Computer (Report No. 6478). Ottawa: National Research Council.

AHMED, F. R., BARNES, W. H. & MASIRONI, L. DI M. (1963). *Acta Cryst.* **16**, 237.

FARMILO, C. G. & LEVI, L. (1953). *Bull. Narcotics, U.N. Dept. Social Affairs,* **5** (4), 20.

FODOR, G. (1960). in MANSKE, R. H. F. *The Alkaloids,* vol. VI, chap. 5. New York: Academic Press.

FREEMAN, A. J. (1959). *Acta Cryst.* **12**, 261.

GABE, E. J. (1962). *Acta Cryst.* **15**, 759.

HANSON, A. W. (1958). *J. Sci. Instrum.* **35**, 180.

HANSON, A. W. & AHMED, F. R. (1958). *Acta Cryst.* **11**, 724.

HOLMES, H. L. (1950) in MANSKE, R. H. F. & HOLMES, H. L. *The Alkaloids,* vol. I, chap. VI. New York: Academic Press.

KARTHA, G. (1952). *Acta Cryst.* **5**, 549.

KARTHA, G., AHMED, F. R. & BARNES, W. H. (1960). *Acta Cryst.* **13**, 525.

KARTHA, G., AHMED, F. R. & BARNES, W. H. (1961). *Acta Cryst.* **14**, 93.

KARTHA, G., AHMED, F. R. & BARNES, W. H. (1962). *Acta Cryst.* **15**, 326.

LIEBERMANN, C. (1890). *Ber. Dtsch. Chem. Ges.* **23**, 2518.

LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures.* London: Bell.

McWEENY, R. (1951). *Acta Cryst.* **4**, 513.

MERCK, W. (1885). *Ber. Dtsch. Chem. Ges.* **18**, 2952.

PRZYBYLSKA, M. & AHMED, F. R. (1958). *Acta Cryst.* **11**, 718.

RÉRAT, C. (1960). *Acta Cryst.* **13**, 72.

SHOEMAKER, D. P., DONOHUE, J., SCHOMAKER, V. & COREY, R. B. (1950). *J. Amer. Chem. Soc.* **72**, 2328.

SUTTON, L. E. (1958). *Tables of Interatomic Distances and Configurations in Molecules and Ions.* London: The Chemical Society.

VISSER, J. W., MANASSEN, J. & DEVRIES, J. L. (1954). *Acta Cryst.* **7**, 288.

WILLSTÄTTER, R., WOLFES, O. & MÄDER, H. (1923). *Liebigs Ann.* **434**, 111.

WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

WÖHLER, F. (1862). *Ann. Chem. Pharm.* **121**, 372.

Second Review of Al-O and Si-O Tetrahedral Distances

BY J. V. SMITH

Department of Geophysical Sciences, University of Chicago, Chicago 37, Illinois, U.S.A.

AND S. W. BAILEY

Department of Geology, University of Wisconsin, Madison 6, Wisconsin, U.S.A.

In the same tetrahedron, individual Si-O (or Al-O) distances have been found to vary by amounts up to 0·1 Å even when the random experimental error is less than 0·01 Å. In a single structure the differences between the mean values of the four distances in a tetrahedron are much smaller, for variations between chemically identical tetrahedra rarely amount to more than 0·02 Å. The average of all the Si-O distances in a structure depends on the extent of the tetrahedral linkage, changing from 1·61 Å in frameworks to 1·63 Å in structures with isolated tetrahedra. Correspondingly, the average Al-O distance changes from 1·75 to 1·80 Å, the latter figure requiring confirmation. The mean tetrahedral distance in a feldspar structure varies linearly with percentage Al from 1·61 for Si-O to 1·75 Å for Al-O. Individual tetrahedral means for ordered structures confirm these end values. The deviations from linearity are not greater than 0·003 Å and may merely result from random experimental error. Mean values for other framework structures deviate from the linear relation by about 0·01 Å. The less accurate data for layer silicates suggest a linear relation for the overall mean Si, Al-O distance between Si-O 1·62 and Al-O 1·77 Å.

Estimation of the Al-content of an individual tetrahedron from the measured Si, Al-O distances must take into account the effects of structural type and of local environment of the tetrahedron. Even after correction for the structural type, it seems that the local environment may lead to errors of ±5% Al (in round figures) in addition to the effect of experimental error.

It is hoped that further studies along these lines may lead to empirical relations between bond distances and atomic environment for complex structures, and ultimately to estimation of the internal energy from observed atomic coordinates.

1. Introduction

In 1954 J. V. Smith examined measured Si, Al-O distances and suggested standard values for estimating the substitution of aluminum and silicon atoms in tetrahedra. The available data were mainly of low accuracy and the predicted values (Si-O, 1·60; Al-O, 1·78 Å) were somewhat uncertain. Nevertheless, these values have been used considerably in discussion of feldspar structures, sometimes without full awareness

of the possible uncertainties. Since the advent of electronic computers, refinement of atomic coordinates has become more sophisticated, and better values of Si, Al–O distances are now available. In 1954, errors were usually so large that it was not necessary to ascribe variation of distances to factors other than that of chemical content; the only data of high reliability (those for high sanidine, Cole, Sörum & Kennard (1949)) gave individual Si, Al–O distances that varied only over 0·007 Å. However, recent values for Si–O bonds have varied by as much as 0·1 Å even when the standard deviation was less than 0·01 Å, demonstrating that the Si–O bond is affected by factors other than atomic substitution. At the Fifth International Congress of Crystallography, it was reported that the overall mean Si–O distance appeared to increase from 1·61 Å in a framework silicate to 1·63 Å for a silicate with isolated tetrahedra.

At the University of Wisconsin, S. W. Bailey was finding that the Si, Al–O distances in layer silicates appeared to be about 0·01 Å higher than in feldspars for the same Si : Al ratio. At the same time, Megaw, Kempster & Radoslovich (1962) were finding that the Si–O or Al–O distances in anorthite increased by about 0·05 Å as the oxygen atoms were attached to 0, 1 or 2 calcium atoms. Several other scientists (especially Prof. M. J. Buerger and C. W. Burnham at the Massachusetts Institute of Technology and Dr G. V. Gibbs at the Pennsylvania State University) were finding similar variations in Si–O distances as a result of secondary coordination. Thus there was a growing feeling that a careful re-examination of the factors that control interatomic distances was needed. Rather than publish separate accounts of our work, we have integrated our results so that the reader's task will be simplified. As our work is based so much on the thoughts and measurements of others, we wish to draw especial attention to the acknowledgements to them at the end of this paper.

Extensive discussion in the scientific literature has shown that error in interatomic distances arises from several factors, including inaccuracy of the cell dimensions, error of intensity measurements and incomplete refinement of the atomic coordinates. The latter factor, which arises from incorrect signs for the weaker terms in the Fourier series, and from overlapping of electron density from adjacent atoms, gives errors whose direction and magnitude cannot be calculated: such errors are especially serious for atomic coordinates determined by two-dimensional (2D) methods where overlapping of peaks is common, and are insignificant in structures determined by three-dimensional (3D) methods in which many cycles of refinement have been made. In addition, intensity errors have less proportional effect in 3D refinement and, consequently, reliance will be placed wherever possible on the latter type of result.

