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

by

Dana T. Griffen

Dissertation submitted to the Graduate Faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

Geological Sciences

APPROVED:

______________________________
G.V. Gibbs, Chairman

______________________________  ______________________________
P.H. Ribbe  F.D. Bloss

______________________________  ______________________________
D.A. Hewitt  J.C. Schug

June, 1975

Blacksburg, Virginia
ACKNOWLEDGMENTS

The author has benefitted from discussions with Drs. G.V. Gibbs, P.H. Ribbe, D.A. Hewitt, F.D. Bloss, and J.C. Schug, all of whom served as members of his advisory committee, and with .

and are gratefully acknowledged for the typing of the manuscript and drafting of the figures, respectively. The following agencies provided partial financial support: The National Science Foundation (Grant GA-30864X), the Research Division of the Virginia Polytechnic Institute and State University (computing and microprobe facilities), and the Office of Education (National Defense Education Act, Title IV Fellowship).
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>ii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vi</td>
</tr>
<tr>
<td><strong>I. DISTORTIONS IN THE TETRAHEDRAL OXYANIONS OF CRYSTALLINE SUBSTANCES</strong></td>
<td>1</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>2</td>
</tr>
<tr>
<td>THE GEOMETRICAL NATURE OF POLYHEDRAL DISTORTIONS</td>
<td>4</td>
</tr>
<tr>
<td>Bond-length and edge-length distortions</td>
<td>4</td>
</tr>
<tr>
<td>Distortion parameters</td>
<td>5</td>
</tr>
<tr>
<td>COMPARISON OF BLDP AND ELDP WITH OTHER DISTORTION PARAMETERS</td>
<td>11</td>
</tr>
<tr>
<td>Type I methods</td>
<td>11</td>
</tr>
<tr>
<td>Type II methods</td>
<td>13</td>
</tr>
<tr>
<td>Type III methods</td>
<td>14</td>
</tr>
<tr>
<td>ANALYSIS OF OBSERVED DISTORTIONS IN TETRAHEDRAL OXYANIONS</td>
<td>16</td>
</tr>
<tr>
<td>Tetrahedral oxyanions of non-transition elements</td>
<td>16</td>
</tr>
<tr>
<td>Relationships among bond lengths, edge lengths, and bond angles</td>
<td>25</td>
</tr>
<tr>
<td>Tetrahedral oxyanions of transition metals</td>
<td>32</td>
</tr>
<tr>
<td>Relationships among bond lengths, edge lengths, and bond angles</td>
<td>34</td>
</tr>
<tr>
<td>ANALYSIS OF DISTORTION RANGES OBSERVED FOR TETRAHEDRAL OXYANIONS</td>
<td>37</td>
</tr>
<tr>
<td>Tetrahedral oxyanions of non-transition elements</td>
<td>37</td>
</tr>
<tr>
<td>Tetrahedral oxyanions of transition metals</td>
<td>49</td>
</tr>
<tr>
<td>TABLE OF CONTENTS (CONTINUED)</td>
<td>Page</td>
</tr>
<tr>
<td>---------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>CONCLUSION</td>
<td>57</td>
</tr>
<tr>
<td>II. THE CRYSTAL STRUCTURE OF SLAWSONITE (SrAl₂Si₂O₈)</td>
<td>60</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>61</td>
</tr>
<tr>
<td>EXPERIMENTAL PROCEDURES</td>
<td>63</td>
</tr>
<tr>
<td>DISCUSSION</td>
<td>69</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td>69</td>
</tr>
<tr>
<td>The tetrahedral framework</td>
<td>73</td>
</tr>
<tr>
<td>III. REFINEMENT OF THE CRYSTAL STRUCTURE OF CELSIAN</td>
<td>76</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>77</td>
</tr>
<tr>
<td>EXPERIMENTAL METHODS</td>
<td>81</td>
</tr>
<tr>
<td>DISCUSSION</td>
<td>88</td>
</tr>
<tr>
<td>Ordering of the tetrahedral sites</td>
<td>88</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>91</td>
</tr>
<tr>
<td>APPENDIX A</td>
<td>97</td>
</tr>
<tr>
<td>APPENDIX B</td>
<td>134</td>
</tr>
<tr>
<td>VITA</td>
<td>145</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td></td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Linear regression analyses for plots of $T-0$ vs. $&lt;0-T-O&gt;_3$</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>Regression statistics for relations among $T-0$, $O\cdots O$, and $O-T-0$ for oxyanions of five transition metals</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>Grand mean interatomic distances, mean distortion parameters, and ranges in distortion parameters for sixteen oxyanions</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>Revised effective ionic radii for tetrahedral coordination</td>
<td>44</td>
</tr>
<tr>
<td>5</td>
<td>Crystallographic data for slawsonite</td>
<td>62</td>
</tr>
<tr>
<td>6</td>
<td>Final atomic positional parameters for slawsonite</td>
<td>65</td>
</tr>
<tr>
<td>7</td>
<td>Isotropic and anisotropic temperature factors</td>
<td>66</td>
</tr>
<tr>
<td>8</td>
<td>Interatomic distances and angles in slawsonite</td>
<td>67</td>
</tr>
<tr>
<td>9</td>
<td>Crystallographic data for five paracelsian analogs and danburite</td>
<td>70</td>
</tr>
<tr>
<td>10</td>
<td>Crystal data for $M^{2+}T_2^{3+}T_4^{4+}O_8$ feldspar-type compounds</td>
<td>80</td>
</tr>
<tr>
<td>11</td>
<td>Fractional coordinates for celsian</td>
<td>84</td>
</tr>
<tr>
<td>12</td>
<td>Temperature factors and thermal ellipsoid data for celsian</td>
<td>85</td>
</tr>
<tr>
<td>13</td>
<td>Interatomic distances and angles in celsian</td>
<td>86</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>Linear relationships between distortions and distortion parameters</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>ELDP vs. BLDP for composite of all oxyanions studied</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>ELDP vs. BLDP for oxyanions of individual non-transition elements</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>Variation in distortion parameters with the number of shared tetrahedral edges and with tetrahedral polymerization</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>Distribution of data within the maximum distortion boundary for silicon oxyanions as a function of the number of shared edges</td>
<td>23</td>
</tr>
<tr>
<td>6</td>
<td>Distribution of data within the maximum distortion boundary for silicon oxyanions as a function of tetrahedral polymerization</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>Variations in tetrahedral bond angle with the mean length of the bonds forming the angle, and with the length of the edge subtended by the angle</td>
<td>28</td>
</tr>
<tr>
<td>8</td>
<td>Bond length vs. $&lt;O-T-O&gt;_3$ for oxyanions of non-transition elements</td>
<td>29</td>
</tr>
<tr>
<td>9</td>
<td>ELDP vs. BLDP for oxyanions of individual transition metals</td>
<td>33</td>
</tr>
<tr>
<td>10</td>
<td>Relationships between grand mean tetrahedral edge length and (a) mean ELDP and (b) range in ELDP for oxyanions of non-transition elements</td>
<td>38</td>
</tr>
<tr>
<td>11</td>
<td>Relationships between grand mean tetrahedral bond length and (a) mean BLDP and (b) range in BLDP for oxyanions of non-transition elements</td>
<td>39</td>
</tr>
<tr>
<td>12</td>
<td>Grand mean bond lengths vs. grand mean edge lengths and effective ionic radii for twenty species of tetrahedral oxyanions</td>
<td>43</td>
</tr>
</tbody>
</table>
LIST OF FIGURES (CONTINUED)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>Electronegativity of cation vs. (a) mean ELDP and (b) range in ELDP for non-</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>transition cations</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Electronegativity of cation . (a) mean BLDP and (b) range in BLDP for non-</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>transition cations</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Electronegativity as a function of effective ionic radii</td>
<td>52</td>
</tr>
<tr>
<td>16</td>
<td>Relationships between grand mean tetrahedral edge length and (a) mean ELDP</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>and (b) range in ELDP for oxyanions of transition metals</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Relationships between grand mean tetrahedral bond length and (a) mean BLDP</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>and (b) range in BLDP for oxyanions of transition metals</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Variations in cell dimensions as a function of the mean M-O bond lengths</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>in paracelsian analogs and danburite</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Cell dimensions vs. grand mean tetrahedral bond lengths for paracelsian</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>analogs and danburite</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Mean T-O-T angle as a function of mean M-O and grand mean T-O bond lengths</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>for paracelsian analogs and danburite</td>
<td></td>
</tr>
</tbody>
</table>
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 B03 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) =**

\[
\frac{1}{<T-0>} \left( \frac{4}{3} \sum_{i=1}^{4} \left( (T-0)_i - <T-0> \right)^2 \right)^{1/2} = \frac{1}{<T-0>} [\hat{\sigma}(T-0)], \text{ and (1)}
\]

**Edge-length distortion parameter (ELDP) =**

\[
\frac{1}{<O...O>} \left( \frac{6}{5} \sum_{i=1}^{6} \left( (O...O)_i - <O...O> \right)^2 \right)^{1/2} = \frac{1}{<O...O>} [\hat{\sigma}(O...O)] \text{ (2)}
\]

where \(T-0\) and \(O...O\) are individual bond lengths and edge lengths, \(\hat{\sigma}\) represents an unbiased estimated standard deviation (e.s.d.), and "O" represents a ligand which, for the applications to be considered in this study, is oxygen. The terms \(<T-0>\) and \(<O...O>\) are mean values for individual tetrahedra. Multiplication by \(1/<T-0>\) or \(1/<O...O>\) 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

\[
(C-O)^2 = (x_i - x)^2 + (y_i - y)^2 + (z_i - z)^2, \quad i = 1,2,3,4 \text{ (3)}
\]
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 \( <T-O> \) and \( <O_{\cdots}O> \) are population means; thus division by \( n = 4 \) or 6) is appropriate. In the latter case \( <T-O> \) and \( <O_{\cdots}O> \) 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 \( T_04 \) 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 Å; for the exceptional cases, the averages of the e.s.d.'s of the bond lengths were less than 0.010 Å and no individual bond length e.s.d. exceeded 0.013 Å. 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

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

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

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 \( <T-0> \) and \( \hat{\sigma}(T-0) \) 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 \( <O\cdots O> \) 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 \( T-0 \) distance is not in general equal to the circumcenter-to-oxygen distance, a theoretically better parameter for estimating bond length distortion is

\[
\text{BLDP}' = \frac{1}{C-0} \left\{ \frac{\sum_{i=1}^{4} \left[ (T-0)_i - (C-0) \right]^2}{3} \right\}^{1/2},
\]

where \( C-0 \) 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

\[ \langle \lambda_{\text{tet}} \rangle = \frac{4}{i=1} \left( \frac{l_i}{l_o} \right)^2 / 4 \quad \text{and} \]

\[ \sigma^2_{\theta(\text{tet})} = \frac{6}{i=1} \left( \theta_i - 109.47^\circ \right)^2 / 5. \]

Here \( l_i \) and \( \theta_i \) are the \( i^{\text{th}} \) 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 \( 109.47^\circ \) is generally not the true mean angle, \( \sigma^2_{\theta(\text{tet})} \) 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 \( \sigma^2_{\theta(\text{tet})} \) 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 $\sigma_{\theta}(\text{tet})$ could be substituted for either BLDP or ELDP in a two-parameter method of characterizing distortions; however the relationships between $\sigma_{\theta}(\text{tet})$ 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 $<\lambda_{\text{tet}}>$ and $\sigma_{\theta}(\text{tet})$ for a large variety of tetrahedral oxyanions, but observed that there are some cases in which $\sigma_{\theta}(\text{tet})$ might not give a reliable estimate of $<\lambda_{\text{tet}}>$. A comparison of the values of BLDP, ELDP, $\sigma_{\theta}(\text{tet})$, and $<\lambda_{\text{tet}}>$ for the tetrahedra used in Figure 1 shows that, for most species of tetrahedral oxyanions, $\sigma_{\theta}(\text{tet})$ and $<\lambda_{\text{tet}}>$ 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., $\text{BO}_{4}^{5-}$, $\text{PO}_{4}^{3-}$, and $\text{SO}_{4}^{2-}$, as discussed below); these show good correlations between $<\lambda_{\text{tet}}>$ or $\sigma_{\theta}(\text{tet})$ and BLDP, but poor correlations with ELDP. The second type consists of those oxyanions whose $0-T-0$ angles tend to be close to 109.47° (i.e., $\text{VO}_{4}^{3-}$, $\text{CrO}_{4}^{2-}$, and $\text{MoO}_{4}^{2-}$, as discussed below); for these $\sigma_{\theta}(\text{tet})$
is generally very small, and is not correlated well with BLDP, ELDP, or \( \lambda_{\text{tet}} \). Robinson et al. (1971) have given other examples of the failure of \( \sigma^2_{\theta(\text{tet})} \) to accurately predict \( \lambda_{\text{tet}} \). Since \( \lambda_{\text{tet}} \) is difficult to compute, is not always accurately predicted by \( \sigma^2_{\theta(\text{tet})} \), and cannot resolve edge-length and bond-length distortions, its use is not recommended. On the other hand, \( \sigma^2_{\theta(\text{tet})} \) 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 \( \sigma \), where

\[
\sigma^2 = \frac{1}{6} \sum_{i=1}^{6} [(O-T-O)_i - <O-T-O>]^2 / 6
\]

If \( <O-T-O> \) is considered as an exact population mean, then \( \sigma^2 \) is a true population variance. This parameter differs conceptually from \( \sigma^2_{\theta(\text{tet})} \) in that \( <O-T-O> \) is the mean angle rather than the ideal angle. Like \( \sigma^2_{\theta(\text{tet})} \), however, \( \sigma^2 \) 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

\[
\text{Distortion} = \left( \frac{\Delta R}{R} \right)^2.
\]

Applied to tetrahedra and rewritten, equation (9) becomes

\[
\left( \frac{\Delta R}{R} \right)^2 = \frac{1}{4} \sum_{i=1}^{4} \frac{[(T-O)_i - <T-0>]^2}{<T-0>} = \frac{1}{<T-0>} \sigma^2(T-0) = 0.75(\text{BLDP})^2. \tag{10}
\]

It is apparent that \( \left( \frac{\Delta R}{R} \right)^2 \) is a true population variance if the \( (T-0)_i \)
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, \( \alpha \), and angular distortion, \( \psi \), which are defined as follows:

\[
\alpha = \sum_{j=1}^{N} \log \frac{L_j}{L_1}
\]

\[
\psi = \sum_{j=1}^{3N-6} \tan \theta_j
\]
where \( N \) is the number of bonds, \( \ell_j \) and \( \ell_i \) are observed and ideal bond lengths, respectively, and \( \theta_i \) is the difference between observed and ideal angles. From the foregoing discussions it is clear that \( \alpha \) and \( \psi \) are generally not independent parameters.

