROMIUM

69	ACBCA	825	2170	CA2 CR O4 CL
70	ACBCA	826	222	CR O3
70	ACBCA	826	437	(N H4)2 CR O4
72	ACBCA	828	2845	K2 CR O4
72	ACBCA	828	2880	NA RB CR2 O7
73	ACBCA	829	2141	RB2 CR4 O13
73	ACSAA	27	177	ZR4 (O H)6 (CR O4)5 . H2 C
73	MRBUA	8	271	K2 CR2 O7

COPPER

73	JSSCB	7	17	CU6.8 V6 C18.8
----	-------	---	----	----------------

GALLIUM

65	ACCRA	18	481	LI GA O2
65	ACCRA	19	971	LU3 GA2 GA3 O12
65	ACCRA	19	971	YB3 GA2 GA3 O12
65	ACCRA	19	971	Y3 GA2 GA3 O12
65	JCPSA	42	3957	GA(2-x) FE(x) O3
75	ACBCA	831	560	SR GA2 S12 O8
75	ACBCA	831	560	BA GA2 S12 O8
#1				SR GA2 S12 O8
#1				SR GA2 GE2 O8
#2				SR GA2 S12 O8

GERMANIUM

64	ACCRA	17	842	GE O2
67	ACSAA	21	1281	NA8 SN4 GE10 O30 (O H)4
69	ZEKGA	129	427	MN3 FE2 GE3 O12
70	JSSCB	2	612	MG28 GE10 C48
70	KRISA	15	47	FR2 GE2 O7
72	AMMIA	57	62	MN2 GE O4

72	JSSCB	4	262	MG28 GE7.5 O38 F10
#1				SR GA2 GE2 O8
IRON				
65	ACCRA	19	971	LU3 FE2 FE3 O12
65	ACCRA	19	971	YE3 FE2 FE3 O12
65	ACCRA	19	971	DY3 FE2 FE3 O12
65	ACCRA	19	971	SM3 FE2 FE3 O12
65	ACCRA	19	971	Y3 FE2 FE3 O12
67	ACCRA	22	766	NA3 FE5 O9
70	ACBCA	826	1469	CA2 FE2 O5
74	JSSCB	10	122	Y3 SC FE4 O12
74	JSSCB	10	122	Y2.3 PR0.7 SC FE4 O12
74	JSSCB	10	122	Y PR2 SC FE4 O12
74	JSSCB	10	122	PR3 SC FE4 O12

LITHIUM

65	ACCRA	18	717	LI2 S O4 . H2 O
66	JCPSA	44	3348	LI R O2
72	ZEKGA	135	175	LI AL SI O4
73	AMMIA	58	681	LI AL SI O4
73	AMMIA	58	681	LI AL SI O4
73	AMMIA	58	681	LI AL SI O4
73	AMMIA	58	681	LI AL SI O4
73	JSSCB	6	538	LI3 V O4
74	ACBCA	830	831	LI N2 H5 S O4

BETA EUCRYPTITE
BETA EUCRYPTITE
BETA EUCRYPTITE, 200 DEGREES
BETA EUCRYPTITE, 335 DEGREES
BETA EUCRYPTITE, 400 DEGREES

MANGANESE

66	NBSCA	539	9,35	MA AL2 O4
67	INCCA	6	503	K MN O4
67	INCCA	6	507	K2 MN O4

GALAXITE

MOLYBDENUM

67	JCPSA	46	2052	ALPHA ZN MC O4
68	JCPSA	48	2619	CU MJ O4
72	ACBCA	828	60	PROTOTYPIC GD2 (MC O4)3
72	ACBCA	828	60	FERROIC GD2 (MJ O4)3