In order to discover the effect of Si, Al substitution or of complexity of tetrahedral linkage, it is best to average the individual distances over the appropriate structural unit so that factors that affect only individual distances have reduced effects. The relation between error of an individual value and error of a mean value, either for the whole structure or for a single tetrahedron, is quite complex. If the four Si–O distances in a tetrahedron are all unrelated by symmetry, error in the fractional coordinates of a silicon atom has no significant effect on the mean of the four Si–O distances. This arises because displacement of the silicon atom towards one oxygen atom is compensated by lengthening of bonds to the other oxygen atoms. When oxygen atoms are each joined to two silicon atoms, errors in the fractional coordinates do not have full effect on the overall mean Si–O distances. If all Si–O–Si bond angles were 180°, errors in the position of the oxygen atoms would have no significant effect on the mean Si–O distance. As the angle deviates from 180°, the effect increases continuously until a maximum is reached at zero degrees which corresponds to an isolated tetrahedron. In silicates, the Si–O–Si bond angles lie between 120° and 180° with a mean value near 140° (Liebau, 1961c): consequently the overall mean distance in framework structures is affected only slightly by errors in the fractional coordinates of the silicon and oxygen atoms.

Errors in interaxial angles directly affect individual Si–O distances, but have no significant effect on mean values taken for Si–O distances isotropically distributed. Errors in the cell edges have serious effects both on individual and mean Si–O distances, especially if the measured cell edges are all too large or too small. Some of the cell dimensions for silicates studied by 3D methods were determined by forward-reflection techniques. These may be in error by 0·5%, and all three dimensions are likely to be affected in the same direction. Consequently a systematic error as large as 0·01 Å might occur for Si–O distances determined by this type of method, though a smaller value is more likely. Dimensions for other silicates, whose atomic coordinates were determined by 3D methods, were estimated with an accuracy of 0·1% or better, thus giving a negligible maximum error of 0·002 Å from this cause.

Although pictorial display of data has been made as comprehensive as possible, and the tables contain the essential data for all the relevant structures determined by 3D methods, and for some of the more accurate of the structures studied by 2D techniques, it has not been feasible to include all the data necessary for evaluation of error. However, it is felt that any reader who wishes to examine with full rigour the validity of the present arguments should examine the original references anyway: as a help, a few notes on individual structure determinations have been included to deal with the more important points not suitable for tabular presentation.

Table 1. Si–O and Al–O *Tetrahedral distances*

Name	Formula	Si, Al-O Distances				Standard Deviation	Mean for Tetrahedron	Overall Mean	Reference
a) Data based on three-dimensional refinement									
afwillite	$Ca_3(SiO_3OH)_2 2H_2O$	Si-O: 1.57	1.58	1.60		0.037			Megaw (1952)
		1.61	1.61	1.61					
		Si-OH: 1.65	1.71						
albite (low)	$NaAlSi_3O_8$	1.730 1.745	1.751	1.751		0.01 approx.	1.744	1.646	Ribbe (1952a) preliminary values:
		1.601 1.604	1.612	1.623			1.610		refinement not quite
		1.592 1.614	1.621	1.635			1.616		complete
		1.585 1.602	1.620	1.643			1.613		
andalusite	Al_2SiO_5	1.615 1.631	twice	1.635		0.005	1.628	1.628	Burnham and Buerger (1961)
anorthite (primitive)	$CaAl_2Si_2O_8$	1.559 1.601	1.603	1.646		0.004	1.602	1.681	Megaw, Kempster and Radoslovich (1962)
		1.571 1.617	1.618	1.626			1.608		
		1.566 1.606	1.617	1.652			1.610		
		1.575 1.589	1.641	1.647			1.613		
		1.589 1.611	1.624	1.629			1.613		
		1.585 1.599	1.620	1.661			1.616		
		1.600 1.623	1.637	1.643			1.626		
		1.622 1.628	1.629	1.634			1.628		
		1.695 1.755	1.757	1.757			1.741		
		1.706 1.747	1.754	1.769			1.744		
		1.708 1.733	1.747	1.796			1.746		
		1.723 1.730	1.749	1.784			1.746		
		1.723 1.735	1.754	1.794			1.752		
		1.696 1.738	1.780	1.792			1.752		
		1.692 1.745	1.782	1.792			1.753		
		1.701 1.755	1.755	1.820			1.758		
benitoite	$BaTiSi_3O_9$	1.605 twice	1.630	1.648		0.003	1.622	1.622	Fischer (1961)
coesite	SiO_2	1.593 1.605	1.616	1.641		0.008	1.614	1.613	Zoltai and Buerger (1959)
		1.589 1.610	1.618	1.629			1.612		Zoltai (1961)
cordierite	a	1.573 1.602	1.615	twice		0.005	1.601	1.673	Gibbs (1962b)
		1.606 1.620	1.628	twice			1.620		
		1.627 four	times				1.627		the third tetrahedron
		1.700 1.718	1.764	twice			1.736		is only half as frequent
		1.747 twice	1.767	twice			1.757		as the others
cummingtonite*	b	1.616 1.617	1.617	1.635		0.01. approx.	1.622	1.627	Ghose (1961); further
		1.613 1.626	1.646	1.646			1.633		refinement, Fischer (1962)
danburite	$CaB_2Si_2O_8$	1.612 1.617	1.621	1.625		0.010	1.619	1.619	Johansson (1959): partly 2D
dickite	$Al_2(Si_2O_5)(OH)_4$	1.614+ 1.615	1.637	1.642		0.017	1.627	1.620	Newnham (1961)
		1.604 1.614	1.617+	1.617			1.613		values recalculated
gismondine	$Ca(Al_2Si_2O_8)4H_2O$	1.611 1.617	1.621	1.625		0.004	1.619	1.678	Fischer (1962)
		1.611 1.614	1.622	1.636			1.621		
		1.725 1.733	1.734	1.735			1.732		
		1.725 1.732	1.741	1.759			1.739		
grossular	c	1.637 four	times			0.006	1.637	1.637	Abrahams and Geller (1958)
grunerite*	d	1.597 1.624	1.642	1.654		no estimate	1.629	1.631	Ghose and Hellner (1959)
		1.598 1.613	1.624	1.700			1.634		
hexagonal form	$CaAl_2Si_2O_8$	1.656 1.707	thrice			0.03 .	1.694	1.694	Takéuchi and Donnay (1959)
kyanite	Al_2SiO_5	1.603 1.621	1.622	1.639		0.006	1.621	1.626	Burnham (1962a)
		1.615 1.631	1.635	1.642			1.631		
microcline (intermediate)	$(K,Na)AlSi_3O_8$	1.608 1.609	1.611	1.614		0.009	1.610	1.642	Bailey and Taylor (1955)
		1.607 1.615	1.616	1.618			1.614		
		1.643 1.644	1.646	1.647			1.645		
		1.697 1.698	1.698	1.700			1.698		
microcline (maximum) (Pellotsalo)	do.	1.574 1.614	1.621	1.633		0.006	1.611	1.644	Brown and Bailey (1963a)
		1.592 1.593	1.617	1.644			1.612		
		1.592 1.608	1.628	1.629			1.614		
		1.738 1.739	1.741	1.745			1.741		
microcline (maximum) (Pontiskalk)	do.	1.593 1.598	1.615	1.638		0.016	1.611	1.644	Finney and Bailey
		1.586 1.619	1.622	1.622			1.612		
		1.582 1.623	1.627	1.650			1.620		
		1.719 1.721	1.744	1.753			1.734		
muscovite	e	1.683 1.689	1.698	1.710+		0.023	1.695	1.654	Radoslovich (1960)
		1.582 1.596	1.623	1.648+			1.612		Values recalculated
narsarsukite	f	1.601 1.614	1.626	1.639		0.006	1.620	1.620	Peacor and Buerger (1962)
natrolite	$Na_2Al_2Si_3O_{10}H_2O$	1.622 twice	1.629	twice		0.01	1.624	1.670	Meier (1960)
		1.600 1.611	1.620	1.635			1.616		values recalculated
		1.722 1.733	1.761	1.772			1.747		
nepheline	$KNa_3Al_4Si_4O_{16}$	1.64 1.64	thrice			0.03 approx.	1.64	1.687	Hahn and Buerger (1955)
		1.665 1.670	1.680	1.685			1.676		values given to nearest
		1.665 1.675	1.695	1.700			1.684		0.005
		1.790 1.775	thrice				1.78		
octa methyl cyclo-tetrasiloxane	$(SiO_2(CH_3)_2)_4$	1.64 1.65	1.65	1.66		0.018	1.65	1.65	Steinfink, Post and Fankuchen (1955)
octa methyl sil-sesquioxane	$(SiO_{1.5}CH_3)_8$	1.603 1.604	1.615	1.620		0.025	1.610	1.610	Larsson (1960)
proto-amphibole	g	1.605 1.616	1.619	1.630		0.01	1.618	1.621	Gibbs (1962a)
		1.600 1.611	1.633	1.654			1.624		
pyrope	$Mg_3Al_2Si_3O_{12}$	1.639 four	times			0.006	1.639	1.639	Gibbs and Smith (1962)
quartz (low)	SiO_2	1.603 twice	1.611	twice		0.003	1.607	1.607	Young and Post (1962)
do.	do.	1.597 twice	1.617	twice		0.003	1.607	1.607	Smith and Alexander (1963)
reedmergnerite*	$NaBSi_3O_8$	1.589 1.600	1.602	1.621		0.01	1.603	1.613	Clark and Appleman (1960)
		1.576 1.620	1.627	1.630			1.613		
		1.609 1.614	1.618	1.650			1.623		
sanidine	$(K,Na)AlSi_3O_8$	1.643 1.643	1.645	1.647		0.008 approx.	1.644	1.642	Cole, Sörum and Kennard (1949)
		1.631 1.638	1.645	1.645			1.640		new refinement by Ribbe (1962b)
sillimanite	Al_2SiO_5	1.564 1.629	1.633	twice		0.006	1.615	1.692	Burnham (1962b)
		1.721 1.758	1.800	twice			1.770		
spurrite	$Ca_5(SiO_4)_2CO_3$	1.580 1.625	1.641	1.656		0.023	1.625	1.631	Smith, Karle, Hauptman
		1.597 1.626	1.658	1.668			1.637		and Karle (1960)
thortveitite	$Sc_2Si_2O_7$	1.607 1.620	1.630	twice		0.015	1.622	1.622	Cruickshank, Lynton and Barclay (1962)
tourmaline	h	1.603 1.606	1.635	1.639		0.005	1.621	1.621	Buerger, Burnham and Peacor (1962)
yoderite	$Mg_2Al_{5.3}Fe_{0.5}Ca_{0.2}Si_4 O_{20}H_{2.4}$	1.627 1.639	1.639	1.647		0.004 approx.	1.638	1.635	Fleet and Megaw (1962)
		1.582 1.639	1.639	1.664			1.631		
xanthophyllite		1.710+ 1.725	1.730	1.754		0.014	1.730	1.730	Takéuchi and Sadanaga (1959)

