Acta Cryst. (1954). **7**, 479

A Review of the Al–O and Si–O Distances

By J. V. Smith

Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C., U.S.A.

(*Received* 21 *January* 1954 *and in revised form* 19 *February* 1954)

A review of the measured Al–O and Si–O distances leads to the values Al–O = 1·78±0·02 Å and Si–O = 1·60±0·01 Å. These values are of use in locating the positions of Al and Si atoms in felspar or other structures by accurate measurements of distances in oxygen tetrahedra.

Introduction

Because the atomic scattering factors of silicon and aluminium are similar, it is difficult to distinguish between these atoms in tetrahedral positions of crystal structures. It has been realized for some time by many crystallographers that the only direct way of doing this in complicated structures* is by accurately determining the distances in oxygen tetrahedra. It is important, therefore, to know accurately the expected values for the Al–O and Si–O distances. This problem is especially important in felspar structure determinations in which it is thought that the main difference between the polymorphs lies in the state of order of the silicon and aluminium atoms. In view of the large amount of work being expended on the felspar structures at the present time, it was thought desirable to review the measured Al–O and Si–O distances and to determine the best values for them.

Evaluation of accuracy

Because of the paucity of the data for Al–O distances it is essential to examine the accuracy as closely as possible. This is difficult because of the various methods used in determining the atomic parameters. In recent years, methods have been developed for systematically refining atomic parameters by successive Fourier series. In addition, accurate estimates of the errors in the parameters can now be obtained by the use of statistical methods based on observed fluctuations of electron density in Fourier series. Before the advent of these methods, however, it was possible to obtain high accuracy (∼ 0·02 Å) only in structures where most of the parameters were fixed by symmetry. In most early determinations of complex structures, the parameters were not systematically refined and are not reliable to better than 0·1 Å. Usually no estimates of error were given, and in this paper an attempt has been made to estimate the errors where these were not given. These estimates are based on a consideration of (*a*) the number of arbitrary parameters, (*b*) the method of adjusting the parameters, and (*c*) the type of linkage of the tetrahedra. The effects of (*a*) and (*b*) are obvious. The effect of (*c*) arises in this way: if any two tetrahedra containing the same atoms share a corner, then, to a first approximation, the mean of the two (Si, Al–O) distances at that corner is independent of the position of the oxygen atom. Framework structures whose tetrahedra contain the same atoms are therefore more favourable for accurate work than structures with isolated tetrahedra. For the framework structures with alternating Si and Al tetrahedra, however, the errors in the oxygen parameters have the same effect on the individual Si–O and Al–O distances as if the tetrahedra were isolated.

In order to simplify the problem of comparing data obtained by such different methods, the following classification is used. For structures whose parameters were systematically refined a numerical error is given. For structures whose parameters were not systematically refined, the letters *A* and *B* are used. *A* denotes that the structure is favourable for the determination of accurate distances and *B* that the structure is unfavourable. For especially favourable structures a numerical error is given which has been estimated by myself. *A* represents an accuracy of about 0·03 Å, and *B* an accuracy of 0·05–0·10 Å; it should be emphasized that these errors are based merely on personal judgement without an accurate mathematical backing.

Review of the structures

(*a*) Al–O *distances*

1. $Na_8Al_4Si_4O_{18}$ (Borchert & Keidel, 1947).—Small cubic cell, eight parameters. Accuracy not stated; probably *B*. Al–O = 1·85 Å; Si–O = 1·55 Å.

2. *Barium aluminate*, $BaAl_2O_4$ (Wallmark & Westgren, 1937).—Hexagonal, small cell, two parameters. Accuracy not stated, but structure is so favourable that a numerical estimate of 0·02 Å is used. This agrees with the observed variation of 1·75–1·79 Å. Al–O = 1·78±0·02 Å.

3. $Na_2O.11Al_2O_3$ (Beevers & Ross, 1937).—Hexagonal, large cell, seven parameters. Complicated struc-

---

* Neutron diffraction can at present be used only in simple structures with which we are not concerned. Comparison with synthetic crystals which have gallium substituted for aluminium and germanium substituted for silicon provides an indirect method if the crystals are isostructural (see Goldsmith & Laves, 1951).