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

\[
\text{DI(TO)} = \frac{1}{\langle T-O \rangle} \left[ \frac{4}{6} \sum_{i=1}^{4} \left| (T-O)_i - \langle T-O \rangle \right| \right], \quad \text{and} \quad \text{DI(OTO)} = \frac{1}{\langle O-T-O \rangle} \left[ \frac{6}{6} \sum_{i=1}^{6} \left| (O-T-O)_i - \langle O-T-O \rangle \right| \right], \quad \text{DI(OO)} = \frac{1}{\langle O\cdots O \rangle} \left[ \frac{6}{6} \sum_{i=1}^{6} \left| (O\cdots O)_i - \langle O\cdots O \rangle \right| \right].
\]

(13) (14) (15)

It is obvious that \( \text{DI(TO)} \) and \( \text{DI(OO)} \) measure the same quantities as do BLDP and ELDP, respectively, whereas \( \text{DI(OTO)} \) is analogous to \( \sigma^2 \) 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 \( \sigma^2 \) 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 \( \text{DI(TO)} \) and \( \text{DI(OO)} \) 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 $T_0^4$ 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 0-T-0 angles of a tetrahedron were ideal ($109.47^\circ$). 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 $O\cdot\cdot\cdot O$ 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, $O\cdot\cdot\cdot O$ 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 $\text{AsO}_4^{3-}$ 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 $O\cdot\cdot\cdot O$ 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 $\Delta p_o$, 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 $\Delta p_o$ 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 $\Delta p_o$ 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 indi-
cates 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 dis-
tortions 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 influ-
ence 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 varia-
tions 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:

\[
\log[\sin(0-T-0/2)] = a + b[\log<T-0>], \quad \text{(16)}
\]

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

In equation (16) \( <T-0> \) is the mean length of the two \( T-0 \) bonds which form the sides of the \( O-T-O \) 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 \( O\cdots O \) 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 \( T = \text{Al}, \text{Si}, \text{P}, \text{S} \) but increased again for \( \text{Cl} \). They also found that the correlation coefficient for equation (16) increased from \( \text{Al} \) to \( \text{Si} \) to \( \text{P} \), but decreased from \( \text{P} \) to \( \text{S} \) to \( \text{Cl} \); a generally similar trend was observed in plots of \( T-O \) vs. \( <O-T-O> \), where \( <O-T-O> \) is the average of the three angles common to a bond. They concluded that variations in \( O-T-O \) angles are dependent on changes in both bond lengths and edge lengths for oxyanions of \( \text{Si}, \text{P}, \text{S}, \) and \( \text{Cl} \), but almost entirely on changes in edge lengths for
oxygen ions of Al. Ribbe et al. (1972) examined the applicability of equations (16) and (17) to the \( \text{SiO}_4 \) and \( \text{AlO}_4 \) 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 oxygen ions 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. \( <O - T - O>_3 \), 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 oxygen ions, 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 oxygen ions of Li, Be, Al, Ga, Ge, and As. In addition, most of the angular variation for \( \text{BO}_4^{5-} \), \( \text{SiO}_4^{4-} \), \( \text{PO}_4^{3-} \), and \( \text{SeO}_4^{2-} \) tetrahedra appears to be due to edge length changes, although bond length variations do make a significant contribution. Only for \( \text{SO}_4^{2-} \) 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 $0 \cdots 0$ 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. $<O-T-O>_3$ for oxyanions of non-transition elements, where $<O-T-O>_3$ is the mean of the three angles in which a given bond is involved.
### Table 1

Linear regression analyses for plots of $T-O$ vs. $<O-T-O>_3$*

| 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 $\Delta p_0$ (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 $p_0$ with bond length is better for more electronegative cations, and that there is a moderate correlation between $p_0$ and $n(T-O)$, suggesting that $p_0$ (and hence $\Delta p_0$) 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. BLD 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 VI B 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 $d^3 s$ hybrid bonds as compared to $sp^3$ hybrid bonds, suggesting that small deviations from the ideal tetrahedral angle would cause a greater reduction in $\sigma$-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. $<O-T-O>_3$ 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 $<O-T-O$ for oxanions of five transition metals*

| Cation | $r$  | $a$    | $b$    | $|t|$ |
|--------|------|--------|--------|------|
| 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. $\log<T-O>$

| Cation | $r$  | $a$    | $b$    | $|t|$ |
|--------|------|--------|--------|------|
| 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 |

$log[\sin(O-T-O/2)]$ vs. $\log(O\cdots O)$

| Cation | $r$  | $a$    | $b$    | $|t|$ |
|--------|------|--------|--------|------|
| 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 | 2.777  | -0.003 | 1.2  |

$T-O$ vs. $<O-T-O>_3$

| Cation | $r$  | $a$    | $b$    | $|t|$ |
|--------|------|--------|--------|------|
| 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 | 2.777  | -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

<table>
<thead>
<tr>
<th>Cation</th>
<th>&lt;&lt;T-O&gt;&gt;</th>
<th>&lt;&lt;O•••O&gt;&gt;</th>
<th>Mean BLDP</th>
<th>Mean ELDP</th>
<th>Range in BLDP</th>
<th>Range in ELDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>2.009</td>
<td>3.249</td>
<td>0.0025</td>
<td>0.1365</td>
<td>0.0176</td>
<td>0.1923</td>
</tr>
<tr>
<td>Be</td>
<td>1.641</td>
<td>2.672</td>
<td>0.0095</td>
<td>0.0480</td>
<td>0.0276</td>
<td>0.1107</td>
</tr>
<tr>
<td>B</td>
<td>1.477</td>
<td>2.410</td>
<td>0.0197</td>
<td>0.0163</td>
<td>0.0859</td>
<td>0.0232</td>
</tr>
<tr>
<td>Al</td>
<td>1.750</td>
<td>2.854</td>
<td>0.0081</td>
<td>0.0316</td>
<td>0.0241</td>
<td>0.0808</td>
</tr>
<tr>
<td>Si</td>
<td>1.621</td>
<td>2.644</td>
<td>0.0112</td>
<td>0.0219</td>
<td>0.0405</td>
<td>0.0635</td>
</tr>
<tr>
<td>P</td>
<td>1.536</td>
<td>2.506</td>
<td>0.0168</td>
<td>0.0150</td>
<td>0.0600</td>
<td>0.0319</td>
</tr>
<tr>
<td>S</td>
<td>1.474</td>
<td>2.406</td>
<td>0.0153</td>
<td>0.0076</td>
<td>0.1340</td>
<td>0.0197</td>
</tr>
<tr>
<td>Ga</td>
<td>1.829</td>
<td>2.980</td>
<td>0.0078</td>
<td>0.0394</td>
<td>0.0162</td>
<td>0.0594</td>
</tr>
<tr>
<td>Ge</td>
<td>1.757</td>
<td>2.865</td>
<td>0.0059</td>
<td>0.0300</td>
<td>0.0180</td>
<td>0.0545</td>
</tr>
<tr>
<td>As</td>
<td>1.685</td>
<td>2.748</td>
<td>0.0080</td>
<td>0.0257</td>
<td>0.0372</td>
<td>0.0505</td>
</tr>
<tr>
<td>Se</td>
<td>1.643</td>
<td>2.679</td>
<td>0.0195</td>
<td>0.0192</td>
<td>0.0792</td>
<td>0.0365</td>
</tr>
<tr>
<td>V</td>
<td>1.716</td>
<td>2.802</td>
<td>0.0253</td>
<td>0.0261</td>
<td>0.0558</td>
<td>0.0456</td>
</tr>
<tr>
<td>Cr</td>
<td>1.654</td>
<td>2.701</td>
<td>0.0452</td>
<td>0.0276</td>
<td>0.0727</td>
<td>0.0449</td>
</tr>
<tr>
<td>Mo</td>
<td>1.759</td>
<td>2.873</td>
<td>0.0192</td>
<td>0.0189</td>
<td>0.0484</td>
<td>0.0496</td>
</tr>
<tr>
<td>Fe</td>
<td>1.871</td>
<td>3.051</td>
<td>0.0038</td>
<td>0.0488</td>
<td>0.0198</td>
<td>0.0585</td>
</tr>
<tr>
<td>Zn</td>
<td>1.963</td>
<td>3.199</td>
<td>0.0074</td>
<td>0.0372</td>
<td>0.0152</td>
<td>0.0604</td>
</tr>
</tbody>
</table>
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 0.304Å to 0.315Å. The placement of
the stippled bar depends, of course, on the choice of oxygen radius. Among the more recent estimates, Slater (1964) has given 0.60Å as the atomic radius of oxygen, Fumi and Tosi (1964) have given a crystal radius of 1.21-1.28Å (depending on coordination number and based on a radius for six-coordinated fluorine of 1.19Å), and Shannon and Prewitt (1969) have given an effective ionic radius of 1.35-1.42Å (depending on coordination number and based on an assumed radius of 1.40Å 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-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-O and O⋯O distances obey the linear relationship required by tetrahedral geometry. The other line, grand mean T-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

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radii of Shannon and Prewitt (1969)</th>
<th>Radii from this work</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(^{5+})</td>
<td>0.335</td>
<td>0.325</td>
</tr>
<tr>
<td>Be(^{2+})</td>
<td>0.27</td>
<td>0.28</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>--</td>
<td>0.63</td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>0.49</td>
<td>0.50</td>
</tr>
<tr>
<td>Li(^{+})</td>
<td>0.59</td>
<td>0.64</td>
</tr>
<tr>
<td>Mo(^{6+})</td>
<td>0.42</td>
<td>0.40</td>
</tr>
<tr>
<td>Ti(^{4+})</td>
<td>--</td>
<td>0.44</td>
</tr>
</tbody>
</table>
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 $Si_2O_6^-$ 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 $O\cdot\cdot\cdotO$ distances in crystals are $\sim2.2Å$ (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 ac-
cordance 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 inter-
action between ligands. Figure 10b is suggestive of coulombic inter-
actions 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 CaO$_4^{5-}$), 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

57
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 $109.47^\circ$, 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

\((\text{SrAl}_2\text{Si}_2\text{O}_8)\)
INTRODUCTION

The structure of paracelsian (BaAl$_2$Si$_2$O$_8$, $P2_1/α$), 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 (CaBe$_2$P$_2$O$_8$; Lindbloom, Gibbs, and Ribbe, 1974) and synthetic SrGa$_2$Si$_2$O$_8$\(^1\) and SrGa$_2$Ge$_2$O$_8$ (Phillips, Kroll, Pentinghaus, and Ribbe, 1975). Danburite (CaB$_2$Si$_2$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 SrAl$_2$Ge$_2$O$_8$ (Kroll and Phillips, in preparation) and BaGa$_2$Ge$_2$O$_8$ (Cali, pers. comm.). This study presents the structure of a new mineral, slawsonite (SrAl$_2$Si$_2$O$_8$), the Sr analog of paracelsian.

Barrer and Marshall (1964) synthesized pseudo-orthorhombic SrAl$_2$Si$_2$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, $P2_1/α$, suggest that slawsonite is isomorphous with paracelsian (Table 5).

\(^{1}\) SrGa$_2$Si$_2$O$_8$ has also been refined by Calleri and Gazzoni (Periodico di Mineralogia, XLIV, in press).
Table 5

Crystallographic data for slawsonite

<table>
<thead>
<tr>
<th></th>
<th>Barrer and Marshall (1964)</th>
<th>Erd, Nolf, and Smith (pers. comm.)</th>
<th>This study</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>8.910</td>
<td>8.895(1)*</td>
<td>8.888(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.343</td>
<td>9.359(1)</td>
<td>9.344(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.345</td>
<td>8.333(1)</td>
<td>8.326(3)</td>
</tr>
<tr>
<td>β (°)</td>
<td>~90</td>
<td>90.24(1)</td>
<td>90.33(2)</td>
</tr>
<tr>
<td>Vol. (Å³)</td>
<td>−</td>
<td>693.7(1)</td>
<td>691.5</td>
</tr>
</tbody>
</table>

* 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 62µm thick with sides measuring 140 × 217 × 155µm. 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 MoKα 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}Al_{2}Si_{2}O_{8}.

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-2θ scanning rate of 1°/min was used and intensities were measured in the range 0.12<sinθ/λ<1.22. Observed intensities were corrected for Lorentz-polarization effects and for absorption (μ_L = 93.4 cm^{-1}), and converted to F_{obs}² with the program DATALIB. These were weighted according to 1/σ², 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 SrGa$_2$Si$_2$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 3σ were omitted, and the remaining reflections were weighted according to $1/\sigma^2$. An extinction correction was applied, and refinement with isotropic temperature factors yielded an unweighted residual of 0.050 ($\omega R = 0.055$) for 1617 reflections. With the introduction of anisotropic temperature factors the refinement converged to $R = 0.048$ ($\omega R = 0.053$). 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

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>0.8902(1)*</td>
<td>0.4122(1)</td>
<td>0.2503(1)</td>
</tr>
<tr>
<td>T10</td>
<td>0.2321(2)</td>
<td>0.9249(2)</td>
<td>0.9311(2)</td>
</tr>
<tr>
<td>T1m</td>
<td>0.2405(2)</td>
<td>0.9199(2)</td>
<td>0.5605(2)</td>
</tr>
<tr>
<td>T20</td>
<td>0.0595(2)</td>
<td>0.2006(2)</td>
<td>0.9440(2)</td>
</tr>
<tr>
<td>T2m</td>
<td>0.0541(2)</td>
<td>0.1944(2)</td>
<td>0.5706(2)</td>
</tr>
<tr>
<td>O10</td>
<td>0.1910(4)</td>
<td>0.0934(4)</td>
<td>0.0100(5)</td>
</tr>
<tr>
<td>O1m</td>
<td>0.1875(4)</td>
<td>0.0740(4)</td>
<td>0.4937(5)</td>
</tr>
<tr>
<td>O20</td>
<td>0.1192(4)</td>
<td>0.3658(4)</td>
<td>0.9458(5)</td>
</tr>
<tr>
<td>O2m</td>
<td>0.1236(4)</td>
<td>0.3699(4)</td>
<td>0.5573(5)</td>
</tr>
<tr>
<td>O30</td>
<td>0.9202(4)</td>
<td>0.1919(4)</td>
<td>0.0699(4)</td>
</tr>
<tr>
<td>O3m</td>
<td>0.8979(4)</td>
<td>0.1923(4)</td>
<td>0.4399(5)</td>
</tr>
<tr>
<td>O4</td>
<td>0.0092(5)</td>
<td>0.1545(4)</td>
<td>0.7662(5)</td>
</tr>
<tr>
<td>O5</td>
<td>0.3139(4)</td>
<td>0.9252(4)</td>
<td>0.7407(5)</td>
</tr>
</tbody>
</table>

* e.s.d.'s, given in parentheses, refer to last decimal place.
<table>
<thead>
<tr>
<th>Atom</th>
<th>B (Å²)</th>
<th>Anisotropic temperature factors (× 10⁴)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>β₁₁</td>
</tr>
<tr>
<td>Sr</td>
<td>0.66(1)*</td>
<td>30(1)</td>
</tr>
<tr>
<td>T10</td>
<td>0.34(2)</td>
<td>9(2)</td>
</tr>
<tr>
<td>T1m</td>
<td>0.31(2)</td>
<td>6(2)</td>
</tr>
<tr>
<td>T20</td>
<td>0.27(2)</td>
<td>8(2)</td>
</tr>
<tr>
<td>T2m</td>
<td>0.30(2)</td>
<td>9(2)</td>
</tr>
<tr>
<td>O10</td>
<td>0.62(6)</td>
<td>21(4)</td>
</tr>
<tr>
<td>O1m</td>
<td>0.67(6)</td>
<td>25(5)</td>
</tr>
<tr>
<td>O20</td>
<td>0.48(6)</td>
<td>13(4)</td>
</tr>
<tr>
<td>O2m</td>
<td>0.59(6)</td>
<td>17(5)</td>
</tr>
<tr>
<td>O30</td>
<td>0.51(6)</td>
<td>13(4)</td>
</tr>
<tr>
<td>O3m</td>
<td>0.63(6)</td>
<td>10(4)</td>
</tr>
<tr>
<td>O4</td>
<td>0.89(6)</td>
<td>42(5)</td>
</tr>
<tr>
<td>O5</td>
<td>0.61(6)</td>
<td>12(4)</td>
</tr>
</tbody>
</table>