Table 1 (cont.)

b) Data based on two-dimensional refinement

Mineral	Formula	Distances	σ	Mean	Overall mean	Reference
albite (high)	$NaAlSi_3O_8$	1.645 1.652 1.654 1.658 1.633 1.636 1.641 1.646 1.635 1.640 1.645 1.646 1.633 1.637 1.649 1.668	0.018	1.652 1.639 1.641 1.647	1.645	Ferguson, Traill and Taylor (1958)
amesite	i	1.670 thrice 1.713⁺ 1.670 thrice 1.713⁺	0.025	1.681	1.681	Steinfink and Brunton (1956)
beta form	$Na_2Si_2O_5$	1.50⁺ 1.62 1.63 1.65 1.52⁺ 1.64 1.65 1.65	?	1.60 1.615	1.608	Grund (1954)
celsian	$(Ba_{0.84}K_{0.18})(Al_{1.90}Si_{2.11})O_8$	1.617 1.637 1.640 1.645 1.633 1.633 1.640 1.651 1.698 1.702 1.714 1.733 1.703 1.711 1.722 1.733	0.012	1.635 1.639 1.712 1.717	1.676	Newnham and Megaw (1960)
clino-enstatite	$MgSiO_3$	1.61 1.63 1.65 1.67 1.58 1.62 1.70 1.74	0.05	1.64 1.66	1.65	Morimoto, Appleman and Evans (1960)
corundophyllite	k	1.636 1.640 1.685 1.709⁺ 1.639 1.662 1.682 1.709⁺ 1.646 1.673 1.682 1.709⁺ 1.652 1.676 1.693 1.710⁺	0.016	1.667 1.673 1.677 1.683	1.675	Steinfink (1958)
Cr-chlorite	l	1.616 1.637₊ 1.642 1.648⁺ 1.646 1.662⁺ 1.715 1.717	0.02	1.636 1.685	1.660	Brown and Bailey (1963b)
dioptase	$Cu_6(Si_6O_{18})6H_2O$	1.55 1.60 1.63 1.67	?	1.612	1.612	Heide et al (1955)
egyptian blue	$CaCuSi_4O_{10}$	1.59⁺ 1.59 1.60 1.60	0.04	1.595	1.595	Pabst (1959)
epidote	$Ca_2FeAl_2Si_3O_{10}(OH)$	1.59 1.66 twice 1.70 1.60 1.61 1.65 twice 1.60 twice 1.63. 1.66	0.04	1.652 1.627 1.622	1.634	Ito, Morimoto and Sadanaga (1954)
euclase	$Be_2(OH)_2(SiO_4)_2$	1.61 1.62 1.62 1.65	0.015	1.625	1.625	Mrose and Appleman (1962)
gillespite	$BaFe(Si_4O_{10})$	1.56 1.59 1.59 1.64⁺	?	1.595	1.595	Pabst (1943)
harmotome	$Ba_2Al_4Si_{12}O_{32}12H_2O$	1.57 1.59 1.62 1.67 1.57 1.59 1.62 1.67 1.59 1.59 1.62 1.67 1.59 1.59 1.62 1.68 1.61 1.63 1.64 1.65 1.59 1.62 1.67 1.68 1.61 1.64 1.65 1.67 1.58 1.62 1.64 1.74	0.03?	1.612 1.612 1.617 1.620 1.632 1.640 1.642 1.645	1.628	Sadanaga, Marumo and Takéuchi (1961)
kaolinite	$Al_2Si_2O_5(OH)_4$	1.610 1.625 1.629* 1.637 1.623 1.623 1.627 1.635*	0.02	1.625 1.627	1.625	Drits and Kashaev (1960) Values recalculated
keatite	SiO_2	1.57 1.57 1.61 1.61 1.58 1.59 1.61 1.61	?	1.59 1.597	1.594	Shropshire, Keat and Vaughan (1959)
orthoclase	$(K_{0.9}Na_{0.1})AlSi_3O_8$	1.624 1.633 1.634 1.639 1.650 1.651 1.651 1.654	0.014	1.632 1.651	1.642	Jones and Taylor (1961)
petalite	$LiAlSi_4O_{10}$	1.584 1.601 1.602⁺ 1.605 1.584 1.601 1.602⁺ 1.620 1.588 1.597 1.627 1.629⁺ 1.597 1.627 1.629⁺ 1.640 1.707 1.707 1.733 1.733	0.01	1.599 1.602 1.610 1.623 1.720	1.631	Liebau (1961b)
pigeonite	m	1.55 1.59 1.62 1.69 1.58 1.63 1.63 1.68	0.05	1.612 1.63	1.62	Morimoto, Appleman and Evans (1960)
prochlorite (monoclinic)	n	1.567₊ 1.609 1.674 1.682⁺ 1.676⁺ 1.706 1.760 1.762	0.024	1.633 1.762	1.680	Steinfink (1961)
sanbornite	$BaSi_2O_5$	1.60⁺ 1.64 1.65 1.68	?	1.642	1.642	Douglass (1958)
vermiculite	o	1.630 1.633 1.638 1.669⁺	0.015	1.643	1.643	Mathieson (1958)
zircon	$ZrSiO_4$	1.612 four times	0.02	1.612	1.612	Krstanovic (1958)
zunyite	$Al_{13}(OH)_8Si_5O_{20}Cl$ approx.	1.802 four times 1.638 four times 1.621 1.651 thrice	0.016 0.018 0.019, 0.007	1.802 1.638 1.644	1.674	Kamb (1960)
	$Li_2Si_2O_5$	1.56⁺ 1.66 1.67 1.69 1.57⁺ 1.57 1.66 1.67	0.02	1.645 1.617	1.631	Liebau (1961a)