PHOSPHORUS

60	ACCRA	13	325	LI MN P O4	
63	ACCRA	16	79	H16 C10 N5 O4 P O4	
64	ACCRA	17	1097	(CL C6 H4 O)2 P O (O H)	
64	ACCRA	17	1139	NA4 P4 O12 . 4(H2 O)	
65	ACCRA	18	226	NA3 P3 O9	
65	ZEKGA	121	87	CU AL6 (P O4)4 (O H)8 . 4(H2 O)	TURQUOIS
66	ZEKGA	123	161	AL P O4	
67	CJCHA	45	2303	BETA ZN3 (P O4)2	
67	INOCA	6	119	LI3 P O4	
68	INOCA	7	1345	ALPHA CA2 P2 O7	
68	ACBCA	824	1621	NA P O3	
68	AMMIA	53	1096	AL2 P O4 (O H)3	AUGELLITE
68	ZEKGA	127	21	AL3 (P O4)2 (O H)3 . N(H2 O)	WAVELLITE
69	ACBCA	825	2170	CA2 P O4 CL	
69	ZEKGA	130	1	(MN,FE)2 F P O4	TRIPLITE
69	ZEKGA	130	148	K ZR2 (P O4)3	
69	ZEKGA	130	261	ZN3 (P O4)2 . 4(H2 O)	PARAHOPEITE
70	ACBCA	826	840	CA2 MN (P O4)2 . 2(H2 O)	FAIRFIELDITE
70	CIWYA	88	290	LI FEO.8 MNO.2 P O4	TRIPHYLITE
70	JSSCB	1	120	ALPHA ZN2 P2 O7	
71	ACBCA	827	2124	NA3 P O4 . (NA O H)0.2 . 12(H2 O)*	
71	AMMIA	56	1527	MN3 (O H)2 B (O H)4 P O4	SEAMANITE
71	TMPMA	16	79	CA7 MG9 (CA,MG)2 (P O4)12	
72	ACBCA	828	201	CU2 P4 O12	
72	ACBCA	828	2505	NM2 P O4 CL	
72	ACBCA	828	2525	MA2 P O4 F	
72	ACBCA	828	2721	CU NA2 (P O3)4	
72	ACBCA	828	2740	NA6 P6 O18 . 6(H2 O)	
72	ACBCA	828	2883	CO2 P2 O7	
72	ACBCA	828	3461	MG2 P O4 CL	
72	ACBCA	828	3668	SR5 (P O4)3 O H	
72	AMMIA	57	45	FEO.7 MNO.3 P O4	HETEROSITE
72	AMMIA	57	397	K2 FE4 (O H)2 (H2 O)2 (P O4)4*	LEUCOPHOSPHITE
72	AMMIA	57	1333	NA MN P O4	NATROPHILITE
72	BJFGA	55	47	K TI2 (P O4)3	
72	CJCHA	16	2519	NA4 P2 O7	
72	JSSCB	5	432	BETA V P O5	
73	ACBCA	829	141	LU P O4	
73	ACBCA	829	808	CD5 (P O4)3 CL	
73	ACBCA	829	2046	CA4 (P O4)2 O	
73	ACBCA	829	2541	MN5 (H O P O3)2 (P O4)2 . 4(H2 O)*	MUREAULITE
73	ACBCA	829	2721	N H4 H2 P O4	
74	ACBCA	830	1311	NA AL3 (P O4)2 (O H)4	BRAZILIANITE
74	ACBCA	830	1381	SR5 (P O4)3 CL	
74	AMMIA	59	280	NA2 FE2 AL (P O4)3	NYLLITE

74	AMMIA	59	567	EA (MN,FE)2 AL2 (C H)3 (P O4)3	BJAREBYITE
74	AMMIA	59	573	(CU,ZN)2 ZN P O4 (C H)3	VESZELYITE
74	AMMIA	59	1267	CA BE2 P2 O8	MURLBUTITE
74	CJCHA	52	1155	CA18 MG2 H2 (P O4)14	WHITLOCKITE
74	JSSCB	10	12	NA7 MG4.5 (P2 O7)4	
74	JSSCB	10	232	BETA CA3 (P O4)2	