* e.s.d.'s, given in parentheses, refer to last decimal place.
Table 8
Interatomic distances (Å) and angles (°)

<table>
<thead>
<tr>
<th>T-0</th>
<th>0...0</th>
<th>0-T-0</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T10 tetrahedron</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T10-010</td>
<td>1.745(4)*</td>
<td>010-020</td>
</tr>
<tr>
<td>-020</td>
<td>1.757(4)</td>
<td>-030</td>
</tr>
<tr>
<td>-030</td>
<td>1.741(4)</td>
<td>-05</td>
</tr>
<tr>
<td>-05</td>
<td>1.749(4)</td>
<td>020-030</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>030-05</td>
</tr>
<tr>
<td>Mean</td>
<td>1.748</td>
<td></td>
</tr>
</tbody>
</table>

| **T1m tetrahedron** |        |        |
| T1m-01m    | 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  | 2.642(5) | 108.7(2) |
| Mean      | 1.623    |         | 2.649    | 109.5    |

| **T20 tetrahedron** |        |        |
| T20-010    | 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  | 2.675(5) | 111.8(2) |
| Mean      | 1.624    |         | 2.651    | 109.5    |

| **T2m tetrahedron** |        |        |
| T2m-01m    | 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  | 2.909(6) | 113.5(2) |
| Mean      | 1.748    |         | 2.853    | 109.4    |

* e.s.d.'s, given in parentheses, refer to last decimal place.
<table>
<thead>
<tr>
<th>Sr-O distances</th>
<th>T-O-T angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr-01</td>
<td>T10-010-T20</td>
</tr>
<tr>
<td>-01m</td>
<td>T1m-01m-T2m</td>
</tr>
<tr>
<td>-020</td>
<td>T10-020-T20</td>
</tr>
<tr>
<td>-02m</td>
<td>T1m-02m-T2m</td>
</tr>
<tr>
<td>-030</td>
<td>T10-030-T20</td>
</tr>
<tr>
<td>-03m</td>
<td>T1m-03m-T2m</td>
</tr>
<tr>
<td>-05</td>
<td>T20-04-T2m</td>
</tr>
<tr>
<td></td>
<td>T10-05-T1m</td>
</tr>
<tr>
<td>Mean</td>
<td>2.630</td>
</tr>
</tbody>
</table>
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, $\text{SrGa}_2\text{Ge}_2\text{O}_8$, with the largest framework, has larger cell dimensions than $\text{BaAl}_2\text{Si}_2\text{O}_8$, which contains the largest $M$ cation.

It appears from Figure 18 that variations in lattice parameters with $<M-O>$ 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 $\text{BaGa}_2\text{Ge}_2\text{O}_8$ (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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Paracelsian BaAl$_2$Si$_2$O$_8$</th>
<th>Slawsonite SrAl$_2$Si$_2$O$_8$</th>
<th>(Synthetic) SrGa$_2$Si$_2$O$_9$</th>
<th>(Synthetic) SrGa$_2$Ge$_2$O$_8$</th>
<th>Hurlbutite CaBe$_2$P$_2$O$_8$</th>
<th>Danburite CaB$_2$Si$_2$O$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>9.065(3)*</td>
<td>8.888(2)</td>
<td>9.001(1)</td>
<td>9.206(1)</td>
<td>8.299(1)</td>
<td>8.038(3)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.568(1)</td>
<td>9.344(2)</td>
<td>9.484(1)</td>
<td>9.660(1)</td>
<td>8.782(2)</td>
<td>8.752(5)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.574(5)</td>
<td>8.326(3)</td>
<td>8.399(1)</td>
<td>8.581(1)</td>
<td>7.798(3)</td>
<td>7.730(3)</td>
</tr>
<tr>
<td>β (°)</td>
<td>90.00(1)</td>
<td>90.33(2)</td>
<td>90.68(1)</td>
<td>90.43(1)</td>
<td>90.5</td>
<td>90.0</td>
</tr>
<tr>
<td>$&lt;M^{VII-0}&gt;$ (Å)</td>
<td>2.801</td>
<td>2.630</td>
<td>2.626</td>
<td>2.630</td>
<td>2.469</td>
<td>2.461</td>
</tr>
<tr>
<td>$&lt;T^{3+}-0&gt;$ (Å)</td>
<td>1.747</td>
<td>1.748</td>
<td>1.823</td>
<td>1.825</td>
<td>---</td>
<td>1.474</td>
</tr>
<tr>
<td>$&lt;T^{4+}-0&gt;$ (Å)</td>
<td>1.619</td>
<td>1.624</td>
<td>1.628</td>
<td>1.748</td>
<td>---</td>
<td>1.617</td>
</tr>
<tr>
<td>$&lt;&lt;T-0&gt;&gt;$ (Å)</td>
<td>1.683</td>
<td>1.686</td>
<td>1.726</td>
<td>1.786</td>
<td>1.577</td>
<td>1.546</td>
</tr>
<tr>
<td>Symbol</td>
<td>BASP</td>
<td>SASP</td>
<td>SGSP</td>
<td>SGGP</td>
<td>CBePP</td>
<td>CBSD</td>
</tr>
</tbody>
</table>

* 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 $<M-0>/<<T-0>>$ 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 $<M-0>$ and with increasing $<<T-0>>$, thus providing a physical interpretation for the parameter $<M-0>/<<T-0>>$. 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 Å 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 $\mathcal{M}$ 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 (BaAl$_2$Si$_2$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, \( \ell \) odd, indicating that celsian is body-centered and that the \( c \)-dimension of its unit cell is \( \sim 14.4 \text{Å} \), 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, \( \text{O}7; \) bytownite, \( \text{I}7 \)).

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, \( \ell \) even) and refining in space group \( C2/m \) with \( c = 7.2\text{Å} \), the Ba atom and one oxygen (O$_A^2$) on the mirror plane, one oxygen (O$_A^1$) 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_A, and O_A 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 $T_{10}$, $T_{1z}$, $T_{20}$, $T_{2z}$; $O_B^0$, $O_B^z$; $O_C^0$, $O_C^z$; $O_D^0$, $O_D^z$ to indicate that they are related by a pseudo-c/2 translation in the doubled cell.¹

Newnham and Megaw found that the mean $T$-0 bond lengths at $T_{10}$ and $T_{2z}$ (1.639 and 1.635Å) and at $T_{20}$ and $T_{1z}$ (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 $I2/a$ strontium feldspar (SrAl$_2$Si$_2$O$_8$, 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 $T$-0 bond lengths ($T_{10} = 1.626$; $T_{2z} = 1.630$; $T_{20} = 1.735$; $T_{1z} = 1.732$Å), when compared to the grand mean Si-0 bond length of 1.614Å and Al-0 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).
\( \text{Cn}_{0.84} \text{Or}_{1.18} \) 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

<table>
<thead>
<tr>
<th>Source, reference*</th>
<th>Celsian ($C_{n_{95}}O_{5.5}$)</th>
<th>Celsian ($C_{n_{84}}O_{18}$)</th>
<th>SrAl$_2$Si$_2$O$_8$</th>
<th>CaAl$_2$Si$_2$O$_8$</th>
<th>SrGa$_2$Si$_2$O$_8$</th>
<th>BaGa$_2$Si$_2$O$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>I2/α</td>
<td>I2/α</td>
<td>I2/α</td>
<td>P/̅I</td>
<td>I2/α</td>
<td>I2/α</td>
</tr>
<tr>
<td>$a$</td>
<td>8.622(4)**</td>
<td>8.627</td>
<td>8.388(3)</td>
<td>8.173(1)</td>
<td>8.481(2)</td>
<td>8.727(5)</td>
</tr>
<tr>
<td>α</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>93.11(1)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β</td>
<td>115.09(2)</td>
<td>115.2</td>
<td>115.2(1)</td>
<td>115.91(1)</td>
<td>115.48(4)</td>
<td>115.00(6)</td>
</tr>
<tr>
<td>γ</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>91.26(1)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Volume</td>
<td>1471.6</td>
<td>1467.0</td>
<td>1404.4</td>
<td>1337.7</td>
<td>1453.3</td>
<td>1530.0</td>
</tr>
</tbody>
</table>

* (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 Pasmeda, 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 x 60 x 70µm) 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 $\text{Ba}_{0.95}\text{K}_{0.05}\text{Al}_{1.95}\text{Si}_{2.05}\text{O}_8$ (Cn~95 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 $\text{M}_{2+}\text{T}_{3+}\text{T}_{4+}\text{O}_8$ 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 MoKα radiation in the range 0.1<sinθ/λ<1.2 for 'a' reflections and 0.1<sinθ/λ<1.0 for 'b' reflections; 'a' reflections were scanned at 1.0°2θ/min, and the weaker 'b' reflections at 0.25°2θ/min. In order to place the 'a' and 'b' reflections on the same scale, 20 weak 'a' reflections were measured at 0.25°2θ/min and 20 strong 'b' reflections were measured at 1°2θ/min. The best-fit conversion factor for scaling the raw 'b' intensities to a 1°2θ/min scan rate was then determined, and the 'b' $F_{\text{obs}}$ 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 DATALIB. 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 $1\sigma$ 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 $1/\sigma^2$.

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 $|F_{\text{obs}}| > 1\sigma$ 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 $<\text{Si-O}>$ increased and $<\text{Al-O}>$ decreased by 0.013Å, while the e.s.d.'s of all distances decreased by approximately 30 percent.
Table 11

Fractional coordinates

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>0.2827(1)*</td>
<td>0.0000(1)</td>
<td>0.0653(0)</td>
</tr>
<tr>
<td>T10</td>
<td>0.0096(3)</td>
<td>0.1820(2)</td>
<td>0.1103(2)</td>
</tr>
<tr>
<td>T1z</td>
<td>0.0076(3)</td>
<td>0.1830(2)</td>
<td>0.6148(2)</td>
</tr>
<tr>
<td>T20</td>
<td>0.7054(4)</td>
<td>0.1214(2)</td>
<td>0.1730(2)</td>
</tr>
<tr>
<td>T2z</td>
<td>0.7019(3)</td>
<td>0.1163(2)</td>
<td>0.6743(2)</td>
</tr>
<tr>
<td>O1A</td>
<td>0.0005(9)</td>
<td>0.1377(4)</td>
<td>-0.0002(5)</td>
</tr>
<tr>
<td>O2A</td>
<td>0.6206(7)</td>
<td>-0.003(5)</td>
<td>0.1438(4)</td>
</tr>
<tr>
<td>O1B</td>
<td>0.8349(8)</td>
<td>0.1368(5)</td>
<td>0.1119(5)</td>
</tr>
<tr>
<td>O2B</td>
<td>0.8198(8)</td>
<td>0.1370(5)</td>
<td>0.6136(5)</td>
</tr>
<tr>
<td>O1C</td>
<td>0.0220(8)</td>
<td>0.3062(5)</td>
<td>0.1210(5)</td>
</tr>
<tr>
<td>O2C</td>
<td>0.0293(8)</td>
<td>0.3120(5)</td>
<td>0.6312(5)</td>
</tr>
<tr>
<td>O1D</td>
<td>0.1836(8)</td>
<td>0.1296(5)</td>
<td>0.1958(5)</td>
</tr>
<tr>
<td>O2D</td>
<td>0.1900(8)</td>
<td>0.1231(5)</td>
<td>0.7017(5)</td>
</tr>
</tbody>
</table>

* e.s.d.'s, given in parentheses, refer to last decimal place.
Table 12

Isotropic and anisotropic temperature factors

<table>
<thead>
<tr>
<th>Atom</th>
<th>B(Å)</th>
<th>Anisotropic temperature factors ($\times 10^4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\beta_{11}$</td>
</tr>
<tr>
<td>Ba</td>
<td>0.99(1)*</td>
<td>28(1)</td>
</tr>
<tr>
<td>T10</td>
<td>0.70(5)</td>
<td>28(5)</td>
</tr>
<tr>
<td>T1z</td>
<td>0.49(5)</td>
<td>13(5)</td>
</tr>
<tr>
<td>T20</td>
<td>0.51(5)</td>
<td>22(5)</td>
</tr>
<tr>
<td>T2z</td>
<td>0.54(5)</td>
<td>16(4)</td>
</tr>
<tr>
<td>O1A</td>
<td>0.70(10)</td>
<td>47(9)</td>
</tr>
<tr>
<td>O2A</td>
<td>0.84(10)</td>
<td>31(9)</td>
</tr>
<tr>
<td>OB0</td>
<td>1.40(13)</td>
<td>64(14)</td>
</tr>
<tr>
<td>OBz</td>
<td>1.04(12)</td>
<td>39(12)</td>
</tr>
<tr>
<td>OC0</td>
<td>1.21(13)</td>
<td>55(13)</td>
</tr>
<tr>
<td>OCz</td>
<td>1.08(12)</td>
<td>24(12)</td>
</tr>
<tr>
<td>OD0</td>
<td>1.13(12)</td>
<td>38(12)</td>
</tr>
<tr>
<td>ODz</td>
<td>1.14(12)</td>
<td>41(12)</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>r.m.s. displacement</th>
<th>Angle (°) with respect to</th>
</tr>
</thead>
<tbody>
<tr>
<td>r</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>1</td>
<td>0.093(2)</td>
</tr>
<tr>
<td>2</td>
<td>0.109(2)</td>
</tr>
<tr>
<td>3</td>
<td>0.133(1)</td>
</tr>
</tbody>
</table>

* e.s.d.'s, given in parentheses, refer to last decimal place.
<table>
<thead>
<tr>
<th>T-O distances</th>
<th>0-O distances</th>
<th>0-T-0 angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{10}) tetrahedron</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T_{10}-0) &amp; (O_{1-0})</td>
<td>1.664(6)* &amp; 2.570(8) &amp; 102.7(3)</td>
<td></td>
</tr>
<tr>
<td>(-0_B) &amp; (-0_C) &amp; 1.628(7) &amp; 2.768(8) &amp; 114.4(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_C) &amp; (-0_D) &amp; 1.630(7) &amp; 2.589(9) &amp; 103.4(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_D) &amp; (O_B-O_C) &amp; 1.634(7) &amp; 2.710(8) &amp; 112.6(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_D) &amp; (O_C-O_D) &amp; 1.630(7) &amp; 2.725(9) &amp; 113.3(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1.639</td>
<td>2.673</td>
</tr>
<tr>
<td>(T_{1z}) tetrahedron</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T_{1z}-0) &amp; (O_{1-0_z})</td>
<td>1.727(6) &amp; 2.686(8) &amp; 102.4(3)</td>
<td></td>
</tr>
<tr>
<td>(-0_B) &amp; (-0_C) &amp; 1.721(7) &amp; 2.900(8) &amp; 115.5(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_C) &amp; (-0_D) &amp; 1.701(7) &amp; 2.669(9) &amp; 101.1(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_D) &amp; (O_B-O_C) &amp; 1.728(7) &amp; 2.859(8) &amp; 113.3(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_D) &amp; (O_C-O_D) &amp; 1.722(7) &amp; 2.898(8) &amp; 114.3(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1.719</td>
<td>2.803</td>
</tr>
<tr>
<td>(T_{20}) tetrahedron</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T_{20}-0) &amp; (O_{2-0})</td>
<td>1.728(7) &amp; 2.749(9) &amp; 106.5(3)</td>
<td></td>
</tr>
<tr>
<td>(-0_B) &amp; (-0_C) &amp; 1.702(6) &amp; 2.654(8) &amp; 100.7(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_C) &amp; (-0_D) &amp; 1.719(7) &amp; 2.788(9) &amp; 107.8(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_D) &amp; (O_B-O_C) &amp; 1.722(7) &amp; 2.856(8) &amp; 113.2(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_D) &amp; (O_C-O_D) &amp; 1.722(7) &amp; 2.843(8) &amp; 112.3(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1.718</td>
<td>2.799</td>
</tr>
</tbody>
</table>