* Three-dimensional determinations with cell dimensions determined by precession methods.   + unshared oxygen in sheet structure

a $(Mg_{1.58}Fe^2_{.43})(Al_{1.96}Fe^3_{.03}Mn_{.02}Si_{1.00})(Al_{2.00}Si_{4.00})O_{18}(H_2O)_{0.55}$;   b $(Mg_{0.60}Fe^3_{0.37}Mn_{0.03})_7(Si,Al)_8O_{22}(OH)_2$, Al/Si less than 1%

c $(Ca_{2.86}Mg_{0.14})(Al_{1.58}Fe^3_{0.25}Mg_{0.15}Ti_{0.02})(Si_{2.96}Al_{0.04})O_{12}$;   d $(Fe_{0.67}Mg_{0.30}Mn_{0.03})_7(Si,Al)_8O_{22}(OH)_2$, Al/Si less than 0.2%

e $(K_{0.94}Na_{0.06})(Al_{1.83}Fe^3_{0.12}Mg_{0.06})(Si_{3.11}Al_{0.89}O_{10})(OH)_2$;   f $(Na_{7.58}K_{0.14}Ca_{0.05})(Ti_{3.22}Fe^2_{0.60}Mg_{0.18}Fe^2_{0.10})(Si_{15.90}Al_{0.10})O_{43.5}$

g $(Li_{0.64}Na_{0.05})(Li_{0.48}Mg_{6.52})Si_{7.93}O_{21.9}F_{2.09}$;   h $(Na_{0.39}K_{0.01}Ca_{0.60})B_3Mg_3(Al_{5.42}Mg_{0.55}Fe_{0.03})(Si_{5.84}Al_{0.16})O_{30.6}F_{0.5}H_{3.0}$

i $Ca_{1.10}(Mg_{2.18}Al_{0.72})(Si_{1.05}Al_{2.95}Al_{2.95})O_{10}(OH)_2$;   j $(Mg_{1.98}Al_{1.00}Fe_{0.02})(Si_{1.07}Al_{0.95})O_5(OH)_4$

k $(Mg_{4.9}Al_{0.75}Cr^2_{0.18}Fe^3_{0.17}Fe^2_{0.07})(Si_{2.6}Al_{1.4})O_{10}(OH)_2$;   l $(Mg_{5.0}Cr_{0.7}Al_{0.2}Fe^2_{0.1})(Si_{3.0}Al_{1.0})O_{10}(OH)_8$

m $(Ca_{0.10}Mg_{0.34}Fe_{0.56})SiO_3$;   n $(Mg_{2.6}Al_{1.2}Fe_{0.2}Fe^3_{1.5})(Si_{2.2}Al_{1.8})O_{10}(OH)_2$:   o $(Mg_{2.36}Fe_{0.48}Al_{0.16})(Si_{2.72}Al_{1.28})O_{10}(OH)_2(H_2O)_{4.3}$

2. Variation of individual distances

Examination of Table 1 shows that there are variations up to 0·1 Å between the four distances in the same tetrahedron even when the random experimental error is less than 0·01 Å. A comprehensive evaluation of possible factors will not be attempted here, but a few illustrative examples will be presented. We are indebted to the variously cited authors for pointing out these effects, and recommend examination of the individual publications for further details.

In proto-amphibole (Gibbs, 1962a, b), there are three types of Si-O bonds in the double chains: (a) to oxygen atoms linked to only one silicon atom, (b) to oxygen atoms linked to two silicon atoms, and belonging to a tetrahedron that shares two corners with other tetrahedra, and (c) to oxygen atoms like (b) but in tetrahedra sharing three corners. The respective distances are (a) 1·600, 1·605, 1·611, (b) 1·633, 1·654, (c) 1·615, 1·619, 1·630 Å. Because the standard error is 0·007 Å, the differences between the groups are highly significant.

In the polymorphs of Al_2SiO_5, there is considerable variation of Si–O bond lengths, especially for sillimanite where Burnham (1962a, b) has found a spread of 0·08 Å in both the silicon and aluminum tetrahedra.

In kyanite and andalusite (Burnham & Buerger, 1961) the ranges are smaller, 0·036 and 0·020 Å respectively. Burnham & Buerger have shown that the linkage of the aluminum polyhedra in andalusite imposes some awkward geometrical problems, leading to drastic shortening of shared edges, and it seems likely that Burnham will find similar effects in his forthcoming detailed analyses of kyanite and sillimanite.

In anorthite (Megaw, Kempster & Radoslovich, 1962) each oxygen atom in the ordered framework is linked to one silicon and one aluminum atom: four of these oxygen atoms are bonded to two calcium atoms, twenty to only one calcium, and eight are not bonded to any calcium. The mean Si–O distances for zero, one and two calcium neighbours are 1·588, 1·622 and 1·632 Å respectively, while the corresponding Al–O distances are 1·719, 1·755 and 1·779 Å. Although the average distances change regularly with linkage to calcium atoms, the individual tetrahedral distances of each group vary greatly: Si–O for 0 Ca neighbours, 1·566–1·623; 1 Ca, 1·589–1·661; 2 Ca, 1·618–1·647; Al–O for 0 Ca neighbours, 1·695–1·723; 1 Ca, 1·708–1·796; 2 Ca, 1·747–1·820 Å. The differences between the group means, however, are shown to be significant, even allowing for this scatter within the groups. This latter variation is much larger than that to be expected from the random experimental error, since the standard error of an individual distance is only 0·004 Å. It seems that some additional factor or factors other than number of neighbouring calcium atoms affects the interatomic distances.

In the potassium feldspars, there is no corresponding enlargement of the tetrahedral distance with increase in number of external cation neighbours; in fact, the reverse occurs. For example, in maximum microcline which has been refined to the same degree as anorthite (Brown & Bailey, 1963a) the Si–O distances for 0, 1 and 2 potassium neighbours are 1·622, 1·609 and 1·592 Å. In sodium feldspars (Ribbe, 1962a, b) the variation is within the standard error.

Data are available for two types of sheet structure, those in the clay minerals group consisting of superimposed tetrahedral and octahedral sheets, both essentially planar, and those with corrugated tetrahedral sheets only, linked by medium-to-large cations to give compositions $A_m(Si_2O_5)_n$. In all of these structures individual tetrahedra share three corners with adjacent tetrahedra, the fourth apical oxygen being free. It should be noted, however, that for some of the corrugated sheet structures the apical oxygen is shared with tetrahedra containing other than Si cations, for example Li in $Li_2Si_2O_5$ and Li and Al in petalite. These structures could be considered frameworks from the point of view of the total tetrahedral linkage.