SELENIUM

51	JCSOA	1951	968	H2 SE O4
65	ACCRA	18	795	SE O3
68	ZAACA	358	125	MN SE O4
68	ZAACA	358	125	CO SE O4
68	ZAACA	358	125	NI SE O4
69	ACBCA	825	19	CU (N H3)4 SE O4
69	ACSAA	23	1607	HG2 SE O4
70	ACBCA	826	436	NA2 SE O4
70	ACBCA	826	1451	K2 SE O4
70	ACBCA	826	2062	CU (N H2 (C H2)3 N H2)2 SE O4 *
70	ZAACA	379	204	NI SE O4 . 6(H2 O)
71	ACBCA	827	2341	C10 H11 N O . H2 SE O4
73	CRSC1	2	163	K2 CO (SE O4)2 . 2(H2 O)
74	JSSCB	9	63	NA2 CU (SE O4)2 . 2(H2 O)

SILICON

61	ZEKGA	115	269	AL2 SI O5	ANDALUSITE
62	ACCRA	15	583	(CA,NA) (MG,AL)6 (H,AL)6 SI6 O30	TOURMALINE
62	ZEKGA	118	127	AL2 SI O5	SILLIMANITE
63	ACCRA	16	462	SI O2	ALPHA QUARTZ
63	ZEKGA	118	337	AL2 SI O5	KYANITE
66	ACCRA	20	301	CA4 (BE O H)2 AL2 SI9 O26	BAVENITE
66	AMMIA	51	1068	AL3 MG2 SI5 AL O18 . N(H2 O)	CORDIERITE
67	ACCRA	23	434	NA8 SI6 AL6 (24 CL2	SODALITE
67	ZEKGA	124	180	ZN4 SI2 O7 (C H)2 . H2 O	HEMIMORPHITE
68	AMMIA	53	807	MG1.8 FEG.2 SI O4	FORSTERITE
68	AMMIA	53	807	MG1.1 FEG.9 SI O4	HYALOSIDERITE
68	AMMIA	53	807	MG FE SI O4	HORTONALITE
68	AMMIA	53	807	FE2 SI O4	FAYALITE
68	AMMIA	53	1139	AL18 FE4 SI8 O44 (C H)4	STAUROLITE
68	LITHA	1	275	AL2 BE3 SI6 O18	BERYL
68	LITHA	1	275	AL1.9 CRO.1 BE3 SI6 O18	EMERALD
68	LITHA	1	275	AL2 BE3 SI6 O13 . N(H2 O)	HYDROUS BERYL
68	LITHA	1	275	AL1.9 CRO.1 BE3 SI6 O18 . N(H2 O)*	HYDROUS EMERALD
69	ACBCA	525	1503	NA AL SI3 O8	LOW ALBITE
69	AMMIA	54	376	MG2 SI O4 . MG F1.8 (C H)0.2	NORBERGITE