* e.s.d.'s, given in parentheses, refer to last decimal place.
Table 13: continued

<table>
<thead>
<tr>
<th>T-O distances</th>
<th>0-O distances</th>
<th>0-T-O angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{2z} ) tetrahedron</td>
<td>( T_{2z}-0_{\text{A}} )</td>
<td>( 0_{\text{A}}-0_{\text{B}} )</td>
</tr>
<tr>
<td>( T_{2z}-0_{\text{A}} )</td>
<td>1.650(7)</td>
<td>2.639(9)</td>
</tr>
<tr>
<td>(-0_{\text{B}} )</td>
<td>1.621(6)</td>
<td>2.561(8)</td>
</tr>
<tr>
<td>(-0_{\text{C}} )</td>
<td>1.643(7)</td>
<td>2.668(9)</td>
</tr>
<tr>
<td>(-0_{\text{D}} )</td>
<td>1.630(7)</td>
<td>2.707(7)</td>
</tr>
<tr>
<td>Mean</td>
<td>1.636</td>
<td>2.668</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ba polyhedron</th>
<th>( T_{1}-0_{\text{A}} )</th>
<th>( T_{1}-0_{\text{B}} )</th>
<th>( T_{1}-0_{\text{C}} )</th>
<th>( T_{1}-0_{\text{D}} )</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 0_{\text{A}} )</td>
<td>2.641(5)</td>
<td>( T_{1}-0_{\text{A}}-T_{1z} )</td>
<td>139.6(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_{\text{A}} )</td>
<td>2.847(6)</td>
<td>( T_{1}-0_{\text{B}}-T_{2z} )</td>
<td>133.9(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_{\text{A}} )</td>
<td>2.854(6)</td>
<td>( T_{1}-0_{\text{C}}-T_{2} )</td>
<td>149.9(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_{\text{D}} )</td>
<td>2.903(6)</td>
<td>( T_{1z}-0_{\text{B}}-T_{2z} )</td>
<td>148.9(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_{\text{B}} )</td>
<td>2.916(6)</td>
<td>( T_{1z}-0_{\text{C}}-T_{2} )</td>
<td>130.3(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_{\text{D}} )</td>
<td>2.924(7)</td>
<td>( T_{1z}-0_{\text{D}}-T_{2} )</td>
<td>139.4(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_{\text{C}} )</td>
<td>3.124(6)</td>
<td>( T_{1z}-0_{\text{D}}-T_{2z} )</td>
<td>137.8(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-0_{\text{D}} )</td>
<td>3.150(7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>2.862 (CN=7)</td>
<td>138.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.923 (CN=9)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
DISCUSSION

The results of this structure refinement are surprisingly similar to those obtained for \( \text{Cn}_{84}\text{Or}_{18} \) by Newnham and Megaw (1960), particularly with regard to the tetrahedral 0···O distances, O-T-O angles, and mean T-O and Ba,K-O bond lengths. Only for \( T_2O \) do the corresponding \( <T-O> \) distances in the two structures differ by more than 0.002Å. Despite the difference in chemical composition the mean Ba,K-O distances are also statistically identical, whether the \( M \)-site is considered 7- or 9-coordinated. As in \( \text{Cn}_{84}\text{Or}_{18} \) the Ba,K and \( O_{A1} \) atoms lie statistically on the \( \sigma \)-glide and \( O_{A2} \) 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 Al:Si ratio is 1:1 and every oxygen atom forms a bridge between an \( \text{AlO}_4 \) and an \( \text{SiO}_4 \) tetrahedron. The ordering scheme in celsian does not appear to be as straightforward. In both \( \text{Cn}_{84}\text{Or}_{18} \) and \( \text{Cn}_{95}\text{Or}_{5} \) some degree of disorder is inevitable since the Al: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-O bond lengths, when compared to those in anorthite (Wainwright and Starkey, 1971), indicate the presence of an additional \( \sim 0.35 \) 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, SrGa$_2$Si$_2$O$_8$, has mean Si-O and Ga-O distances of 1.614 and 1.821Å, respectively, clearly indicating complete order in the tetrahedral framework. By contrast the mean Si-O and Ga-O distances in BaGa$_2$Si$_2$O$_8$ are 1.634Å and 1.805Å, 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 (~0.02Å), 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 BaGa$_2$Si$_2$O$_8$ is unnecessary. At least three circumstances mitigate against their conclusion. First, with one exception the temperature factors for the T-atoms of Cn$_{95}$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$_{10}$ is slightly higher than those in anorthite. Second, $<\text{Si-O}>$ increases from SrGa$_2$Si$_2$O$_8$ to BaGa$_2$Si$_2$O$_8$ by about the same amount that $<\text{Ga-O}>$
decreases, a highly fortuitous circumstance if BaGa$_2$Si$_2$O$_8$ is not partially disordered. Third, Phillips and Kroll (pers. comm.) have completed the refinement of another synthetic BaGa$_2$Si$_2$O$_8$ in which the <Si-O> distances are shorter and the <Ga-O> 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 SrAl$_2$Si$_2$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, $\ell$ odd) and 'd' ($h+k$ odd, $\ell$ even) reflections indicative of a primitive space group and (possibly) complete Al/Si order. This specimen would be analogous to anorthite, CaAl$_2$Si$_2$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 SrAl$_2$Si$_2$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 BaGa$_2$Si$_2$O$_8$. 
REFERENCES


Calleri, M., and G. Gazzoni (1975) The structures of (Sr,Ba)[(Al,Ga)\textsubscript{2} (Si,Ge)\textsubscript{2}O\textsubscript{8}]. I. The crystal structures of synthetic feldspars SrGa\textsubscript{2}Si\textsubscript{2}O\textsubscript{8} and BaGa\textsubscript{2}Si\textsubscript{2}O\textsubscript{8}. Acta Crystallogr. B31, 560-568.


Smith, J.V. (1953) The crystal structure of paracelsian, $\text{BaAl}_2\text{Si}_2\text{O}_8$. *Acta Crystallogr.* 6, 613-620.


APPENDIX A
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 PLOTTING MACHINE. 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 CCDE DETERMINES THE TYPES OF PLOTS OBTAINED, AS FOLLOWS:

CCDE 0 - NO PLOTS DESIRED
CCDE 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.
CCDE 4 - PLOT 1 AND PLOT 2
CODE 5 - PLOT 1 AND PLOT 3
CODE 6 - PLOT 2 AND PLOT 3
CODE 7 - PLOT 1, PLOT 2, AND PLOT 3

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

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

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

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

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

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

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

T-C(1) BOND LENGTH
T-C(2) BOND LENGTH
T-C(3) BOND LENGTH
T-C(4) BOND LENGTH
C(1)-T-C(2) ANGLE
C(1)-T-C(3) ANGLE
C(1)-T-C(4) ANGLE
C(2)-T-C(3) ANGLE
C(2)-T-C(4) ANGLE
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 ACCOMODATE UP TO SIX HUNDRED TETRAHEDRA.

REAL SIGT0(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 CATION(600),TYPE(600),NAME(600,12),TITLE(12)
REAL CHRS(20)
REAL BL(600),EG(600),BOND(600),EDGE(600)
INTEGER CODE
REAL SUMT0(20),SUM00(20),SUMSIG(20),SUMSG0(20),MEANT0(20),
1 MEAN00(20),MEANSG(20),MEANSL(20)
REAL TJ(20)
INTEGER JJ(20)
COMMON/PASS/C012,0013,0014,023,024,0C34,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(513)
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

3 FORMAT('0', 'REGRESSION SUM OF SQUARES = ',F11.8,///, ', 'RESIDUAL SUM OF SQUARES = ',F11.8,///, ', 'MEAN SQUARE ERROR = ',F11.8,///,  
2 ', 'FOR THE TEST OF THE NULL HYPOTHESIS THAT THE SLOPE IS ZERO, 1  
3T| = ',F7.3)  
4 FORMAT('1')  
5 FORMAT('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  

6 FORMAT('0', 'REGRESSION SUM OF SQUARES = ',F11.8,///, ', 'RESIDUAL SUM OF SQUARES = ',F11.8,///, ', 'MEAN SQUARE ERROR = ',F11.8,///,  
2 ', 'FOR THE TEST OF THE NULL HYPOTHESIS THAT THE SLOPE IS ZERO, IT)  
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 CALCULATION FOLLOWS: ', ///)  
10 FORMAT(',5X,12A4,10X,1A4)  
150 FORMAT('1', 12X, 'MEAN BOND LENGTH', 10X, 'MEAN EDGE LENGTH', 14X,  
1 'MEAN BLP', 14X, 'MEAN ELP', ///)  
151 FORMAT('0', 'A4,13X,F5.3,21X,F5.3,22X,F6.4,18X,F6.4)  
152 FORMAT('0', 'A4,13X', 'NONE FOUND IN INPUT DATA')

READ(5,1) CCCE,NOPRT,*,LIST,MRPLT  
IF(M.EQ.0) GO TO 15  
READ(5,8) (TYPE(I),I=1,M)  
15 DC 725  I=1,20
MEANTO(I)=0.
MEANOO(I)=0.
MEANSG(I)=0.
MEANSL(I)=0.
JJ(I)=0
SUMTO(I)=0.0
SUMCO(I)=0.0
SUMSIG(I)=0.0
725 SUMSGO(I)=0.0

CALL SUBROUTINE READY TC 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=1,6CC
CALL READY(SIG,DIST,SIGC,DISP,CEASE,I)
IF(CEASE.GT.0.0) GO TO 21
SIGTO(I)=SIG
DFGC(I)=DIST
SIGLIG(I)=SIGG
DISPID(I)=DISP
CATION(I)=ATCM
BCNO(I)=AVTO
EDGE(I)=AVGO
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(1,7)=TITLE(7)
NAME(1,8)=TITLE(8)
NAME(1,9)=TITLE(9)
NAME(1,10)=TITLE(10)
NAME(1,11)=TITLE(11)
NAME(1,12)=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
SUMGO(N)=SUMGO(N)+AVCO
SUMSIG(N)=SUMSIG(N)+SIG
SUMSGO(N)=SUMSGO(N)+SIGO
20 L=1
21 CONTINUE
DO 63 \=1,20
  IF(SUMTO(I) .EQ. 0.) GO TO 63
  TJ(I) = FLCAT(JJ(I))
  MEANTO(I) = SUMTC(I) / TJ(I)
  MEANO(I) = SUMO(I) / TJ(I)
  MEANSG(I) = SUMSIG(I) / TJ(I)
  MEANSL(I) = SUMSIGO(I) / TJ(I)
63 CONTINUE
  IF(L .LT. 3) GO TO 16

CALL SUBROUTINE STAT TO DETERMINE THE LEAST SQUARES REGRESSION
LINE WITH DISTANCE OF THE TETRAHEDRALY-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,CCRCO
WRITE(6,3) SSREG, SSE, MSE, TZERO
WRITE(6,7) NDF

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,DISPIC,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 CONTINUE
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)

CALL SUBROUTINE PLOT TO OBTAINT DESIRED PLOTS AS SPECIFIED BY CODE

IF(COE.EQ.0.AND.MORPLT.EQ.0) GO TO 60
IF(COE.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
26 ST(I)=SIGTC(I)
DF(I)=DFGC(I)
CALL AXIS(0.,5,0.,7,'BCND-LENGTH DISTORTION PARAMETER',32,-10..",1.000,.01401)
CALL AXIS(0.,5,0.,7,'DISTANCE FROM CIRCUITER',-26,-1.,90.,.GO,1.,C3201)
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 CONTINUE
CALL PLOT(13., C., -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(L.5, L.7, 'EDGE-LENGTH DISTORTION PARAMETER', 32, -10., 0.,
   1.000, 0.02001)
   CALL AXIS(L.5, L.7, 'AVERAGE OXYGEN DISPLACEMENT', -27, -10., 90.,
   0.000, 1.07401)
   DC 41 I=1,L
   EXPT=(SL(I)/0.020) + 0.5
   WYPT=(DI(I)/0.074) + 0.7
   CAT=CATINC(I)
   CALL SYMBOL(EXPT, WYPT, 1.0, 0., 1., -1)
41 CONTINUE
CALL PLOT(13., C., -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(L.5, L.7, 'BCND-LENGTH DISTORTION PARAMETER', 32, -10., 0.,
   1.000, 0.01401)
   CALL AXIS(L.5, L.7, 'EDGE-LENGTH DISTORTION PARAMETER', -32, -10., 90.,
   1.0, 0.02001)
   DC 43 I=1,L
IF(M.EQ.0) GO TO 44
IF(CATION(I).NE.TYPE(J)) GC TO 43
44 XPLT=(ST(I)/.014) + 0.5
EXPT=(SL(I)/.020) + 0.7
CAT=CATION(I)
CALL SYMBOL(XPLT,EXPT,.1,G,,",-1)
CONTINUE
IF(M.EQ.0) GC TO 45
CALL SYMBOL(7.5,7.5,1.5,CAT,0,,2)
CALL PLOT(13,,0,,-,3)
CONTINUE
C
IF MORPLT IS NCN-ZERO, MAKE PLCTS GF BLDP VS. MEAN BCND LENGTH AND
ELDP VS. MEAN EDGE LENGTH.
C
85 IF(MORPLT.EQ.0) GO TC 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.CHPS(I)) GC TO 81
JCOUNT=JCOUNT+1
BLN(JCOUNT)=BL(J)
EGL(JCOUNT)=EG(J)
SIT(JCOUNT)=ST(J)
SIL(JCOUNT)=SL(J)
CONTINUE
CALL SCALE(SIT,JCOUNT,1C,,SITMIN,DSIT,1)
CALL AXIS(0.5,0.6,'BOND-LENGTH DISTORTION PARAMETER',32,-1C,,J,,)
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)
BLCPAR=SIT(K) + 0.5
BONDL=BLN(K) + 0.6
CALL SYMBOL(BLCPAR,BONDL,.1,.0,.0,-1)
CONTINUE
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,-16.,-16.,
1SILMIN,DSIL)
CALL SCALE(EGL,JCOUNT,10.,XMIN,D,1)
D=D+0.00001
CALL AXIS(0.5,0.6,'MEAN EDGE LENGTH',-16,-10.,90.,XMIN,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)
CONTINUE
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)=C.
SIT(NN)=C.
84 SIL(NN)=C.
80 CONTINUE
50 CALL PLOT(C.,0.,-4)
60 RETURN
END
SUBROUTINE CENT(X,Y,Z)

C SUBROUTINE CENT IS CALLED BY SUBROUTINE TETFIT, AND DETERMINES THE C CENTROID OF THE TETRAHEDRON. CENT IS ADAPTED FROM DOLLAEB'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

SUBROUTINE LLS IS CALLED BY SUBROUTINE TETFIT. IT DETERMINES
THE PARAMETER P IN ORDER TO TEST FOR LEAST SQUARES CONVERGENCE.
THE TEST IS MADE IN SUBROUTINE TETFIT. LLS IS ADAPTED FROM
DCLLASE'S PCLFT (SEE COMMENTS IN SUBROUTINE TETFIT).