Values in the literature indicate that the bond from the tetrahedral cation to the apical unshared oxygen may be either longer or shorter than the bonds

to the three basal shared oxygens. For example, for 5 of the 15 compounds for which data are available the apical bond is longer, in 5 it is shorter, and in 5 it is approximately the same length as the basal bonds. For most of the corrugated Si_2O_5 sheets the bond to the apical oxygen is shorter than those to the basal oxygens whereas for the planar Si_2O_5 sheets the reverse is usually true. With substitution of Al for Si in the tetrahedra of the planar clay mineral sheets, the bonds to the basal oxygens tend to increase in length faster than the bond to the apical oxygen, with the result that the basal bonds become longer than the apical bond at Al-rich compositions. The individual bond lengths, therefore, are affected not only by the size of the tetrahedral cation but also by the sheet configuration, the sheet charge, and the size and charge of the octahedral and interlayer cations. Because of the several variables affecting the individual bonds, only the mean of all four T–O bond lengths within a tetrahedron has been found to give a smooth variation with tetrahedral composition.

It is obvious that the factors that control interatomic distances are numerous, and that the effects are complex: evaluation of these factors should prove to be a profitable field of research.
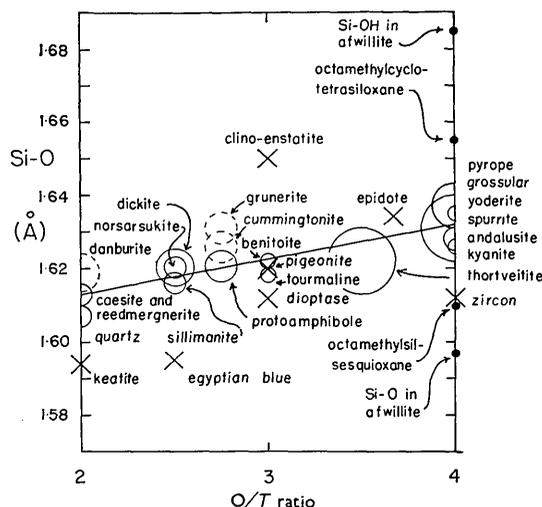
Fig. 1. Relation between the average of all the Si–O distances in a structure and the ratio of oxygen to tetrahedrally coordinated atoms. Only those oxygen atoms linked to tetrahedrally coordinated atoms are counted; for afwillite the hydroxyl group is counted as an oxygen atom. Si–O distances for two siloxane compounds are arbitrarily plotted on the diagram. The average of the Si–O distances is weighted by the multiplicity if the symmetry repeats some tetrahedra more than others. Data obtained by 3D methods are shown by circles whose vertical diameters give twice the standard error of an individual distance divided by the square root of the number of individually determined distances. The crosses denote data obtained by 2D methods; estimates of accuracy, where available, are given in Table 1. The structure of danburite was carried out by a combination of 2D and 3D techniques.

3. Variation of the overall mean Si-O and Al-O distances

(a) Effect of tetrahedral linkage

From the earliest days of silicate crystal chemistry, attention has been focused on the nature of the Si-O linkage (probably too much attention!) and it is obvious to look for a correlation between the overall mean Si-O distance and the extent of the tetrahedral linkage. Fig. 1 shows the relationship, using the O/T ratio as a measure of the linkage (where T is the number of tetrahedrally coordinated atoms). For framework structures, like quartz and coesite, the ratio is 2, whereas in garnet, andalusite and other structures with isolated tetrahedra the ratio is 4. Although the data are not as extensive as might be desired, there is certainly an increase in the Si-O distance from the tektosilicates where Si-O is 1·61 Å to the meso-silicates where Si-O is near 1·63 Å. The line of best fit chosen visually is from 1·613 to 1·632 Å, but there is no justification, at this time, for claiming any significance for the third figure after the decimal point. The errors shown on the diagram were obtained by merely dividing the standard error of an individual Si-O distance by the square root of the number of independent distances. The reduction of error of the mean because of oxygen atoms shared by two silicon atoms has not been calculated, although it is quite important in the structures with a low ratio of $O : T$. The possible effect of error on the cell dimensions has been shown in a qualitative way by the use of broken circles for grunerite, cummingtonite and reedmergnerite, whose cell dimensions were determined by precession techniques. The resulting error in the Si-O distances might amount to 0·008 Å although it is likely to be smaller. Data obtained by 3D refinement are shown by complete circles, those by 2D refinement by crosses and the value for danburite by a broken circle to indicate partial 2D and 3D refinement. Chemical analyses of four of the specimens indicate the possible substitution of Al for Si — in grossular, cummingtonite and grunerite (Table 1). The amount is too small to affect the bond length significantly, but in tourmaline the amount may be of importance. The tourmaline was unanalysed, but analyses of similar material indicate that 0·16 out of the six Si atoms are replaced by Al. To cover this substitution a reduction of the average T-O distance from 1·621 to 1·618 has been made in Fig. 1. All the data obtained by 3D refinement fit within two standard errors of the line drawn from 1·613 to 1·632 Å, except for the mean value for kyanite which lies within three standard errors (using the special definition of error of the mean as given earlier in this paragraph). There seems to be no reason to doubt that there is a close relationship between the overall mean Si-O distance and the O/T ratio, though it is, of course, possible that fluctuations at least as large

as 0·01 Å from this relation might be masked by the errors of the determination.

Evaluation of the effect of tetrahedral linkage on the Al-O distance is difficult because of the scarcity of the data. In the next section it will be shown that the mean tetrahedral distance in feldspars may be represented by a linear relation from Si-O 1·61 to Al-O 1·75 Å. This latter value is obtained by extrapolation, but is confirmed by measured values for individual tetrahedra in ordered structures. In the following section it will be shown that the mean tetrahedral distances in layer silicates may be represented by a linear relation from Si-O 1·62 Å to Al-O 1·77 Å. In sillimanite there is an infinite band of linked four-membered rings of tetrahedra, the composition of which, $Si_2Al_2O_{10}$, is like that in layer silicates formed from linked six-membered rings. The mean value of 1·770 Å ($\pm 0·007$ for an individual distance) obtained by Burnham (1962b) for the Al-O distance is close to the extrapolated value for the layer silicates. Zunyite has an isolated aluminum tetrahedron with an Al-O distance of 1·802 Å ($\pm 0·016$, all four distances in the tetrahedron being related by symmetry). Thus it seems that there is a similar increase in the Al-O distance from 1·75 Å in frameworks to an ill-defined value near 1·80 Å in structures with isolated tetrahedra. The increase (0·05 Å) is larger than that assigned to silicon tetrahedra (0·02 Å), and would be consistent with the lesser strength of the tetrahedral bond and the greater charge of external cations associated with the aluminum tetrahedra.

(b) Variation with chemical content

Because of the effect of structural linkage, it is necessary to consider different structural types separately in order to evaluate the effect of Si, Al substitution on the interatomic distance. For each structure an overall mean tetrahedral distance can be calculated which is relatively unaffected by random experimental error, and which is not dependent on knowledge of ordering. By considering several structures with different Si : Al ratios it is possible to determine the relation between the mean Si, Al-O distance and the Si : Al ratio. The predicted endpoints for Si-O and Al-O distances can then be compared with observed means for individual tetrahedra in ordered structures.