69	PJTOA	6	102	K AL LI2 SI4 O10 F2	FLUOR-POLYLITHIONITE
69	MSAPA	2	31	LI AL SI2 O6	SPODUMENE
69	MSAPA	2	31	LI FE SI2 O6	
69	MSAPA	2	31	NA AL SI2 O6	JADEITE
69	MSAPA	2	31	NA CR SI2 O6	UREYITE
69	MSAPA	2	31	NA FE SI2 O6	ACMITE
69	MSAPA	2	31	NA IN SI2 O6	
69	MSAPA	2	31	CA MG SI2 O6	
69	MSAPA	2	101	LI1.2 MG6.5 SI7.8 O21.7 F2.3	DIOPSIDE
69	MSAPA	2	117	FE6.2 AL0.8 SI8 O22 (O H)2	PROTOAMPHIBOLE
69	MSAPA	2	117	CA0.4 MG5.6 MN SI8 O22 (O H)2	GRUNERITE
69	MSAPA	2	117	CA1.9 NA0.1 MG5 SI8 O22 (O H)2	P. MANGANOAN CUMMINGTONITE
69	MSAPA	2	117	CA0.2 MG4.1 FE0.5 MN2.0 SI8 O*	TREMOLITE
69	MSAPA	2	117	NA1.8 CA0.2 AL1.6 MG2.4 FE SI*	C. MANGANOAN CUMMINGTONITE
69	ZEKGA	129	381	SI O2	GLAUCOPHANE
69	ZEKGA	130	185	CA SI O3	COESITE
69	ZEKGA	130	427	CA2 ZN SI2 O7	
70	AMMIA	55	1146	MN7 SI3 O12 (O H)2	HARDYSTONITE
70	AMMIA	55	1182	MG5 (SI O4)2 F1.3 (O H)0.7	LEUCOPHOENICITE
70	AMMIA	55	1541	H NA BE SI3 O8	CHONDRODITE
70	AMMIA	55	1945	NA0.5 (AL,MG,FE)7.0 (SI,AL)8.0*	EPIDIDYMITE
70	AMMIA	55	1945	NA0.6 (AL,MG,FE)6.9 (SI,AL)8.0*	GEDRITE
70	ZEKGA	131	314	CA NA AL SI2 O7	GEORITE
70	ZEKGA	132	288	CA5 SI2 O7 (C O3)2	SODA MELILITE
71	ACCSA	101	250	CA AL2 SI2 O8 . 4(H2 O)	TILLEYITE
71	AMMIA	56	24	AL2 SI O4 F2	GISMONDITE
71	AMMIA	56	782	ZR SI O4	TOPAZ
71	AMMIA	56	791	MG3 AL2 SI3 O12	ZIRCON
71	AMMIA	56	791	FE3 AL2 SI3 O12	PYROPE
71	AMMIA	56	791	CA3 AL2 SI3 O12	ALMANDINE
71	ZEKGA	133	75	CA AL2 SI2 O8	GROSSULAR
72	ACBCA	828	114	MN4 (BE SI O4)3 S	ANGRTHITE
72	AMMIA	57	1089	AL13 SI5 F4 (O H)14 O20 CL	HELVITE
72	AMMIA	57	1345	NA2 BE2 SI6 O15 . H2 O	ZUNYITE
72	KRISA	16	1167	BE2 SI O4	EUDIDYMITE
72	ZEKGA	135	175	LI AL SI O4	PHENACITE
73	ACBCA	829	73	CA7 SI6 O18 C O3 . 2(H2 O)	BETA EUCRYPTITE
73	AMMIA	58	676	NA2 AL2 SI3 O10 . 2(H2 O)	SCAWTITE
73	AMMIA	58	676	NA2 AL2 SI3 O10 . 2(H2 O)	NATROLITE
73	AMMIA	58	676	NA2 AL2 SI3 O10 . 2(H2 O)	NATROLITE, 88 DEGREES
73	AMMIA	58	676	NA2 AL2 SI3 O10 . 2(H2 O)	NATROLITE, 146 DEGREES
73	AMMIA	58	681	LI AL SI O4	NATROLITE, 198 DEGREES
73	AMMIA	58	681	LI AL SI O4	BETA EUCRYPTITE
73	AMMIA	58	681	LI AL SI O4	BETA EUCRYPTITE, 200 DEGREES
73	AMMIA	58	681	LI AL SI O4	BETA EUCRYPTITE, 335 DEGREES
73	AMMIA	58	909	CA B SI O4 (O H)	BETA EUCRYPTITE, 400 DEGREES
73	ZEKGA	138	419	CA FE SI2 O6	DATOLITE
74	ACBCA	830	1882	NA IN SI2 O6	

74	AMMIA	59	486	FE2 S1 O4	
74	AMMIA	59	486	NI2 S1 O4	
74	AMMIA	59	1166	BA FE S14 C10	GILLESPIE
75	ACBCA	331	560	SR GA2 S12 O8	
75	ACBCA	831	560	BA GA2 S12 O8	
#1				SR GA2 S12 O8	
#2				SR GA2 S12 O8	