Table 1. Al–O *and* Si–O *distances*

Type	Distance (Å)	Source
Al–O	$1{\cdot}85 \pm B$	$Na_8Al_4Si_4O_{18}$ (Borchert & Keidel, 1947)
Al–O	$1{\cdot}78 \pm 0{\cdot}02$	$BaAl_2O_4$ (Wallmark & Westgren, 1937)
Al–O	$1{\cdot}7 \pm B$	'βAl_2O_3' (Beevers & Ross, 1937)
Al–O	$1{\cdot}75 \pm A$	$12CaO.7Al_2O_3$ (Büssem & Eitel, 1936)
Al–O	$1{\cdot}72 \pm B$	Sillimanite (Hey & Taylor, 1931)
Al–O	$1{\cdot}76 \pm A$	Sodalite (Pauling, 1930)
$\frac{1}{2}$(Al–O)+$\frac{1}{2}$(Si–O)	$1{\cdot}69_6 \pm 0{\cdot}01$	Paracelsian (Smith, 1953*b*)
$\frac{1}{2}$(Al–O)+$\frac{1}{2}$(Si–O)	$1{\cdot}69 \pm 0{\cdot}01$	Eucryptite (Winkler, 1948)
$Al_{\frac{1}{2}}Si_{\frac{1}{2}}$–O	$1{\cdot}64 \pm B$	Sodalite (Barth, 1932)
$Al_{\frac{1}{2}}Si_{\frac{1}{2}}$–O	$1{\cdot}66 \pm B$	Noselite (Barth, 1932)
$Al_{\frac{1}{3}}Si_{\frac{2}{3}}$–O	$1{\cdot}62 \pm A$	Analcite (Taylor, 1930)
$Al_{\frac{1}{4}}Si_{\frac{3}{4}}$–O	$1{\cdot}64_2 \pm 0{\cdot}003$	Sanidine (Cole *et al.*, 1949)
$\frac{1}{4}$(Al–O)+$\frac{3}{4}$(Si–O)	$1{\cdot}63 \pm A$	Orthoclase (Chao *et al.*, 1940)
Si–O	$1{\cdot}60 \pm 0{\cdot}01$	Afwillite (Megaw, 1952)
Si–O	$1{\cdot}61 \pm 0{\cdot}01$	Tilleyite (Smith, 1953*a*)
Si–O*	$1{\cdot}60 \pm 0{\cdot}02$	High-cristobalite (Nieuwenkamp, 1937)
Si–O	$1{\cdot}59 \pm A$	Low-cristobalite (Nieuwenkamp, 1935)
Si–O	$1{\cdot}59 \pm A$	Low-quartz (Machatschki, 1936)
Si–O	$1{\cdot}61_5 \pm 0{\cdot}02$	Low-quartz (Wei, 1935)
Si–O*	$1{\cdot}61_2 \pm 0{\cdot}01$	High-quartz (Wyckoff, 1926)

* Determined at high temperatures. All other values determined at room temperature.

ture with 14Al in octahedra and 8Al in tetrahedra. Values for Al–O tetrahedra vary from 1·64 to 1·78 Å. Accuracy *B*.

4. $12CaO.7Al_2O_3$ (Büssem & Eitel, 1936).—High symmetry, cubic, large cell, six parameters. Values for Al–O distances vary from 1·72 to 1·78 Å. Accuracy *A*. Al–O = 1·75 Å.

5. *Sillimanite*, Al_2SiO_5 (Hey & Taylor, 1931).—Small orthorhombic cell, isolated tetrahedra. No estimate of error given. Al–O = 1·72 Å. Accuracy *B*.

6. *Sodalite*, $Na_4Al_3Si_3O_{12}Cl$ (Pauling, 1930; Barth, 1932).—Cubic; space group uncertain. Pauling gives structure with segregated Al and Si atoms: Al–O = 1·76 Å and Si–O = 1·58 Å (values recalculated from Pauling's atomic positions). Barth, on the other hand, gives a structure with disordered Si and Al atoms; $Si_{\frac{1}{2}}Al_{\frac{1}{2}}$–O = 1·64 Å. For the isomorphous noselite he gives $Si_{\frac{1}{2}}Al_{\frac{1}{2}}$–O = 1·66 Å. Pauling has systematically varied his parameters and considers that his oxygen positions are accurate to at least 0·05 Å. Accuracy taken as *A*. Barth did not systematically vary his parameters and so probably is not accurate to better than *B*.