COMMON/DCLL/F(3),C(12,3),S(12),W(12),NP,NO
DIMENSION A(9),B(3,3),T(3),AO(3,3)
REAL A,B,AO,T,P,ER,ERM
N=0
DO 44 I=1,NP
DO 44 J=I,NP
K=N+1
A(N)=0.
DC 4 K=1,NO
4 A(N)=A(N)+C(K,I)*C(K,J)*W(K)
AC(J,I)=A(N)
AC(I,J)=A(N)
CALL SMI(A,NP,INC)
M=0
DO 65 J=1,NP
M=M+1
B(J,I)=A(M)
65 B(I,J)=A(M)
ERM=0.
DO 68 I=1,NP
68 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, NC
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)


REAL TITLE(12),ELNAME(3),CHAR(68)
CCMPCN/PASS/0012,0013,0C14,0023,0C24,0G34,AVTO,AVOO
CCMPCN/COORD/XC1,XO2,XO3,XO4,YO1,YO2,YC3,YO4,ZO1,ZO2,ZO3,ZO4
CCMPCN/PRINT/NOPRNT,ATCM,TITLE
DATA CHAR/ 'Al', 'ALUM', 'INUM', 'AS', 'ARSE', 'NIC', 'B',
1 'BORO', 'N', 'BE', 'BERRY', '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 FCRMAT(9F6.4)
2 FCRMAT(12A4,1X,A4)
3 FCRMAT(0', 'INPUT DATA IS AS FOLLOWS: T=O = ', F5.3, 10X, 'ANGLES =
4 FCRMAT( ', 12A4, ' //', 'THE TETRAHECRALLY COORDINATED ATOM IS ' 1,3A4)
5 FCRMAT( ', 'COORDINATES OF THE CIRCUMCENTER OF THE TETRAHEDR 1GN ARE: X ', F8.5/02X,'Y ', F8.5/62X,'Z ', F8.5//)
6 FORMAT('0', 21X,'THE DISTANCE OF THE CENTRAL ATCM FRCM THE CIRCUM
CENTER IS ',F5.3,' ANGSTROMS')
7 FORMAT('0',//,'10X','*** THE BOND-LENGTH DISTORTION PARAMETER IS ',F6.4)
8 FORMAT('1','TETRAHEDRON NUMBER ',I3,' :',//,' THE ATOMIC SPECIE IS CONTAINED IN THIS TETRAHEDRON IS NOT ONE',//,' OF THOSE INITIALIZED IN THE ARRAY NAME CHAR BY THE DATA',//,' STATEMENT. CHECK 3K TO INSURE THAT THE ELEMENT SYMBOL HAS NOT BEEN',//,' MISPUNCHE 4D ON THE TITLE CARD. IF NOT, THEN A NEW TYPICAL OF ',//,' TETRAHEDRAL ATOM HAS BEEN ADDED, AND THIS MUST BE ADDED TO',//,' THE ARRAY CHAR, AND THE DIMENSION OF CHAR INCREASED ACCORDINGLY.')
9 FORMAT('0',10X,*** THE EDGE-LENGTH DISTORTION PARAMETER IS ',1F6.4)
10 FORMAT('0',21X,'THE AVERAGE DISPLACEMENT OF THE OXYGEN ATOMS FROM AN IDEAL TETRAHEDRAL ARRAY IS ',F5.3,' ANGSTROMS')
11 FORMAT('1','CARTESIAN COORDINATES FOR THE OXYGEN ATOMS ARE: ',//,
        '0(1) ',21X,'0(1) ',23X,'0(2) ',23X,'0(3) ',23X,'0(4) ',//,
        '4(14X,X)',24X,F8.5,'/',4(14X,Y),4X,F8.5,'/',4(14X,Z),4X,F8.5,'/',2
        '/,,',0...0 SEPARATIONS (IN ANGSTROMS) BASED ON THESE COORDINATES ARE: ',//,
        '0(1) ',4X,F5.3,'10X', '0(2) ',4X,F5.3,'10X', '0(3) ',4X,F5.3,'10X', '0(4) ',4X,F5.3,'10X', '0(3)...0(4) ',4X,F5.3,'10X', '0(3)...0(4) ',4X,F5.3,'10X', '0(3)...0(4) ',4X,F5.3,'10X', '0(3)...0(4) ',4X,F5.3,'10X', '0(3)...0(4) '),21X
12 FORMAT('1',//)
13 FORMAT('1')
14 FORMAT('0', 'AVERAGE BOND LENGTH = ',F5.3,' ANGSTROMS.',20X,
        '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*RAC
A13=A13*RAD
A14 = A14 * RAD
A23 = A23 * RAD
A24 = A24 * RAD

CGMUTE 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(1.0 - ((COS(A23) - (COS(A12) * CCS(A13))) / SIN(A12)) * ((COS(A123) - (COS(A12) * COS(A13))) / SIN(A12)) - (COS(A13)) * COS(A13)))
YC3 = R3 * ((COS(A23) - (COS(A12) * COS(A13))) / SIN(A12))
ZC3 = R3 * CCS(A13)

XC4 = R4 * (SQRT(1.0 - ((COS(A24) - (COS(A12) * COS(A14))) / SIN(A12)) * ((COS(A124) - (COS(A12) * COS(A14))) / SIN(A12)) - (COS(A14)) * COS(A14)) * (-1.0)
YC4 = R4 * ((COS(A24) - (COS(A12) * COS(A14))) / SIN(A12))
ZC4 = R4 * CCS(A14)

CGMUTE 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))
0012 = SQRT((Y02 * Y02) + (Z01 - Z02) * (ZC1 - Z02))
OC13 = SQRT((XC3 * X03) + (Y03 * Y03) + (ZC1 - Z03) * (Z01 - Z03))
OC14 = SQRT((X04 * X04) + (Y04 * Y04) + (ZC1 - Z04) * (Z01 - Z04))
\[ r_{023} = \sqrt{(x_{03} - x_{c3})^2 + (y_{02} - y_{c3})^2 + (z_{02} - z_{c3})^2} \]
\[ r_{024} = \sqrt{(x_{04} - x_{03})^2 + (y_{02} - y_{04})^2 + (z_{02} - z_{04})^2} \]
\[ r_{g34} = \sqrt{(x_{g3} - x_{04})^2 + (y_{g3} - y_{04})^2 + (z_{g3} - z_{04})^2} \]
\[ \text{AVT} = R_{1} + R_{2} + R_{3} + R_{4} / 4. \]
\[ \text{AVG} = (0.012 + C_{13} + 0.014 + C_{23} + C_{24} + C_{034}) / 6. \]

```
CCMpute Angle 0(3)-T-0(4)

A_{34} = \arccos \left( \frac{r_{034} \cdot r_{034} - r_{3} \cdot r_{3} - r_{4} \cdot r_{4}}{-2 \cdot r_{3} \cdot r_{4}} \right)
A_{12} = A_{12} / \text{RAD}
A_{13} = A_{13} / \text{RAD}
A_{14} = A_{14} / \text{RAD}
A_{23} = A_{23} / \text{RAD}
A_{24} = A_{24} / \text{RAD}
A_{34} = A_{34} / \text{RAD}
```

```
20 IF (ATOM.NE.CHAR(1)) GC TO 20
   ELNAME(1) = CHAR(2)
   ELNAME(2) = CHAR(3)
   ELNAME(3) = CHAR(59)
   GC TO 40
21 IF (ATOM.NE.CHAR(7)) GC TO 22
   ELNAME(1) = CHAR(8)
   ELNAME(2) = CHAR(9)
   ELNAME(3) = CHAR(59)
   GC TO 40
22 IF (ATOM.NE.CHAR(10)) GC TO 23
```
ELNAME(1)=CHAR(11)
ELNAME(2)=CHAR(12)
ELNAME(3)=CHAR(13)
GO TO 40
23 IF(ATOM.NE.CHAR(14)) GC TO 24
   ELNAME(1)=CHAR(15)
   ELNAME(2)=CHAR(16)
   ELNAME(3)=CHAR(17)
   GC TO 40
24 IF(ATOM.NE.CHAR(17)) GC TO 25
   ELNAME(1)=CHAR(18)
   ELNAME(2)=CHAR(19)
   ELNAME(3)=CHAR(20)
   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(26)
   ELNAME(3)=CHAR(27)
   GC TO 40
27 IF(ATOM.NE.CHAR(26)) GC TO 28
   ELNAME(1)=CHAR(28)
   ELNAME(2)=CHAR(29)
   ELNAME(3)=CHAR(30)
   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(55)
   GC TO 40
35 IF(ATOM.NE.CHAR(54)) GO TO 36
   ELNAME(1)=CHAR(55)
   ELNAME(2)=CHAR(56)
   ELNAME(3)=CHAR(59)
   GC TO 40
36 IF(ATOM.NE.CHAR(57)) GO TO 37
   ELNAME(1)=CHAR(58)
   ELNAME(2)=CHAR(59)
   ELNAME(3)=CHAR(59)
   GC TO 40
37 IF(ATOM.NE.CHAR(60)) GO TC 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)
   GC TO 40
39 IF(ATOM.NE.CHAR(66)) GO TO 50
   ELNAME(1)=CHAR(67)
   ELNAME(2)=CHAR(68)
   ELNAME(3)=CHAR(59)
   GC TO 40
50 WRITE(6,8) ICGMAT
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,AV00
WRITE(6,11) X01,X02,X03,X04,YC1,YC2,YC3,YC4,ZC1,ZC2,ZC3,ZC4,  
10012,0013,0C14,0023,0024,0034
42 CONTINUE

C SET UP
C 0-MATRIX IN EQUATION DX=Y, WHERE X IS THE MATRIX OF
C COORDINATES FOR THE CIRCUMCENTER OF THE TETRAHEDRON.

C
D11=0.0
D12=0.-YG2
D13=Z01-Z02
D21=0.-XG3
D22=Y02-YG3
D23=Z02-ZC3
D31=X03-X04
D32=Y03-YC4
D33=Z03-Z04

C SET UP Y-MATRIX
C
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 INVERT D-MATRIX
C
DADJ11=(D22*C33)-(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.)
OADJ31 = (D21*C32) - (D31*D22)
OADJ32 = ((C11*D32) - (D31*D12)) * (-1.)
OADJ33 = (C11*D22) - (D21*C12)
DET = (D11*D22*D33) + (D12*D23*D31) + (D13*D21*C32) - (D31*D22*D13) - 
(1) (D32*D23*D11) - (D33*D21*D12)

DIINV11 = OADJ11 / DET
DIINV12 = OADJ12 / DET
DIINV13 = OADJ13 / DET
DIINV21 = OADJ21 / DET
DIINV22 = OADJ22 / DET
DIINV23 = OADJ23 / DET
DIINV31 = OADJ31 / DET
DIINV32 = OADJ32 / DET
DIINV33 = OADJ33 / DET

DETERMINE CCRRDINATES OF CIRCUMCENTER

X1 = (DIINV11*YA) + (DIINV12*YB) + (DIINV13*YC)
Y1 = (DIINV21*YA) + (DIINV22*YB) + (DIINV23*YC)
Z1 = (DIINV31*YA) + (DIINV32*YB) + (DIINV33*YC)

CCMPUTE BGND-LENGTH DISTORTION PARAMETER

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

CCMPUTE THE DISTANCE OF THE CENTRAL ATOM FROM THE CIRCUMCENTER

DFC = SQRT(X1*X1 + Y1*Y1 + Z1*Z1)

IF (N0PRNT.EQ.1 .OR. N0PRNT.EQ.2) GO TO 44
WRITE(6,5) X1, Y1, Z1
CALL SUBROUTINE TETFIT TO DETERMINE THE EDGE-LENGTH DISTORTION PARAMETER, AND CALCULATE THE OXYGEN DISPLACEMENTS NECESSARY FOR THE OXYGEN ATOMS TO LIE AT THE CORNERS OF A REGULAR TETRAHEDRON.

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)

AT THIS POINT ALL BOND LENGTHS, EDGE LENGTHS, O-T-O ANGLES, DISTORTION VALUES, AND DISTORTION PARAMETERS ARE KNOWN. THIS IS THEREFORE A CONVENIENT LOCATION AT WHICH TO INSERT WRITE STATEMENTS IN ORDER TO OBTAIN ANY OF THESE QUANTITIES ON PUNCHED CARDS. BOND LENGTHS ARE R1, R2, R3, AND R4; EDGE LENGTHS ARE O012, O013, ..., O034; O-T-O ANGLES ARE A12, A13, ..., A34; DISTORTIONS ARE DFC AND DISPL; AND DISTORTION PARAMETERS ARE SIGMA AND SIGCX. FUNCTIONS (LOG, SINE, ETC.) OF THESE QUANTITIES MAY ALSO BE OBTAINED BY INSERTING APPROPRIATE FORTRAN STATEMENTS PRIOR TO THE WRITE STATEMENTS. NOTE, HOWEVER, THAT THE ANGLES ARE IN DEGREES AND MUST BE CONVERTED TO RADIANS BEFORE TRIGONOMETRIC FUNCTIONS MAY BE USED.

GC TO 70
68 QUIT=1.0
70 RETURN
END
SUBROUTINE SMI(A, NY, NR)

SUBROUTINE SMI IS CALLED BY SUBROUTINE LLS. IT IS ADAPTED FROM
DOLLASE'S POLFT (SEE COMMENTS IN SUBROUTINE TETFIT).

DIMENSION R(3), A(9)
REAL*8 R, A, BIGJ, Y, Q

NN = NY
DO 16 1 = 1, NN
16 R(I) = 1.
DC 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
3 Y = CABS(A(J))
17 BIGJ = Y
KK = K
KL = J
CONTINUE
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 DC 102 N = 1, IK
NJ = NJ - 1
J = J + NJ
Y = A(J) * Q
NI = J
MJ = NJ
DO 15 M = N, IK
K = K + 1
A(K) = A(K) - Y * R(M) * A(J)
MJ = MJ - 1
19
J = J + NJ
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
A(K) = A(K) - Y * A(L)
18
102
CONTINUE
103
K = KL + NN - KK
J = KL
IF(JK - NN) 104, 104, 105
104
DC 20 N = JK, NN
J = J + 1
Y = R(N) * A(J) * Q
NI = J
DC 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  CONTINUE
    NR=0
    RETURN
END
SUBROUTINE STAT(EX,WYE,L)

SUBROUTINE STAT COMPUTES THE SIMPLE LEAST SQUARES REGRESSION LINE
BETWEEN TWO VARIABLES, THE RELEVANT SUMS OF SQUARES, THE MEAN
SQUARE ERRCR, AND THE T-STATISTIC FOR THE TEST OF ZERO REGRESSION

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
24 SUMYX=SUMYX+EX(I)*WYE(I)
SUMX=SUMX+EX(I)
SUMY=SUMY+WYE(I)
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 COMPUTE R AND R-SQUARED

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 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(SIGOG,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 CILATION, 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 RESPECT-
IVE OXYGEN ATOMS OF THE REAL AND IDEAL TETRAHEDRA IS TAKEN AS THE
EDGE-LENGTH DISTORTION. SUBROUTINE TETFIT CALLS SUBROUTINES CENT,
LLS, AND SII, EACH OF WHICH HAS BEEN MODIFIED TO A GREATER OR
LESSER EXTENT FROM POLFT. DOLLASE'S SUBROUTINE DIST HAS BEEN
ELIMINATED.