SULPHUR

60	JCSOA	1960	5112	K2 S2 O7	
62	ZEKGA	117	344	MG (N H4)2 (S O4)2 . 6(H2 O)	
64	ACCRA	17	235	MG S O4 . 6(H2 O)	
64	ACCRA	17	863	MG S O4 . 4(H2 O)	
64	ACCRA	17	1167	FE S O4 . 7(H2 O)	MELANTERITE
64	ACCRA	17	1361	MG S O4 . 7(H2 O)	
65	ACCRA	18	717	LI2 S O4 . H2 O	
65	AMMIA	50	1929	K FE (S C4)2 . H2 O	KRAUSITE
67	ACCRA	22	775	FE (N H4)2 (S O4)2 . 6(H2 O)	
67	ACCRA	22	775	CO (N H4)2 (S O4)2 . 6(H2 O)	
67	ZEKGA	124	358	K2 CA (S O4)2 . H2 O	SYNGENITE
68	ACBCA	824	760	FE (ZN,MN,MG,FE) (S C4)2 C H	BOTRYOGEN
68	ZEKGA	127	261	FE2 (S O4)2 C . 7(H2 O)	AMARANTITE
69	ACBCA	825	19	CU (N H3)4 S O4 . H2 O	
69	ACBCA	825	304	BE S O4 . 4(H2 O)	
69	ACBCA	825	676	CU (N H4)2 (S O4)2 . 6(H2 O)	
69	ACBCA	825	1696	K2 S5 O16	
69	ACBCA	825	2298	N H4 LI S O4	
70	ACBCA	826	335	ZN (C (N H2)3)2 (S O4)2	
70	ACBCA	826	536	N2 H6 S O4	
70	AMMIA	55	78	FE3 (S O4)4 . 14(H2 O)	ROEMERITE
70	AMMIA	55	378	NA12 MG7 S13 O52 . 15(H2 O)	LOEWEITE
70	AMMIA	55	1534	FE(2-X) AL(X) (S O4)3 . 9(H2 O)	COQUIMBITE
71	AMMIA	56	1917	K FE (S O4)2	YAVAPAIITE
71	AMMIA	56	1917	K FE (S O4)2 . 4(H2 O)	GOLDICHITE
72	ACBCA	828	236	FE N H4 (S O4)2 . 3(H2 O)	
72	ACBCA	828	2845	K2 S O4	
72	AMMIA	57	1081	NA AL (S O4)2 . 11(H2 O)	MENDOCZITE
72	AMMIA	57	1325	K MG S O4 CL . 2.75(H2 O)	KAINITE
72	TMPMA	18	185	K2 FEB AL (S O4)12 . 18(H2 O)	VOLTAITE
73	ACBCA	829	360	LI2 S O4	
73	ACBCA	829	2732	V O S O4 . 3(H2 O)	
73	ACSAA	27	814	NA2 S O4	THENARDITE
73	ACSAA	27	2614	ZR (O H)2 S O4 . H2 O	
74	ACBCA	830	662	CS TI (S C4)2 . 12(H2 O)	
74	ACBCA	830	831	LI N2 H5 S O4	
74	ACBCA	830	921	CA S O4 . 2(H2 O)	GYPSUM

74 ACBCA 830 1640 BETA RB2 S O4

TITANIUM

73 ACBCA 829 2009 BETA BA2 TI O4

TUNGSTEN

65 ACCRA 18 88 CA W O4
72 ACBCA 828 3174 BETA SN W O4

VANADIUM

68 ACBCA 824 292 Y V O4
70 INOCA 9 2259 CA2 V O4 CL
72 CJCHA 50 3944 CU3 V2 O8
72 JSSCB 4 29 FE V O4
73 ACBCA 829 141 Y V O4
73 ACBCA 829 1338 CU5 V2 O10
73 CJCHA 51 265 LI V O3
73 CJCHA 51 1004 ALPHA ZN2 V2 O7
73 JSSCB 6 538 LI3 V O4
74 ACBCA 830 1628 ALPHA NA V O3
74 ACBCA 830 2491 MG2 V2 O7
74 NJMMA 1974 210 CA5 (V O4)3 O H
75 ACBCA 831 603 ALPHA CUPRIC DIVANADATE