(*b*) $Al_{\frac{1}{2}}Si_{\frac{1}{2}}$–O *distances*

1. *Paracelsian*, $BaAl_2Si_2O_8$ (Smith, 1953*b*).—Error estimated from fluctuations of electron density in Fourier series. $\frac{1}{2}$(Al–O)+$\frac{1}{2}$(Si–O) = $1{\cdot}69_6 \pm 0{\cdot}01$ Å.*

2. *Eucryptite*, $LiAlSiO_4$ (Winkler, 1948).—Small hexagonal cell, three parameters. Oxygen was taken as half-way between Si and Al, which arbitrarily makes the Si and Al tetrahedra equal. This is not required by the space group. Because of the very favourable structure, accuracy was taken to be 0·01 Å. $\frac{1}{2}$(Al–O)+$\frac{1}{2}$(Si–O) = $1{\cdot}69 \pm 0{\cdot}01$ Å.

(*c*) $Al_{\frac{1}{3}}Si_{\frac{2}{3}}$–O *distances*

1. *Analcite*, $NaAlSi_2O_6.H_2O$ (Taylor, 1930).—Large, high symmetry, cubic cell. Si and Al atoms statistically distributed. Four parameters. Error not given; accuracy taken as *A*. $Al_{\frac{1}{3}}Si_{\frac{2}{3}}$–O = 1·62 Å.

(*d*) $Al_{\frac{1}{4}}Si_{\frac{3}{4}}$–O *distances*

1. *Sanidine*, $KAlSi_3O_8$ (Cole, Sörum & Kennard, 1949).—Very accurate three-dimensional Fourier analysis. Si and Al statistically distributed. $Al_{\frac{1}{4}}Si_{\frac{3}{4}}$–O = $1{\cdot}64_2 \pm 0{\cdot}003$ Å.

2. *Orthoclase*, $KAlSi_3O_8$ (Chao, Hargreaves & Taylor, 1940).—In this complicated monoclinic crystal the interatomic distances suggest ordering into Si and $Si_{\frac{1}{2}}Al_{\frac{1}{2}}$ tetrahedra (distances 1·58 Å and 1·68 Å). Cole *et al.* (1949) suggested that the coordinates were not accurate enough to prove that this ordering occurs; accordingly, a mean value of the distance is taken here. Chao *et al.* considered that the individual coordinates are accurate to not worse than ±0·1 Å. For the average distance, $\frac{1}{4}$(Al–O)+$\frac{3}{4}$(Si–O) = 1·63 Å. Accuracy *A*.

(*e*) Si–O *distances*

There are many values for Si–O given in the literature and a detailed description of the accuracy of each will not be given here. Only the more accurate values are listed (Table 1). Some have been recalculated to take into account more accurate lattice parameters determined afterwards.

Discussion

All values which have been assigned a numerical error of 0·02 Å or less have been plotted in Fig. 1, and it

---

* If the (Si, Al–O) distance is not a linear function of aluminium percentage, distinction must be made between an average of Si–O and Al–O distances and between a (Si, Al–O) distance for disordered Si and Al atoms. In paracelsian it was uncertain whether the atoms were disordered or ordered, although the latter was more probable.

will be seen that they may be represented within experimental error by Al–O = 1·78±0·02 Å and Si–O = 1·60±0·01 Å. The values of lower accuracy also agree within their larger errors with these values. In order to test whether there is a linear relation for disordered atoms, values which are averages for ordered atoms cannot be considered. This removes the values for eucryptite and paracelsian at the half-way point. The remaining data are insufficient for a test. Although this test cannot be made, it seems unlikely that there will be much deviation from linearity.

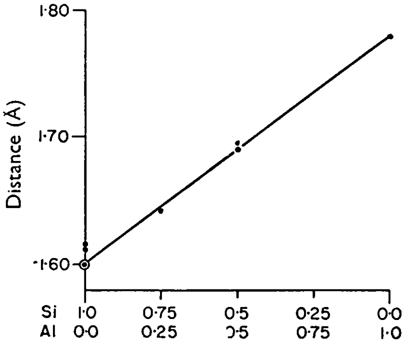

Fig. 1. A graph of the more accurate values for Si–O and Al–O distances. The straight line connects the points Si–O = 1·60 Å, Al–O = 1·78 Å.

Two of the measured values are for high-temperature structures. They do not differ significantly from the values for low-temperature structures, suggesting that the bonds in tetrahedra are almost independent of temperature. It is desirable that considerably more work be carried out to test this suggestion.