The data for feldspars are shown in Table 1 and Fig. 2. The thirteen specimens range in tetrahedral aluminum content from 0 to 50% and the overall mean Si, Al-O distance from 1·61 to 1·68 Å with maximum deviations from linearity of 0·003 Å. These deviations are remarkably small, indicating that the overall mean distance represents the chemical composition very accurately. Extrapolation to pure aluminum gives an Al-O value of 1·75 Å. Several structures are thought for a variety of reasons to be either completely or almost completely ordered, and
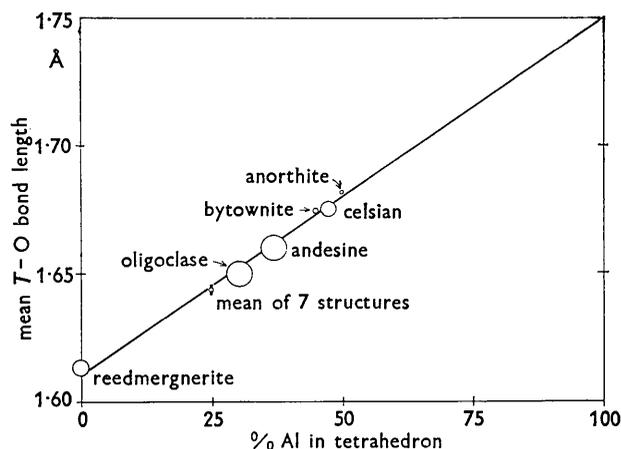
Fig. 2. Relation between overall mean Si, Al–O distance and Al-content for structures with the feldspar framework. The vertical radii of the circles give a measure of the random experimental error, and were obtained by dividing the standard error of an individual distance by the square root of the number of independently determined distances. Because of the reduction of the error of the mean caused by shared oxygen atoms (see text) the true error should be smaller by a factor of 2 or 3. Because of the overlap of values for 25% Al, only the mean and the spread of the eight values for the sodium and potassium feldspars are shown. The straight line was drawn arbitrarily between Si–O 1·61 and Al–O 1·75 Å, and has no statistical significance. In addition to the data listed in Table 1, the following have been used to compile the diagram; high temperature andesine from Linosa, An_{48}, incompletely refined by Kempster (1957), mean T–O, 1·660 Å and σ 0·02 Å; low temperature oligoclase from Amelia County, Va., $Ab_{74}An_{22}Or_{4}$, refined by 2D methods by Waring (1961), mean T–O, 1·650 Å and σ less than 0·02 Å; bytownite, An_{90}, refined by 3D methods by Fleet (1962) following earlier work by Chandrasekhar, mean T–O, 1·674, and σ 0·0065 Å.

the observed tetrahedral distances may be used to check the suggested Si–O and Al–O values. Some of the mean distances in individual tetrahedra of these structures are as follows:

Mineral name	Si-rich tetrahedra	Al-rich tetrahedra
Maximum microcline (Pellotsalo)	1·612 (3)	1·741 (1)
Maximum microcline (Pontiskalk)	1·614 (3)	1·734 (1)
Primitive anorthite	1·614 (8)	1·749 (8)
Low albite	1·613 (3)	1·744 (1)
Reedmergnerite	1·613 (3)	

Other framework structures might be expected to show similar bond distances:

Mineral name	Si-rich tetrahedra	Al-rich tetrahedra
Natrolite	1·620 (2)	1·747 (2)
Coesite	1·613 (2)	
Quartz	1·607 (1)	
Gismondine	1·620 (2)	1·735 (2)
Cordierite	1·616 (3)	1·747 (2)

The bracket after the bond distance gives the number of tetrahedra averaged. Only structures determined by three-dimensional methods are included.

The individual values are consistent with those obtained earlier from consideration of the overall mean distances when account is taken of the random experimental errors and the possibility of some small residual disorder. The data for reedmergnerite, the boron analogue of albite, have been used to anchor the Si end of the graph in Fig. 2, but there is a possible error here due to the uncertainty in the cell dimensions. The points with the smallest standard errors in Fig. 2 are those for anorthite, bytownite, and the mean of all Si₃Al structures. A straight line through these three points extrapolates to Si–O 1·606 Å and Al–O 1·757 Å. When the values of individual tetrahedra are also considered, it seems best to use the rounded-off values of Si–O 1·61 and Al–O 1·75 Å, for the time being, but further refinements of feldspar structures may suggest slight modification of these values.

Data are available for fifteen layer silicates, but the accuracy is generally lower than in the frameworks. Eight structures have been determined for which there is no substitution of Al for Si. The mean Si–O bond length is 1·616 Å. Of these eight structures four have been refined more completely than the others. The mean Si–O bond length is 1·621 Å for them
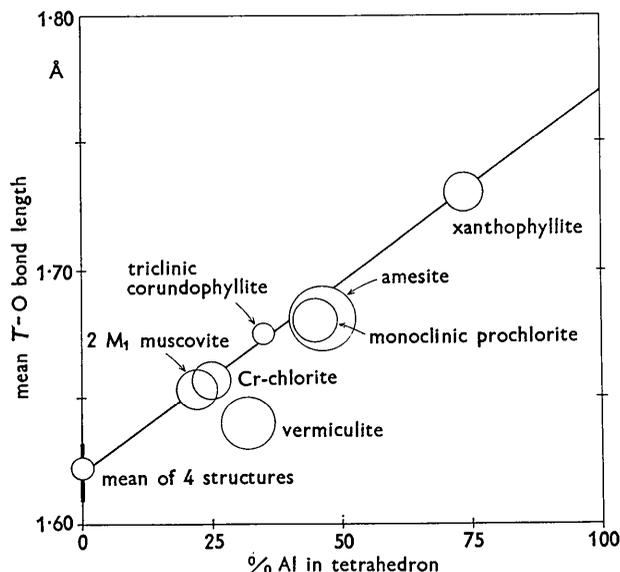
Fig. 3. Relation between mean Si, Al–O distance and Al content for sheet structures. The vertical radii of the circles give a measure of the random experimental error, and were obtained by dividing the standard error of an individual distance by the square root of the number of independently determined distances. There is uncertainty about the error for several of the structures because refinement was carried out by 2D methods in which overlap of peaks led to an additional uncertainty of atomic positions. However the reduction of error of the mean from the sharing of oxygens should help to balance this possible effect. For four structures (dickite, kaolinite, petalite and $Li_2Si_2O_5$) a vertical line has been used to show the range of values: the circle shows the data for dickite. The line from Si–O 1·62 to 1·77 has no statistical significance.

(dickite, kaolinite, petalite, and $Li_2Si_2O_5$) and is 1·620 Å for the structure done with the greatest accuracy (dickite, σ(Si–O) is 0·017 Å). The mean bond length for Si–O is therefore chosen as 1·62 Å.

In Fig. 3 the mean T–O bond lengths averaged over all tetrahedra in the unit cell are plotted against the tetrahedral compositions given by chemical analysis for seven additional layer silicates. These are, in order of increasing Al-content: $2M_1$ muscovite, Cr-chlorite, vermiculite, triclinic corundophyllite, monoclinic prochlorite, amesite and xanthophyllite. Most of the structures were determined by 2D methods and the cell dimensions determined with only moderate precision so that $\sigma(T$–O) is 0·02 Å or greater. For this reason it is not possible to draw as good a line of fit through the points as for the feldspars. The selected line runs from 1·62 ± 0·01 Å at the Si end to 1·77 ± 0·015 Å at the Al end. This line is subject to change as more structures are determined with greater accuracy. The Si, Al–O value for vermiculite is anomalous in that it is the only mean distance that deviates appreciably from a linear variation of bond length with tetrahedral composition. The amount of departure is 0·025 Å, or three times the standard error of the mean calculated from the reported error of an individual bond length.