ZINC

67 ZEKGA 124 180 ZN4 Si2 O7 (O H)2 . H2 O HEMIMORPHITE
69 ACBCA 825 1233 ZN O
69 ZEKGA 130 261 ZN3 (P O4)2 . 4(H2 O) PARASOPEITE
69 ZEKGA 130 427 CA2 ZN Si2 O7 HARDYSTONITE
70 ACBCA 826 335 ZN (O (N H2)3)2 (S O4)2
71 ACBCA 827 672 ZN B4 O7
72 PRREA 27 76 ZN GA2 O4
73 ACSAA 27 1541 ZN S O3 . 2.5(H2 O)
74 AMMIA 59 573 (CU,ZN)2 ZN P O4 (O H)3 VESZELYITE
#3 ACBCA DISODIUM ZINCOSILICATE

* INDICATES TRUNCATED FORMULA

- #1 M. PHILLIPS, H. KROLL, H. PENTINGHAUS, AND P. RIBBE (IN PRESS) (PARACELSIAN STRUCTURE)
- #2 M. CALLERI (PERSONAL COMMUNICATION, 1973) (PARACELSIAN STRUCTURE)
- #3 K. F. HESSE, F. LIEBAU, AND H. BOHM (IN PRESS)

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ABSTRACT

Distortions in coordination polyhedra may be effected by (1) displacement of the central atom from a reference position within the polyhedron (bond-length distortion) and (2) displacement of the ligands from the apices of some reference polyhedron (edge-length distortion). For tetrahedral coordination the bond-length distortion parameter (BLDP) and edge-length distortion parameter (ELDP), which are linearly related to these two types of distortions, have been defined and compared with other distortion parameters currently in use.

Among tetrahedral oxyanions of non-transition elements, ELDP values of those exhibiting small bond-length distortions (e.g., LiO_4^{7-} and GaO_4^{5-}) increase with the number of shared edges. For the oxyanions that show small edge-length distortions (e.g., PO_4^{3-} and SO_4^{2-}) BLDP is related to the degree of tetrahedral polymerization. Although the relationships for oxyanions exhibiting fairly large ranges in both BLDP and ELDP (e.g., SiO_4^{4-}) are not as straightforward, the same trends are recognized. For tetrahedral oxyanions of transition metals these structural trends are not well-developed.

For tetrahedral oxyanions of all but one non-transition element considered, bond angle variations are entirely or largely a function of O...O variations; for SO_4^{2-} , O-T-O variations are mainly a function of T-O bond length variations. With regard to transition metal oxyanions, those of V^{5+} , Cr^{6+} , and Mo^{6+} tend to have bond angles near 109.47° , while those of Fe^{3+} and Zn^{2+} behave much like oxyanions of non-transition elements. Baur's (1970) Rule 5 does not represent a generally adequate

model for tetrahedral oxyanions.

Revised values for five of Shannon and Prewitt's (1971) effective ionic radii are presented, along with new values for the effective tetrahedral ionic radii of Ti^{4+} and Cu^{2+} .

For tetrahedral oxyanions of non-transition elements the maximum value of bond-length distortion appears to be limited by a phenomenon analogous to the "rattling" of the hard-sphere model. The maximum edge-length distortions appear to be limited by coulombic repulsions between bonding electron concentrations, with non-bonded interactions becoming important at very small O...O separations. For transition metal oxyanions it appears that the same factors may limit the maximum edge-length distortions. There is evidence for greater polarization of either the oxygen atoms or cations (or both) in the oxyanions of transition metals than in those of non-transition elements.

The crystal structure of slawsonite ($SrAl_2Si_2O_8$) has been refined to $R = 0.048$. Cell dimensions are positively correlated with both $\langle M-O \rangle$ and $\langle T-O \rangle$. Slawsonite appears to be fully ordered with $\langle Si-O \rangle = 1.624\text{\AA}$ and $\langle Al-O \rangle = 1.748\text{\AA}$. Even where ordering is complete, $\langle Si-O \rangle$ apparently varies with structure type and cation combination.

The crystal structure of a celsian ($Cn_{\sim 95}Or_{\sim 5}$) has been refined to $R = 0.034$. Results are very similar to those of Newnham and Megaw (1960). In both celsians, bond lengths suggest that there is ~ 17 percent disorder in excess of that required by the deviation of the Al:Si ratio from 1:1. Considering similar synthetic materials which show partial disorder, it is concluded that the Al-avoidance principle is not operative for compounds with the celsian structure.