COMMON/DCELL/P(3),A(12,3),S(12),W(12),NP,NO
COMMON/PASS/CG12,0013,CL14,0023,CL24,0034,AVLC,AVOD
COMMON/CCRD/XC1,XO2,XC3,XC4,YC1,YO2,YC3,YO4,ZO1,ZO2,ZC3,ZO4
COMMON/PRINT/NCPRT,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),CT(3),CR(3),DC(1),
2FR(3,3),RR(3,3),SU(3),KA(4),LP(3),L(5),DISP(4),SUELS(4)
REAL*8 P
9 FORMAT('O','COORDINATES FOR OXYGENS DISPLACED SC AS TO LIE AT THE
1CORNERS 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):',6X,'O(1)',
12X,F6.4,5X,'O(2)',2X,
2F6.4,5X,'0(3)',2X,F6.4,'5X,'0(4)',2X,F6.4)

C CALCULATE EDGE LENGTH DISTORTION PARAMETER

VARCC=((CC12-AVCO)*(0012-AVCO)+(CC13-AVCC)*(0013-AV00)+(0014-AV00)+(0014-AV00)+(CC34-AVCO)*(CC34-AV00))/5.

SIGCC=(SQR(T(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 S(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 DETERMINE THE CARTESIAN COORDINATES FOR THE IDEAL TETRAHEDRON.

TANG=(109.471/2.)*RAD
TOIC=(AVCO/2.)/(SQR(T(2.3.)))
\[ V(1,1) = -1.0 \cdot T CID \cdot \sin(TANG) \]
\[ V(1,2) = 0.0 \]
\[ V(1,3) = T CID \cdot \cos(TANG) \]
\[ V(2,1) = T CID \cdot \sin(TANG) \]
\[ V(2,2) = 0.0 \]
\[ V(2,3) = T CID \cdot \cos(TANG) \]
\[ V(3,1) = 0.0 \]
\[ V(3,2) = -1.0 \cdot T CID \cdot \sin(TANG) \]
\[ V(3,3) = -1.0 \cdot T CID \cdot \cos(TANG) \]
\[ V(4,1) = 0.0 \]
\[ V(4,2) = T CID \cdot \sin(TANG) \]
\[ V(4,3) = -1.0 \cdot T CID \cdot \cos(TANG) \]

CELL(1) = 1.0
CELL(2) = 1.0
CELL(3) = 1.0
CELL(4) = 90.0
CELL(5) = 90.0
CELL(6) = 90.0

CA = \cos(RAD \cdot CELL(4))
CB = \cos(RAD \cdot CELL(5))
CG = \cos(RAD \cdot CELL(6))
SNB = \sin(RAD \cdot CELL(5))
SNG = \sin(RAD \cdot CELL(6))
ONE = (CA - CB \cdot CG) / SNG
T(1,1) = CELL(1)
T(1,2) = CELL(2) \cdot CG
T(1,3) = CELL(3) \cdot CB
T(2,1) = 0.0
T(2,2) = CELL(2) \cdot SNG
T(2,3) = CELL(3) \cdot ONE
T(3,1) = 0.0
T(3,2) = 0.0
\[ T(3,3) = \text{CELL}(3) \times \text{SQRT} \left( S\text{NB}^2 - C\text{NE}^2 \right) \]

\[ N = 0 \]

\[ \text{DO 110 I=1,4} \]
\[ \text{IF (I.EQ.1) H(1)=X01} \]
\[ \text{IF (I.EQ.1) H(2)=Y01} \]
\[ \text{IF (I.EQ.1) H(3)=Z01} \]
\[ \text{IF (I.EQ.2) H(1)=X02} \]
\[ \text{IF (I.EQ.2) H(2)=Y02} \]
\[ \text{IF (I.EQ.2) H(3)=Z02} \]
\[ \text{IF (I.EQ.3) H(1)=X03} \]
\[ \text{IF (I.EQ.3) H(2)=Y03} \]
\[ \text{IF (I.EQ.3) H(3)=Z03} \]
\[ \text{IF (I.EQ.4) H(1)=X04} \]
\[ \text{IF (I.EQ.4) H(2)=Y04} \]
\[ \text{IF (I.EQ.4) H(3)=Z04} \]
\[ \text{WC(1)=1.0} \]
\[ \text{WC(2)=1.0} \]
\[ \text{WC(3)=1.0} \]

\[ \text{DC 110 J=1,3} \]
\[ N = N + 1 \]
\[ E(I,J)=0.0 \]

\[ \text{DO 102 K=1,3} \]
\[ E(I,J)=E(I,J)+T(J,K) \times H(K) \]

\[ \text{108 } W(N)=1.0 \]
\[ \text{109 } SU(J)=SU(J)+W(N) \]

\[ \text{110 CONTINUE CONTINUE} \]
\[ \text{CALL CENT(E, SU, OT)} \]
\[ \text{CALL CENT(V, SU, H)} \]
\[ \text{DO 130 I=1,3} \]
\[ \text{130 OT(I)=OT(I)-H(I)} \]

\[ N = 0 \]
DO 150 I=1,4
DO 150 J=1,3
E(I,J)=E(I,J)-GT(J)
DO 150 J=1,3
F(I,J)=V(I,J)
DO 152 I=1,3
F(I,J)=V(I,J)
DO 151 J=1,3
RR(I,J)=0.0
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)) GC 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.GT.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

CONTINUE
CALL LLS
TH=DSQRT(P(1)**2+P(2)**2+P(3)**2)
IF(TH.GE.0.00005) NSTOP=1
DL=P(1)/TH
DM=P(2)/TH
DN=P(3)/TH
STH=SIN(TH)
CTH=CO.S(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)=OM**2+CTH*(1.-OM**2)
R(2,3)=AC*DM*DN-CTH*DL
R(3,1)=AC*CL*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
DC 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
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 CONTINUE
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
DELS=E(I,J)-F(I,J)
SDELS(I)=SDELS(I)+DELS
290 CONTINUE
DC 291 I=1,4
291 DISP(I)=SQRT(SDELS(I))
AVDISP=(DISP(1)+DISP(2)+DISP(3)+DISP(4))/4.
IF(NOPRNT.EQ.1.OR.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 CONTINUE
RETURN
END
# Appendix B

## Crystal Structure Studies Used in This Work

<table>
<thead>
<tr>
<th>Year</th>
<th>Publication</th>
<th>Volume</th>
<th>Page</th>
<th>Chemical Formula</th>
<th>Mineral Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
<td>JCPSA</td>
<td>22</td>
<td>1597</td>
<td>Al2O3</td>
<td>Sillimanite</td>
</tr>
<tr>
<td>62</td>
<td>ZEKGA</td>
<td>118</td>
<td>127</td>
<td>Al2SiO5</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>ACCRA</td>
<td>19</td>
<td>396</td>
<td>Gamma LiAlO2</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>ACCRA</td>
<td>19</td>
<td>971</td>
<td>Lu3Al2Al3O12</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>ACCRA</td>
<td>19</td>
<td>971</td>
<td>Yb3Al2Al3O12</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>ACCRA</td>
<td>19</td>
<td>971</td>
<td>Y2Al2Al3O12</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>ACCRA</td>
<td>19</td>
<td>971</td>
<td>GD3Al2Al3O12</td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>AMMIA</td>
<td>51</td>
<td>1068</td>
<td>Al3Mg2Si5AlO18+N(H2O)</td>
<td>Bavellite</td>
</tr>
<tr>
<td>66</td>
<td>ZEKGA</td>
<td>123</td>
<td>161</td>
<td>AlP04</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>ACCRA</td>
<td>23</td>
<td>434</td>
<td>Na8Si6Al6O24Cl2</td>
<td>Sodalite</td>
</tr>
<tr>
<td>69</td>
<td>ACBCA</td>
<td>325</td>
<td>1503</td>
<td>NaAlSi3O8</td>
<td>Low albite</td>
</tr>
<tr>
<td>69</td>
<td>AMMIA</td>
<td>54</td>
<td>31</td>
<td>Mg3.5Al9.O Si1.5C2O</td>
<td>Saphirine</td>
</tr>
<tr>
<td>70</td>
<td>ZEKGA</td>
<td>121</td>
<td>314</td>
<td>Ca Na Al Si2O7</td>
<td>Soda melilitie</td>
</tr>
<tr>
<td>71</td>
<td>ADCSA</td>
<td>101</td>
<td>250</td>
<td>CaAl2Si2O8+4(H2O)</td>
<td>Gismondite</td>
</tr>
<tr>
<td>71</td>
<td>CAMIA</td>
<td>10</td>
<td>822</td>
<td>Ca2Al[Al,Si]2O7</td>
<td>Gehlenite</td>
</tr>
<tr>
<td>71</td>
<td>ZEKGA</td>
<td>133</td>
<td>75</td>
<td>CaAl2Si2O8</td>
<td>Anorthite</td>
</tr>
<tr>
<td>72</td>
<td>AMMIA</td>
<td>57</td>
<td>1089</td>
<td>Al13Si5F4(OH)14O20Cl</td>
<td>Zunyite</td>
</tr>
<tr>
<td>73</td>
<td>ACBCA</td>
<td>829</td>
<td>1550</td>
<td>11(CaO)*7(Al2O3)*CAF2</td>
<td>Beta eucryptite</td>
</tr>
<tr>
<td>73</td>
<td>AMMIA</td>
<td>58</td>
<td>676</td>
<td>Na2Al2Si3O10+2(H2O)</td>
<td>Natrolite, 88 degrees</td>
</tr>
<tr>
<td>73</td>
<td>AMMIA</td>
<td>58</td>
<td>676</td>
<td>Na2Al2Si3O10+2(H2O)</td>
<td>Natrolite, 146 degrees</td>
</tr>
<tr>
<td>73</td>
<td>AMMIA</td>
<td>58</td>
<td>676</td>
<td>Na2Al2Si3O10+2(H2O)</td>
<td>Natrolite, 198 degrees</td>
</tr>
<tr>
<td>73</td>
<td>AMMIA</td>
<td>58</td>
<td>681</td>
<td>LiAlSiO4</td>
<td>Beta eucryptite</td>
</tr>
<tr>
<td>73</td>
<td>AMMIA</td>
<td>58</td>
<td>681</td>
<td>LiAlSiO4</td>
<td>Beta eucryptite, 200 degrees</td>
</tr>
<tr>
<td>73</td>
<td>AMMIA</td>
<td>58</td>
<td>681</td>
<td>LiAlSiO4</td>
<td>Beta eucryptite, 335 degrees</td>
</tr>
<tr>
<td>75</td>
<td>ACBCA</td>
<td>831</td>
<td>1169</td>
<td>Ca8.5NaAl6O18</td>
<td>Beta eucryptite, 400 degrees</td>
</tr>
</tbody>
</table>
### ARSENIC

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>66</td>
<td>ACCRA</td>
<td>21</td>
<td>808</td>
<td>3(AS2 05)</td>
<td>5(H2 0)</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>ACSSA</td>
<td>24</td>
<td>3711</td>
<td>L1 MO 02 AS 04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>CJCHMA</td>
<td>48</td>
<td>881</td>
<td>CG3 (AS 04)2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>CJCHMA</td>
<td>46</td>
<td>890</td>
<td>MG2 AS2 07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>71</td>
<td>INOCA</td>
<td>9</td>
<td>2259</td>
<td>CA2 AS 04 CL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>71</td>
<td>ACBCA</td>
<td>B27</td>
<td>2124</td>
<td>NA3 AS 04</td>
<td>(NA3 H10 2)</td>
<td>12(H2)</td>
</tr>
<tr>
<td>72</td>
<td>ACBCA</td>
<td>B28</td>
<td>3056</td>
<td>CAK AS 04</td>
<td>8(H2 C)</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>BUFCA</td>
<td>95</td>
<td>33</td>
<td>CA5 (H AS 04)2</td>
<td>(AS 04)2</td>
<td>4(H2)</td>
</tr>
<tr>
<td>72</td>
<td>CJCHMA</td>
<td>51</td>
<td>2082</td>
<td>NA4 AS2 G7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>ACBCA</td>
<td>B29</td>
<td>141</td>
<td>LU AS 04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>AGBCA</td>
<td>B29</td>
<td>2611</td>
<td>MG2 AS2 08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>AMMA</td>
<td>58</td>
<td>1634</td>
<td>CA4 MG AS2 B12 O22 (C H)12</td>
<td>14*</td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>JSSCB</td>
<td>6</td>
<td>83</td>
<td>MG8.5 AS3 O16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### BORON

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>ACCRA</td>
<td>19</td>
<td>297</td>
<td>BA O</td>
<td>2(B2 C3)</td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>JCP5A</td>
<td>44</td>
<td>3348</td>
<td>L1 P O2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>ACCRA</td>
<td>22</td>
<td>815</td>
<td>NA2 O</td>
<td>4(B2 C3)</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>ZEKGA</td>
<td>125</td>
<td>423</td>
<td>CS BE4 B12 AL4 J28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>ACBCA</td>
<td>824</td>
<td>869</td>
<td>B2 C3 (II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>ACBCA</td>
<td>B25</td>
<td>955</td>
<td>CA B2 O4 (1II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>ACBCA</td>
<td>B25</td>
<td>965</td>
<td>LA B2 G4 (1IV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>ACBCA</td>
<td>B25</td>
<td>1787</td>
<td>K2 B5 (8 C H)</td>
<td>2(H2 C)</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>ZEKGA</td>
<td>132</td>
<td>241</td>
<td>CA E3 5 (C H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>ACBCA</td>
<td>B28</td>
<td>1571</td>
<td>RETA NA2 C</td>
<td>3(B2: C3)</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>ACBCA</td>
<td>B28</td>
<td>3389</td>
<td>K2 O</td>
<td>3(B2 G3)</td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>AMMA</td>
<td>58</td>
<td>651</td>
<td>MG3 CL 07 013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>ACBCA</td>
<td>B30</td>
<td>578</td>
<td>NA2 O</td>
<td>2(B2 C3)</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>ACBCA</td>
<td>B30</td>
<td>1178</td>
<td>CS2 G</td>
<td>3(B2 C3)</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>ACBCA</td>
<td>B30</td>
<td>1327</td>
<td>SK2 O</td>
<td>19(B2 C3)</td>
<td></td>
</tr>
</tbody>
</table>

### BERILLYUM

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>59</td>
<td>ACCRA</td>
<td>12</td>
<td>833</td>
<td>BE4 O (C H3 C O2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>AMMA</td>
<td>48</td>
<td>804</td>
<td>AL2 BE O4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>JESCA</td>
<td>111</td>
<td>78</td>
<td>RE O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>ACBCA</td>
<td>B24</td>
<td>672</td>
<td>LA2 BE2 O5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>LITHA</td>
<td>1</td>
<td>275</td>
<td>AL2 BE3 S16 O13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>LITHA</td>
<td>1</td>
<td>275</td>
<td>AL2 BE3 S16 O13</td>
<td>N(H2 C)</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>LITHA</td>
<td>1</td>
<td>275</td>
<td>AL1.9 CR0.1 BE3 S15 O18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>LITHA</td>
<td>1</td>
<td>275</td>
<td>AL1.9 CR0.1 BE3 S15 C18</td>
<td>N(H2)</td>
<td></td>
</tr>
</tbody>
</table>