In addition to the two broad classes of feldspars and layer silicates, there are various miscellaneous specimens to be considered, whose data are given in Table 1 and Fig. 4. The distances for these structures
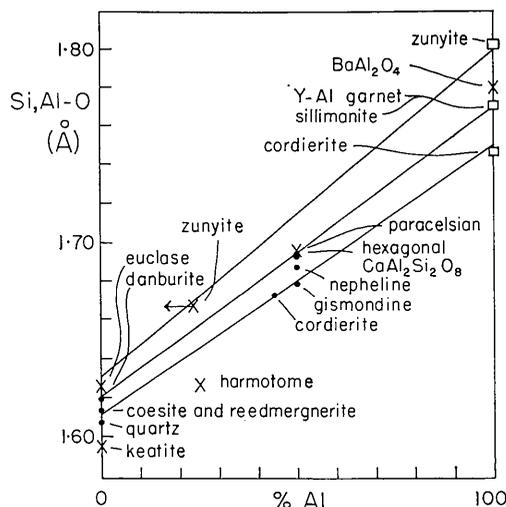
Fig. 4. Relation between Si, Al–O distance and Al content for various structures. The sources of all data, except for $BaAl_2O_4$ and Y–Al garnet, are given in Table 1. A discussion of the accuracy of the data is given in the text. The three lines are, in order of increasing distance, suggested relations for feldspar, sheet structures and structures with isolated tetrahedra. Crosses and solid circles denote, respectively, 2D and 3D determinations. Squares show values for Al-tetrahedra in structures that also contain Si-tetrahedra. The size of the symbols has no significance concerning the experimental error.

are shown in relation to three lines running from 1·61 to 1·75 for feldspars, 1·62 to 1·77 for sheet structures and 1·63 to 1·80 for structures with isolated tetrahedra. The polymorphs of silica (quartz, coesite and keatite) give values consistent with the 1·61 Å distance for Si–O in feldspar structures (the keatite value, 1·594, is low, but the structure was determined by 2D methods). Danburite, which has a framework structure composed of alternating boron and silicon tetrahedra, gives a value, 1·619, which is above the value for the other framework structures, but not significantly when the standard error of 0·01 for an individual distance is considered. Euclase has a curious structure in which each silicon tetrahedron shares one corner with a BeO_3(OH) tetrahedron, and a second corner with two BeO_3(OH) tetrahedra, to form an infinite ribbon of composition $[Be_2(OH)_2(SiO_4)_2]_n$. If only Si and O atoms are used to obtain a T/O ratio, the value of 3 is obtained: for all atoms, the ratio is 2·5. The observed mean value of 1·625 for Si–O with a standard error of 0·015 for an individual distance is consistent with either of the values of 1·62 and 1·615 previously found (Fig. 1) for structures with these ratios. The overall mean value of 1·626 Å for the zeolite harmotome which has a probable Al/(Al+Si) ratio of 0·25 is considerably lower than the value of 1·645 Å found in feldspars with the same ratio. However, the structure was determined by 2D methods, and the chemical composition is uncertain. Zunyite contains AlO_4 tetrahedra and Si_5O_{16} groups; unfortunately, the specimen used for the 2D X-ray analysis was not chemically analysed and it is necessary to use chemical analyses for five other specimens to conclude that up to 0·4 of the Si atoms in the Si_5O_{16} group may be replaced by Al. In Fig. 4 the zunyite is plotted at the composition with maximum Al substitution, and the arrow-head shows the position for no substitution. Considering the standard error of the analysis, and the type of structure, the data for zunyite are consistent with the proposals made in this paper whatever is the real chemical content. In cordierite, pseudohexagonal rings of tetrahedra are cross-linked by other tetrahedra to form a framework structure and although the structure is not of the feldspar type, the overall mean Si, Al–O distance, 1·673 Å, deviates only 0·001 Å from the line determined for feldspars in Fig. 2. There are five structures to be considered, whose Al/Si ratio is unity. The overall mean value for sillimanite (also plotted on Fig. 1) fits well with the line drawn for sheet structures. The overall mean value of 1·678 Å for the very accurate data of the zeolite gismondine fits well with the value of 1·68 Å expected for an Si/Al ratio of unity. The mean values for individual tetrahedra, 1·619, 1·621, 1·732 and 1·739 fit only moderately well with the values 1·61 and 1·75 proposed for a fully ordered feldspar structure, but there might be some residual disorder in gismondine. The other three materials, nepheline, paracelsian and hexagonal $CaAl_2Si_2O_8$,

give values 1·690, 1·696 and 1·694 that are somewhat higher than the value of 1·68 expected for feldspars. It is possible that the distances arise from a genuine structural effect, especially for hexagonal $CaAl_2Si_2O_8$, which has a double-layer structure. However, paracelsian was determined only by 2D methods and the refinement of nepheline, although by 3D techniques, was not complete. The mean distance for the ordered tetrahedron in nepheline is 1·78 Å, which is within one standard error (0·03) of the value of 1·75 Å found in feldspars. A refinement by Hahn, now in progress, should give data of considerable value in checking the effects of tetrahedral environment on tetrahedral distances. Two structures contain tetrahedra free of Si. Unfortunately the structure determination of $BaAl_2O_4$ (Wallmark & Westgren, 1937) is rather old, and although there are only a few variable parameters, recent observations of a superstructure (Hoppe & Schepers, 1960) cast doubt on the significance of the observed Al–O distances. This structure is now being re-investigated by J. V. Smith. No details have become available since the publication of the abstract (Prince, 1957) on a neutron diffraction study of Y–Al garnet: the value of 1·77 Å is lower than that of 1·80 Å in zunyite, equal to that of 1·770 Å for the Al-tetrahedron of sillimanite and greater than the average value of 1·747 Å for the two tetrahedra in cordierite. The tetrahedra in these latter three structures may contain some substituted Si atoms, though the chance of this occurring in sillimanite and zunyite must be rather small.

Although the values for the structures depicted in Fig. 4 are mostly reconcilable with the proposed relations for feldspars (and related framework) structures, sheet (and related) structures and structures with isolated tetrahedra, it is obvious that considerable work will be needed to clarify the true relations, especially for the Al-tetrahedra.

4. Conclusion

Bond lengths in silicates depend on a very complex system of interacting forces, too complicated to be understood in detail by present chemical theory. It is not reasonable to expect in the near future mathematical solutions of the wave equations that will permit calculations of interatomic distances and, more important, thermodynamic functions such as the internal energy. For the time being, an empirical approach in which observed structural dimensions are correlated with the chemical content and the crystalline architecture seems to be the most promising. From such an empirical approach it should be possible to identify those chemical and structural characteristics that primarily determine the properties of the crystal structure.

The present study, which is a modest attempt along these lines, has revealed that the extent of tetrahedral linkage has a significant effect on tetrahedral dis-

tances. Continuation of this work (planned by J. V. Smith), with electronic computers to search for correlations between distances and selected structural properties, should lead to the recognition of other effects, such as those that might arise from external cations and from shared polyhedral edges. (The latter seems an especially good candidate, for Dr G. V. Gibbs has pointed out that the number of shared edges increases as the T–O ratio increases.) The success of such studies will undoubtedly depend on the increasing availability of accurately determined crystal structures.

Both Dr C. W. Burnham and Dr K. Fischer have pointed out the importance of using interatomic distances corrected for temperature motion. As an illustration, Dr Fischer has kindly provided the following data for benitoite:

1·605	1·630	1·648	uncorrected for vibration
1·610	1·634	1·652	O riding on Si
1·614	1·638	1·656	atoms vibrating independently

In this paper it has been necessary to use distances uncorrected for vibration, because so many of the data have been presented in this form. Fortunately temperature motion does not vary very much over the majority of silicates so that the correction tends to be similar for the different substances. However there are a few atoms, such as certain oxygen atoms in nepheline and sillimanite, that appear to have large thermal motions. Consequently, it will be necessary to consider thermal motion in any evaluation of interatomic distances of silicates that attempts to reach a higher level of significance (say 0·001 Å) than the one described in this paper.