Cole *et al.* (1949) suggested that the extreme values were 1·72 and 1·62 Å respectively, on the basis of a survey of the Si–O distances, their value of $1{\cdot}64_2$ Å for $Si_{\frac{1}{2}}Al_{\frac{1}{2}}$–O and the value of 1·72 for Al–O in sillimanite. It is suggested that the new values for the two atoms, which are based on a more complete survey, be substituted for the values of Cole *et al.* The new values differ by 0·18 Å, whereas the old values differ by 0·10 Å, and it therefore seems likely that the problem of distinguishing Al and Si positions is not as difficult as was once thought. Careful two-dimensional analysis should definitely permit the distinction of Al and Si and should permit the distinction of Si and $Si_{\frac{1}{2}}Al_{\frac{1}{2}}$. With three-dimensional analyses (such as that of Cole *et al.*, where σ(Si–O) = 0·0042 Å for the mean value of four independently measured Si–O distances in a tetrahedron), it should be possible to detect differences of about 5% Al in tetrahedra if the distances are governed solely by the percentage of Al.

If we wish to interpret the measurements to this precision, then we have to make sure that the type of bonding and the effect of neighbouring cations such as Ca have a very small effect on the (Si, Al–O) distances. Three measurements in Table 1 provide evidence on this point. In high-quartz, each corner of an SiO_4 group is shared with another SiO_4 group; in afwillite, the tabulated distance of Si–O is the mean of the three Si–O distances in an $SiO_3(OH)$ group; in tilleyite, the Si–O distance is the mean of eight distances in an Si_2O_7 group which has only one shared corner. In spite of these different environments, the respective values $1{\cdot}61_2$, 1·60 and 1·61 differ from the chosen value of 1·60 by no more than the experimental error of 0·01 Å. The effect of neighbouring cations such as Ca which are at distances of 2·5 Å should be less than the effects just described, which are from atoms at a distance of only 1·6 Å. Accordingly, it seems likely that 0·01 Å represents the upper limit of variation to be expected from sources other than (Si, Al) substitution. In the felspars, where the tetrahedra are in three-dimensional linkage, with only a small variation of environment, the effect should be less than the effect on the three structures just described. Accordingly, there is no evidence to suppose that a measured (Si, Al–O) distance will not give a genuine measure of the amount of substituted Al.

I am grateful to Dr H. D. Megaw of the Crystallographic Laboratory, Cambridge, for constructive criticisms of the manuscript and to Dr F. Chayes of this Laboratory for suggestions concerning the comparison of data of varying accuracy.

References

Barth, T. F. W. (1932). *Z. Kristallogr.* **83**, 405.
Beevers, C. A. & Ross, M. A. S. (1937). *Z. Kristallogr.* **97**, 59.
Borchert, W. & Keidel, J. (1947). *Heidelberg Beitr. Min.* **1**, 17.
Büssem, W. & Eitel, A. (1936). *Z. Kristallogr.* **95**, 175.
Chao, S. H., Hargreaves, A. & Taylor, W. H. (1940). *Miner. Mag.* **25**, 498.
Cole, W. F., Sörum, H. & Kennard, O. (1949). *Acta Cryst.* **2**, 280.
Goldsmith, J. R. & Laves, F. (1951). A. C. A. Meeting, Chicago, October 1951. (Abstract, p. 11.)
Hey, J. S. & Taylor, W. H. (1931). *Z. Kristallogr.* **80**, 428.
Machatschki, F. (1936). *Z. Kristallogr.* **94**, 222.
Megaw, H. D. (1952). *Acta Cryst.* **5**, 477.
Nieuwenkamp, W. (1935). *Z. Kristallogr.* **92**, 82.
Nieuwenkamp, W. (1937). *Z. Kristallogr.* **96**, 454.
Pauling, L. (1930). *Z. Kristallogr.* **74**, 213.
Smith, J. V. (1953*a*). *Acta Cryst.* **6**, 9.
Smith, J. V. (1953*b*). *Acta Cryst.* **6**, 613.
Taylor, W. H. (1930). *Z. Kristallogr.* **74**, 1.
Wallmark, S. & Westgren, A. (1937). *Ark. Kemi Min. Geol.* **12**, No. 35.
Wei, P.-H. (1935). *Z. Kristallogr.* **92**, 355.
Winkler, H. G. F. (1948). *Acta Cryst.* **1**, 27.
Wyckoff, R. W. G. (1926). *Amer. J. Sci.* **11**, 101.