### OTHER

- SAINFELDITE
- Rhodizite
- Cubic Boracite
- Terrugite
<table>
<thead>
<tr>
<th>No.</th>
<th>Symbol</th>
<th>Z</th>
<th>Mass</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>69</td>
<td>ACBCA</td>
<td>25</td>
<td>304</td>
<td>BE S 04 * 4(20)</td>
</tr>
<tr>
<td>70</td>
<td>AMMIA</td>
<td>55</td>
<td>1541</td>
<td>H Na BE S13 08</td>
</tr>
<tr>
<td>70</td>
<td>ACBCA</td>
<td>26</td>
<td>1647</td>
<td>SR BE3 04</td>
</tr>
<tr>
<td>72</td>
<td>ACBCA</td>
<td>28</td>
<td>114</td>
<td>MN (BE S1 04) 13 S</td>
</tr>
<tr>
<td>72</td>
<td>AMMIA</td>
<td>57</td>
<td>1345</td>
<td>NA2 BE S16 015 * H2 O</td>
</tr>
<tr>
<td>72</td>
<td>KRISA</td>
<td>16</td>
<td>1167</td>
<td>BE2 S1 04</td>
</tr>
<tr>
<td>74</td>
<td>AMMIA</td>
<td>59</td>
<td>1267</td>
<td>CA BE2 P2 C8</td>
</tr>
<tr>
<td></td>
<td><strong>CHROMIUM</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>ACBCA</td>
<td>25</td>
<td>2170</td>
<td>GA2 CR O4 CL</td>
</tr>
<tr>
<td>70</td>
<td>ACBCA</td>
<td>26</td>
<td>222</td>
<td>CR 03</td>
</tr>
<tr>
<td>70</td>
<td>ACBCA</td>
<td>26</td>
<td>437</td>
<td>(N H4)2 CR O4</td>
</tr>
<tr>
<td>72</td>
<td>ACBCA</td>
<td>28</td>
<td>2845</td>
<td>K2 CR 04</td>
</tr>
<tr>
<td>72</td>
<td>ACBCA</td>
<td>28</td>
<td>2880</td>
<td>NA RB CR2 C7</td>
</tr>
<tr>
<td>73</td>
<td>ACBCA</td>
<td>29</td>
<td>2141</td>
<td>RB2 CR4 013</td>
</tr>
<tr>
<td>73</td>
<td>ACSAA</td>
<td>27</td>
<td>177</td>
<td>ZR4 (O H)6 (CR O4) 15 * H2 C</td>
</tr>
<tr>
<td>73</td>
<td>MRBUA</td>
<td>8</td>
<td>271</td>
<td>K2 CR2 07</td>
</tr>
<tr>
<td></td>
<td><strong>COPPER</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>JSSCB</td>
<td>7</td>
<td>17</td>
<td>Cu6.8 V6 C18.8</td>
</tr>
<tr>
<td></td>
<td><strong>GALLIUM</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>ACCRA</td>
<td>18</td>
<td>481</td>
<td>Li Ga O2</td>
</tr>
<tr>
<td>65</td>
<td>ACCRA</td>
<td>19</td>
<td>471</td>
<td>Li3 Ga2 C3 012</td>
</tr>
<tr>
<td>65</td>
<td>ACCRA</td>
<td>19</td>
<td>471</td>
<td>YH3 Ga2 Ga3 O12</td>
</tr>
<tr>
<td>65</td>
<td>ACCRA</td>
<td>19</td>
<td>471</td>
<td>Y3 Ga2 Ga3 O12</td>
</tr>
<tr>
<td>65</td>
<td>JCPSA</td>
<td>42</td>
<td>3957</td>
<td>Ga(2-X) Fe(X) 03</td>
</tr>
<tr>
<td>75</td>
<td>ACBCA</td>
<td>31</td>
<td>560</td>
<td>Sr Ga2 S12 O8</td>
</tr>
<tr>
<td>75</td>
<td>ACBCA</td>
<td>31</td>
<td>560</td>
<td>Ba Ga2 S12 O8</td>
</tr>
<tr>
<td>#1</td>
<td></td>
<td></td>
<td></td>
<td>Sr Ga2 S12 O8</td>
</tr>
<tr>
<td>#2</td>
<td></td>
<td></td>
<td></td>
<td>Sr Ga2 S12 O8</td>
</tr>
<tr>
<td></td>
<td><strong>GERMANIUM</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>ACCRA</td>
<td>17</td>
<td>842</td>
<td>GE O2</td>
</tr>
<tr>
<td>67</td>
<td>ACSAA</td>
<td>21</td>
<td>1281</td>
<td>Na8 Sn4 Ge10 O32 (C H)4</td>
</tr>
<tr>
<td>69</td>
<td>ZEGGA</td>
<td>129</td>
<td>427</td>
<td>Mn3 Fe2 Ge3 C12</td>
</tr>
<tr>
<td>70</td>
<td>JSSCB</td>
<td>2</td>
<td>612</td>
<td>Mg28 Ge10 C48</td>
</tr>
<tr>
<td>70</td>
<td>KRISA</td>
<td>15</td>
<td>47</td>
<td>Fe2 Ge2 O7</td>
</tr>
<tr>
<td>72</td>
<td>AMMIA</td>
<td>57</td>
<td>62</td>
<td>Mn2 Ge O4</td>
</tr>
<tr>
<td>No</td>
<td>JSSCB</td>
<td>4</td>
<td>262</td>
<td>MG28 GE7.5 C38 F10</td>
</tr>
<tr>
<td>----</td>
<td>-------</td>
<td>---</td>
<td>-----</td>
<td>---------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SR GA2 GE2 08</td>
</tr>
</tbody>
</table>

### Iron

<table>
<thead>
<tr>
<th>No</th>
<th>ACCRA</th>
<th>9</th>
<th>797</th>
<th>LU3 FE2 FE3 O12</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>67</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>JSSCB</td>
<td>10</td>
<td>122</td>
<td>Y3 SC FE4 O12</td>
</tr>
<tr>
<td>74</td>
<td>JSSCB</td>
<td>10</td>
<td>122</td>
<td>Y2+3 PRO.7 SC FE4 O12</td>
</tr>
<tr>
<td>74</td>
<td>JSSCB</td>
<td>10</td>
<td>122</td>
<td>Y PR2 SC FE4 O12</td>
</tr>
<tr>
<td>74</td>
<td>JSSCB</td>
<td>10</td>
<td>122</td>
<td>PR3 SC FE4 O12</td>
</tr>
</tbody>
</table>

### Lithium

<table>
<thead>
<tr>
<th>No</th>
<th>ACCRA</th>
<th>18</th>
<th>717</th>
<th>LI2 S O4 . H2 O</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>JCP SA</td>
<td>44</td>
<td>3348</td>
<td>LI R O2</td>
</tr>
<tr>
<td>72</td>
<td>ZEGGA</td>
<td>135</td>
<td>175</td>
<td>LI AL S1 C4</td>
</tr>
<tr>
<td>73</td>
<td>AMMIA</td>
<td>58</td>
<td>681</td>
<td>LI AL S1 C4</td>
</tr>
<tr>
<td>73</td>
<td>AMMIA</td>
<td>58</td>
<td>681</td>
<td>LI AL S1 C4</td>
</tr>
<tr>
<td>73</td>
<td>AMMIA</td>
<td>58</td>
<td>681</td>
<td>LI AL S1 C4</td>
</tr>
<tr>
<td>73</td>
<td>JSSCB</td>
<td>6</td>
<td>538</td>
<td>LI3 V O4</td>
</tr>
<tr>
<td>74</td>
<td>ACBCA</td>
<td>830</td>
<td>831</td>
<td>LI N2 H5 S O4</td>
</tr>
</tbody>
</table>

### Manganese

<table>
<thead>
<tr>
<th>No</th>
<th>NASCA</th>
<th>539</th>
<th>935</th>
<th>MN AL2 O4</th>
</tr>
</thead>
<tbody>
<tr>
<td>66</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>INOCA</td>
<td>6</td>
<td>503</td>
<td>K MN O4</td>
</tr>
<tr>
<td>67</td>
<td>INCCA</td>
<td>6</td>
<td>507</td>
<td>K2 MN O4</td>
</tr>
</tbody>
</table>

### Molybdenum

<table>
<thead>
<tr>
<th>No</th>
<th>JCP SA</th>
<th>46</th>
<th>2052</th>
<th>ALPHA IN WC O4</th>
</tr>
</thead>
<tbody>
<tr>
<td>67</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>JCP SA</td>
<td>48</td>
<td>2619</td>
<td>CU MO O4</td>
</tr>
<tr>
<td>72</td>
<td>ACBCA</td>
<td>828</td>
<td>60</td>
<td>PROTOTYPIC GD2 (WC C4)</td>
</tr>
<tr>
<td>72</td>
<td>ACBCA</td>
<td>828</td>
<td>60</td>
<td>FRREROIC GD2 (MJ J4)</td>
</tr>
</tbody>
</table>

### Lithium

<table>
<thead>
<tr>
<th>No</th>
<th>JCP SA</th>
<th>46</th>
<th>2052</th>
<th>ALPHA IN WC O4</th>
</tr>
</thead>
<tbody>
<tr>
<td>67</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>JCP SA</td>
<td>48</td>
<td>2619</td>
<td>CU MO O4</td>
</tr>
<tr>
<td>72</td>
<td>ACBCA</td>
<td>828</td>
<td>60</td>
<td>PROTOTYPIC GD2 (WC C4)</td>
</tr>
<tr>
<td>72</td>
<td>ACBCA</td>
<td>828</td>
<td>60</td>
<td>FRREROIC GD2 (MJ J4)</td>
</tr>
<tr>
<td>No.</td>
<td>Symbol</td>
<td>Formula</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>--------</td>
<td>---------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>ACCRA</td>
<td>13 325 LI Mn P O4</td>
<td>Phosphorus</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>Name</td>
<td>No.</td>
<td>Weight</td>
<td>Formula</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>-----</td>
<td>--------</td>
<td>---------</td>
</tr>
<tr>
<td>74</td>
<td>AMMIA</td>
<td>59</td>
<td>567</td>
<td>(Na,Fe)2 Al2 (O,OH)3 (P O4)3</td>
</tr>
<tr>
<td>74</td>
<td>AMMIA</td>
<td>59</td>
<td>573</td>
<td>(Cu,Fe)2 Zn P O4 (Cu H13)</td>
</tr>
<tr>
<td>74</td>
<td>AMMIA</td>
<td>59</td>
<td>1267</td>
<td>Ca Be2 P 08</td>
</tr>
<tr>
<td>74</td>
<td>CJCHA</td>
<td>52</td>
<td>1155</td>
<td>Ca18 Mg2 H2 (P O4)14</td>
</tr>
<tr>
<td>74</td>
<td>JSSCB</td>
<td>10</td>
<td>12</td>
<td>Na7 Mg4*5 (P2 07)4</td>
</tr>
<tr>
<td>74</td>
<td>JSSCB</td>
<td>10</td>
<td>232</td>
<td>Beta Ca3 (P O4)2</td>
</tr>
</tbody>
</table>

**Selenium**

<table>
<thead>
<tr>
<th>Se</th>
<th>Name</th>
<th>No.</th>
<th>Weight</th>
<th>Formula</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>JCSOA</td>
<td>1951</td>
<td>968</td>
<td>H2 Se O4</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>ACCRA</td>
<td>18</td>
<td>795</td>
<td>Se O3</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>ZAACA</td>
<td>358</td>
<td>125</td>
<td>Mn Se O4</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>ZAACA</td>
<td>358</td>
<td>125</td>
<td>C0 Se O4</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>ZAACA</td>
<td>358</td>
<td>125</td>
<td>Ni Se O4</td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>ACBCA</td>
<td>825</td>
<td>19</td>
<td>Cu (N H3)4 Se O4</td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>ACSAA</td>
<td>23</td>
<td>1607</td>
<td>Hg2 Se O4</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>ACBCA</td>
<td>826</td>
<td>436</td>
<td>Na2 Se O4</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>ACBCA</td>
<td>826</td>
<td>1451</td>
<td>K2 Se O4</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>ACBCA</td>
<td>826</td>
<td>2062</td>
<td>Cu (N H2)3 N H2)2 Se O4</td>
<td></td>
</tr>
<tr>
<td>71</td>
<td>ZAACA</td>
<td>379</td>
<td>204</td>
<td>Ni Se O4</td>
<td>61 (H2 0)</td>
</tr>
<tr>
<td>73</td>
<td>CRSC1</td>
<td>2</td>
<td>163</td>
<td>K2 Cd (Se O4)2 2 (H2 C)</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>JSSCB</td>
<td>9</td>
<td>63</td>
<td>Na2 Cu (Se O4)2 2 (H2 C)</td>
<td></td>
</tr>
</tbody>
</table>

**Silicon**

<table>
<thead>
<tr>
<th>Si</th>
<th>Name</th>
<th>No.</th>
<th>Weight</th>
<th>Formula</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>ZEKGA</td>
<td>115</td>
<td>265</td>
<td>Al2 Si C5</td>
<td>Andalusite</td>
</tr>
<tr>
<td>62</td>
<td>ACCRA</td>
<td>15</td>
<td>583</td>
<td>(Ca,Na) (Mg,Al)6 (H,Al)6 Si6 C3</td>
<td>Tourmaline</td>
</tr>
<tr>
<td>62</td>
<td>ZEKGA</td>
<td>113</td>
<td>127</td>
<td>Al2 Si O5</td>
<td>Sillimanite</td>
</tr>
<tr>
<td>63</td>
<td>ACCRA</td>
<td>16</td>
<td>462</td>
<td>Si C2</td>
<td>Alpha Quartz</td>
</tr>
<tr>
<td>63</td>
<td>ZEKGA</td>
<td>118</td>
<td>337</td>
<td>Al2 Si C5</td>
<td>Kyanite</td>
</tr>
<tr>
<td>66</td>
<td>ACCRA</td>
<td>27</td>
<td>301</td>
<td>Ca4 (Re C H2)2 Al2 Si9 O26</td>
<td>Ravenite</td>
</tr>
<tr>
<td>66</td>
<td>AMMIA</td>
<td>51</td>
<td>1068</td>
<td>Al3 Mg2 Si15 P 018 N(H2 O)</td>
<td>Cordierite</td>
</tr>
<tr>
<td>67</td>
<td>ACCRA</td>
<td>33</td>
<td>434</td>
<td>Na18 Si16 Al6 C24 C12</td>
<td>Sodalite</td>
</tr>
<tr>
<td>67</td>
<td>ZEKGA</td>
<td>124</td>
<td>180</td>
<td>Za4 Si12 C7 (C H2)2 H2 C</td>
<td>Hemimorphite</td>
</tr>
<tr>
<td>68</td>
<td>AMMIA</td>
<td>53</td>
<td>867</td>
<td>Mg1.8 Fe0.2 Si C4</td>
<td>Forssterite</td>
</tr>
<tr>
<td>68</td>
<td>AMMIA</td>
<td>53</td>
<td>807</td>
<td>Mg1.1 Fe0.2 Si C4</td>
<td>Hyalosiderite</td>
</tr>
<tr>
<td>68</td>
<td>AMMIA</td>
<td>53</td>
<td>807</td>
<td>Mg Fe Si C4</td>
<td>Horthonialite</td>
</tr>
<tr>
<td>68</td>
<td>AMMIA</td>
<td>33</td>
<td>857</td>
<td>Fe2 Si C4</td>
<td>Fayalite</td>
</tr>
<tr>
<td>68</td>
<td>AMMIA</td>
<td>53</td>
<td>1139</td>
<td>Al18 Fe4 Si8 C44 (C H4)</td>
<td>Staurolite</td>
</tr>
<tr>
<td>68</td>
<td>LITHA</td>
<td>1</td>
<td>275</td>
<td>Al3 Be3 Si6 O18</td>
<td>Beryl</td>
</tr>
<tr>
<td>68</td>
<td>LITHA</td>
<td>1</td>
<td>275</td>
<td>Al3 Be3 Si6 O18</td>
<td>Emerald</td>
</tr>
<tr>
<td>68</td>
<td>LITHA</td>
<td>1</td>
<td>275</td>
<td>Al3 Be3 Si6 O18 N(H2 O)</td>
<td>Hydrous Beryl</td>
</tr>
<tr>
<td>68</td>
<td>LITHA</td>
<td>1</td>
<td>275</td>
<td>Al1.9 Cr0.1 Be3 Si6 O18</td>
<td>Hydrous Emerald</td>
</tr>
<tr>
<td>69</td>
<td>ACBCA</td>
<td>525</td>
<td>1503</td>
<td>Na Al Si3 O8</td>
<td>Low Albite</td>
</tr>
<tr>
<td>69</td>
<td>AMMIA</td>
<td>54</td>
<td>376</td>
<td>Mg2 Si O4 Mg F1.8 (C H)0.2</td>
<td>Norbergite</td>
</tr>
</tbody>
</table>
69  PTOA  6  102  K AL Li2 Si4 O10 F2  FLUOR-POLYLITHIUMITE
69  MSAPA  2  31  Li AL Si2 O6  SPODUMENE
69  MSAPA  2  31  Li FE Si2 O6  JADEITE
69  MSAPA  2  31  Na AL Si2 O6  UREYITE
69  MSAPA  2  31  Na CR Si2 C6  ACMITE
69  MSAPA  2  31  Na FE Si2 C6  DIOPSIDE
69  MSAPA  2  31  Na IN Si2 C6  PROTOPHIBOLE
69  MSAPA  2  117  Li1.2 Mg6.5 Si17.8 O21.7 F2.3  GRUNERITE
69  MSAPA  2  117  Fe6.2 Al0.8 Si18 O22 (O H)2  P. MANGANOAN CUMMINGTONITE
69  MSAPA  2  117  CaO.4 Mg5.6 Mn Si8 G22 (O H)2  TREMOLITE
69  MSAPA  2  117  Ca1.9 NaO.1 Mg5 Si8 O22 (O H)2  C. MANGANOAN CUMMINGTONITE
69  MSAPA  2  117  CaO.2 Mg4.1 Fe0.5 Mn2.0 Si8 O*  GLAUCOPHANE
69  MAAM  129  381  Si02  COESITE
69  ZEGKA  130  185  Ca Si03  HARDYSTONITE
69  ZEGKA  130  427  Ca2 Zn Si2 O7  LEUCOPHACITE
70  AMMA  55  1146  Mn7 Si3 O12 (O H)2  CHONDRODITE
70  AMMA  55  1182  Mg5 (Si04)2 F1.3 (O H)0.7  EPIDIDDYRITE
70  AMMA  55  1541  H Na Be Si3 O8  GEDRITE
70  AMMA  55  1945  NaO.5 (Al, Mg, Fe)7.0 (Si, Al)8.0*  GEDRITE
70  ZEGKA  131  314  Ca Na AL Si2 O7  SODA MELILITE
70  ZEGKA  132  288  Ca5 Si2 O7 (O 03)2  TILLEYITE
71  AOCMA  101  250  Ca AL2 Si2 O8 * 4(H2 O)  GISMONDITE
71  AMMA  56  24  AL2 Si O4 F2  TOPAZ
71  AMMA  56  782  ZR SiO4  ZIRCON
71  AMMA  56  751  Mg3 AL2 Si3 O12  PYROPE
71  AMMA  56  791  Fe3 AL2 Si3 O12  ALMANDINE
71  AMMA  56  791  Ca3 Al2 Si3 O12  GROSSULAR
71  ZEGKA  133  75  Ca AL2 Si2 O8  ANGARHITE
72  ACBCA  928  114  Mn4 (Be Si O4)3 S  HELVITE
72  AMMA  57  1089  Al13 Si5 F4 (O H)14 G20 Cl  ZUNITE
72  AMMA  57  1345  Na2 Be2 Si6 O15 * H2 O  EUDIODYMITE
72  KRISA  16  1167  Be2 Si O4  PHENACITE
72  ZEGKA  135  175  Li AL Si C4  NATROLITE
73  ACBCA  829  73  Ca7 Si6 O18 C 3 * 2(H2 O)  BETA EUCRYPTITE
73  AMMA  58  676  Na2 AL2 Si3 O10 * 2(H2 O)  SCAMITE
73  AMMA  58  676  Na2 AL2 Si3 O10 * 2(H2 O)  NATROLITE
73  AMMA  58  676  Na2 AL2 Si3 c10 * 2(H2 O)  NATROLITE, 88 DEGREES
73  AMMA  58  676  Na2 AL2 Si3 c10 * 2(H2 O)  NATROLITE, 146 DEGREES
73  AMMA  58  681  Li AL Si C4  NATROLITE, 198 DEGREES
73  AMMA  58  681  Li AL Si C4  BETA EUCRYPTITE
73  AMMA  58  681  Li AL Si O4  BETA EUCRYPTITE, 200 DEGREES
73  AMMA  58  681  Li AL Si O4  BETA EUCRYPTITE, 335 DEGREES
73  ZEGKA  138  419  Ca Fe Si12 O6  BETA EUCRYPTITE, 400 DEGREES
74  ACBCA  830  1882  Ka In Si12 C6  DATOLITE
| AMMIA | 59 | 486 | FE₂ S₁ O₄ |
| AMMIA | 59 | 486 | N₂ S₁ O₄ |
| AMMIA | 59 | 486 | BA \(\text{FeSi}_2\) C₁₀ |
| ACBCA | 331 | 560 | S₁₂ S₁₂ O₆ |
| ACBCA | 331 | 560 | BA GA₂ S₁₂ O₆ |
| #1 | SR GA₂ S₁₂ O₆ |
| #2 | SR GA₂ S₁₂ O₆ |

**SULPHUR**

| JCSOA | 1960 | 5112 | K₂ S₂ O₇ |
| ZEKA | 117 | 344 | Mg (N₄41)₂ (S O₄)₂ - 6(H₂ O) |
| ACBCA | 17 | 235 | Mg S O₄ - 6(H₂ O) |
| ACBCA | 17 | 863 | Mg S O₄ - 4(H₂ O) |
| ACBCA | 17 | 1167 | Fe S O₄ - 7(H₂ O) |
| ACBCA | 17 | 1361 | Mg S O₄ - 7(H₂ O) |
| ACBCA | 18 | 717 | Li₂ S O₄ - H₂ O |
| ACBCA | 22 | 775 | Fe (N₄1)₂ (S O₄)₂ - 6(H₂ O) |
| ACBCA | 22 | 775 | Ca (N₄1)₂ (S O₄)₂ - 6(H₂ O) |
| ZEKA | 124 | 358 | K₂ Ca (S O₄)₂ - H₂ O |
| ACBCA | B24 | 760 | Fe (Zn,Mn,Mg,Fe) (S C₄)₂ C₁₀ |
| ZEKA | 127 | 261 | Fe₂ (S O₄)₂ C₁₀ - 7(H₂ O) |
| ACBCA | B25 | 19 | Cu In H₃₄ S O₄ - H₂ C |
| ACBCA | B25 | 304 | Be S O₄ - 4(H₂ O) |
| ACBCA | B25 | 676 | Cu (N₄1)₂ (S O₄)₂ - 6(H₂ C) |
| ACBCA | B25 | 1666 | K₂ S₂ O₁₆ |
| ACBCA | B25 | 2298 | K₄ L₁ S C₄ |
| ACBCA | R₂6 | 335 | Zn (C₁₁ (N₁₄2)₁₂ (S C₄)₂ |
| ACBCA | R₆ | 536 | Na₂ H₁₂ S O₄ |
| AMMIA | 55 | 78 | Fe₃ (S O₄)₄ - 14(H₂ O) |
| AMMIA | 55 | 378 | Na₁₂ Mg₁⁷ S₁₃ O₅₂ - 1₅(H₂ C) |
| AMMIA | 55 | 1534 | Fe₁₂₋₁₂ (H₂ O)₃ - 9(H₂ O) |
| AMMIA | 56 | 1917 | K₂ Fe (S O₄)₁₂ |
| AMMIA | 56 | 1917 | K₂ Fe (S O₄)₁₂ - 4(H₂ C) |
| ACBCA | R₂₆ | 236 | Fe N₄ S O₄ - 3(H₂ C) |
| ACBCA | R₆ | 284₅ | K₂ S O₄ |
| AMMIA | 57 | 1081 | Na₆ Al₁⁷ (S O₄)₂ - 1₁(H₂ O) |
| AMMIA | 57 | 132₅ | K Mg₁² S O₄ - 2₇₅(H₂ O) |
| TPMMA | 1₈ | 1₈₅ | K₂ Fe₈ Al₁² (S O₄)₁₂ - 1₈(H₂ C) |
| ACBCA | B₂₉ | 360 | Li₂ S O₄ |
| ACBCA | B₂₉ | 27₃₂ | V O S O₄ - 3(H₂ O) |
| ACSAA | 2₇ | 8₁₄ | Na₂ S O₄ |
| ACSAA | 2₇ | 2₆₁₄ | Zr (O₁₄ H₂ S O₄ - H₂ O |
| ACBCA | B₃₀ | 6₆₂ | Cs Ti (S C₄)₂ - 1₂(H₂ O) |
| ACBCA | B₃₀ | 8₃₁ | Li H S O₄ |
| ACBCA | B₃₀ | 9₂₁ | Ca S O₄ - 2(H₂ O) |

**GILLESPIE**

**KRAUSITE**

**SYNGENITE**

**BOTRYOGEN**

**AMARANTITE**

**YAVAPAIITE**

**GOLDICHITE**

**REEMERITE**

**LOEWENITE**

**COQUIMBITE**

**VOLTIAITE**

**MENODZITE**

**KAINITE**

**THENARDITE**

**GYPSUM**
<table>
<thead>
<tr>
<th>74</th>
<th>ACBCA</th>
<th>B30</th>
<th>1640</th>
<th>BETA RB2 S 04</th>
</tr>
</thead>
</table>

**TITANIUM**

<table>
<thead>
<tr>
<th>73</th>
<th>ACBCA</th>
<th>B29</th>
<th>2009</th>
<th>BETA BA2 TI 04</th>
</tr>
</thead>
</table>

**TUNGSTEN**

<table>
<thead>
<tr>
<th>65</th>
<th>ACCRA</th>
<th>18</th>
<th>88</th>
<th>CA W 04</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>ACBCA</td>
<td>B28</td>
<td>3174</td>
<td>BETA SN W 04</td>
</tr>
<tr>
<td>-----</td>
<td>---------</td>
<td>------</td>
<td>------</td>
<td>--------------</td>
</tr>
</tbody>
</table>

**VANADIUM**

<table>
<thead>
<tr>
<th>68</th>
<th>ACBCA</th>
<th>B24</th>
<th>292</th>
<th>Y V 04</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>INOCA</td>
<td>9</td>
<td>2259</td>
<td>CA2 V 04 CL</td>
</tr>
<tr>
<td>72</td>
<td>CJCHA</td>
<td>50</td>
<td>3944</td>
<td>CU3 V2 08</td>
</tr>
<tr>
<td>72</td>
<td>JSSCB</td>
<td>4</td>
<td>29</td>
<td>FE V 04</td>
</tr>
<tr>
<td>73</td>
<td>ACBCA</td>
<td>B29</td>
<td>141</td>
<td>Y V 04</td>
</tr>
<tr>
<td>73</td>
<td>ACBCA</td>
<td>B29</td>
<td>1338</td>
<td>CU5 V2 010</td>
</tr>
<tr>
<td>73</td>
<td>CJCHA</td>
<td>51</td>
<td>265</td>
<td>LI V 03</td>
</tr>
<tr>
<td>73</td>
<td>CJCHA</td>
<td>51</td>
<td>1004</td>
<td>ALPHA ZN2 V2 07</td>
</tr>
<tr>
<td>73</td>
<td>JSSCB</td>
<td>6</td>
<td>538</td>
<td>LI3 V 04</td>
</tr>
<tr>
<td>74</td>
<td>ACBCA</td>
<td>B30</td>
<td>1628</td>
<td>ALPHA NA V C3</td>
</tr>
<tr>
<td>74</td>
<td>ACBCA</td>
<td>B36</td>
<td>2491</td>
<td>MG2 V2 07</td>
</tr>
<tr>
<td>74</td>
<td>NJMMA</td>
<td>1974</td>
<td>210</td>
<td>CA5 (V O4)3 O H</td>
</tr>
<tr>
<td>75</td>
<td>ACBCA</td>
<td>B31</td>
<td>603</td>
<td>ALPHA CUPRIC DIVANADATE</td>
</tr>
</tbody>
</table>

**ZINC**

<table>
<thead>
<tr>
<th>67</th>
<th>ZEKGA</th>
<th>124</th>
<th>180</th>
<th>ZN4 S12 O7 (C H12 * H2 O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>69</td>
<td>ACBCA</td>
<td>B25</td>
<td>1233</td>
<td>ZN D</td>
</tr>
<tr>
<td>69</td>
<td>ZEKGA</td>
<td>130</td>
<td>261</td>
<td>ZN3 (P C412 * 4(H2 O))</td>
</tr>
<tr>
<td>69</td>
<td>ZEKGA</td>
<td>130</td>
<td>427</td>
<td>CA2 ZN S12 O7</td>
</tr>
<tr>
<td>70</td>
<td>ACBCA</td>
<td>426</td>
<td>335</td>
<td>ZN (C (N H2)3 )? (S C412</td>
</tr>
<tr>
<td>71</td>
<td>ACBCA</td>
<td>B27</td>
<td>672</td>
<td>ZN B4 C7</td>
</tr>
<tr>
<td>72</td>
<td>PARCA</td>
<td>27</td>
<td>76</td>
<td>ZN GA2 C4</td>
</tr>
<tr>
<td>73</td>
<td>ACSAA</td>
<td>27</td>
<td>1541</td>
<td>ZN S O3 * 2.5(H2 O)</td>
</tr>
<tr>
<td>74</td>
<td>AMMA</td>
<td>59</td>
<td>573</td>
<td>(CU2ZN12 ZN P C4 (O H3)13</td>
</tr>
<tr>
<td>#3</td>
<td>ACBCA</td>
<td>59</td>
<td>573</td>
<td>DISODIUM ZINCOSILICATE</td>
</tr>
</tbody>
</table>

**Publication Codes from Cuden for Periodical Titles, ASTM Data Series OS 23H, Phila., 147**
* 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)
The vita has been removed from the scanned document
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$_2$Si$_2$O$_8$) has been refined to $R = 0.048$. Cell dimensions are positively correlated with both $<M-0>$ and $<T-0>$. Slawsonite appears to be fully ordered with $<Si-0> = 1.624\AA$ and $<Al-0> = 1.748\AA$. Even where ordering is complete, $<Si-0>$ apparently varies with structure type and cation combination.

The crystal structure of a celsian ($Cn_{95}O_{15}$) 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.