The original impetus for the present studies came from a need for standard distances from which the Al-content in Si, Al tetrahedra could be estimated from the mean tetrahedral distance of a tetrahedron. It is now clear that the relation between Si–O 1·60 and Al–O 1·78 Å proposed in 1954 is considerably in error. Because of the effect of structural linkage on Si, Al–O distances, it is necessary to use a different relation for each structural type. Even after making allowance for structural linkage, it is still necessary to take into account the effect of local environment on the mean tetrahedral distance. The stronger the tetrahedral bonds are in relation to the other bonds of the structure, the less should be the effect of local environment. Unfortunately it is not yet possible to predict the effect of local environment on tetrahedral distances, and its effect can only be taken account of by assuming a random error in the estimation of Al content in Si, Al tetrahedra. Study of the data in Table 1 suggests that the use of the mean of the four tetrahedral distances greatly reduces the effect of local environment (see, for example, the data for anorthite and kyanite). Nevertheless it seems prudent to assume that local structural environment may affect the mean distance in feldspars by 0·01 Å and

in structures with more pronounced environmental effects by somewhat larger values. In summary, it appears that after correction for structural type, the estimation of Al content of individual tetrahedra from interatomic distances may have an error due to environmental factors of $\pm 5\%$ Al (in round figures) in addition to the effect of experimental error. For especially favourable structures, such as potassium feldspars, the accuracy may be a little better than this, whereas in others, like the sheet structures and alumino-silicates, it may be worse.

References

ABRAHAMS, S. C. & GELLER, S. (1958). *Acta Cryst.* **11**, 437.

BAILEY, S. W. & TAYLOR, W. H. (1955). *Acta Cryst.* **8**, 621.

BROWN, B. E. & BAILEY, S. W. (1963a). In preparation.

BROWN, B. E. & BAILEY, S. W. (1963b). *Amer. Min.* **48**, 42.

BUERGER, M. J., BURNHAM, C. W. & PEACOR, D. R. (1962). *Acta Cryst.* **15**, 583.

BURNHAM, C. W. & BUERGER, M. J. (1961). *Z. Kristallogr.* **115**, 269.

BURNHAM, C. W. (1962a). Private communication. Available as Ph.D. thesis, Massachusetts Institute of Technology.

BURNHAM, C. W. (1962b). Private communication.

CLARK, J. & APPLEMAN, D. E. (1960). *Science*, **132**, 1837.

COLE, W. F., SÖRUM, H. & KENNARD, O. (1949). *Acta Cryst.* **2**, 280.

CRUICKSHANK, D. W. J., LYNTON, H. & BARCLAY, G. A. (1962). *Acta Cryst.* **15**, 491.

DOUGLASS, R. M. (1958). *Amer. Min.* **43**, 517.

DRITS, V. A. & KASHAEV, A. A. (1960). *Kristallografiya*, **5**, 224.

FINNEY, J. J. & BAILEY, S. W. In preparation.

FISCHER, K. (1961). Private communication.

FISCHER, K. (1962). Private communication.

FLEET, S. G. (1962). Private communication.

FLEET, S. G. & MEGAW, M. D. (1962). *Acta Cryst.* **15**, 721.

GHOSE, S. (1961). *Acta Cryst.* **14**, 622.

GHOSE, S. & HELLNER, E. (1959). *J. Geology*, **67**, 691.

GIBBS, G. V. (1962a). Private communication. Available as Ph.D. thesis, Pennsylvania State University.

GIBBS, G. V. (1962b). Private communication.

GIBBS, G. V. & SMITH, J. V. (1962). In preparation.

GRUND, A. (1954). *Bull. Soc. Franc. Minér. Crist.* **77**, 775.

HAHN, T. & BUERGER, M. J. (1955). *Z. Kristallogr.* **106**, 308.

HEIDE, H. G., BOLL-DORNBERGER, K., THILO, E. & THILO, E. M. (1955). *Acta Cryst.* **8**, 425.

HOPPE, R. & SCHEPERS, B. (1960). *Naturwissenschaften*, **47**, 376.

ITO, T., MORIMOTO, N. & SADANAGA, R. (1954). *Acta Cryst.* **7**, 53.

JOHANSSON, G. (1959). *Acta Cryst.* **12**, 522.

JONES, J. B. & TAYLOR, W. H. (1961). *Acta Cryst.* **14**, 443.

KAMB, W. B. (1960). *Acta Cryst.* **13**, 15.

KEMPSTER, C. J. E. (1957). Ph.D. thesis, University of Cambridge.

KRSTANOVIC, I. R. (1958). *Acta Cryst.* **11**, 896.

LARSSON, K. (1960). *Ark. Kemi Sverige*, **16**, 203.

LIEBAU, F. (1961a). *Acta Cryst.* **14**, 389.

LIEBAU, F. (1961b). *Acta Cryst.* **14**, 399.

LIEBAU, F. (1961c). *Acta Cryst.* **14**, 1103.

MATHIESON, A. M. (1958). *Amer. Min.* **43**, 216.

MEGAW, H. D. (1952). *Acta Cryst.* **5**, 477.

MEGAW, H. D., KEMPSTER, C. J. E. & RADOSLOVICH, E. W. (1962). *Acta Cryst.* **15**, 1005.

MEIER, W. M. (1960). *Z. Kristallogr.* **113**, 430.

MORIMOTO, N., APPLEMAN, D. E. & EVANS, H. T. (1960). *Z. Kristallogr.* **114**, 120.

MROSE, M. E. & APPLEMAN, D. E. (1962). *Z. Kristallogr.* **117**, 16.

NEWNHAM, R. E. (1961). *Miner. Mag.* **32**, 683.

NEWNHAM, R. E. & MEGAW, H. D. (1960). *Acta Cryst.* **13**, 303.

PABST, A. (1943). *Amer. Min.* **28**, 372.

PABST, A. (1959). *Acta Cryst.* **12**, 733.

PEACOR, D. R. & BUERGER, M. J. (1962). *Amer. Min.* **47**, 539.

PRINCE, E. (1957). *Acta Cryst.* **10**, 787.

RADOSLOVICH, E. R. (1960). *Acta Cryst.* **13**, 919.

RIBBE, P. H. (1962a). Private communication. Joint work with R. B. FERGUSON & W. H. TAYLOR.

RIBBE, P. H. (1962b). Private communication.

SADANAGA, R., MARUMO, F. & TAKÉUCHI, Y. (1961). *Acta Cryst.* **14**, 1153.

SEEMAN, H. (1956). *Acta Cryst.* **9**, 251.

SHROPSHIRE, J., KEAT, P. P. & VAUGHAN, P. A. (1959). *Z. Kristallogr.* **112**, 409.

SMITH, G. S. & ALEXANDER, L. E. (1963). *Acta Cryst.* **16**, 462.

SMITH, J. V. (1954). *Acta Cryst.* **7**, 479.

SMITH, J. V., KARLE, I. L., HAUPTMAN, H. & KARLE, J. (1960). *Acta Cryst.* **13**, 454.

STEINFINK, H. (1958). *Acta Cryst.* **11**, 195.

STEINFINK, H. (1961). *Acta Cryst.* **14**, 198.

STEINFINK, H. & BRUNTON, G. (1956). *Acta Cryst.* **9**, 487.

STEINFINK, H., POST, B. & FANKUCHEN, I. (1955). *Acta Cryst.* **8**, 420.

TAKÉUCHI, Y. & DONNAY, G. (1959). *Acta Cryst.* **12**, 465.

TAKÉUCHI, Y. & SADANAGA, R. (1959). *Acta Cryst.* **12**,

945. Also personal communication containing refined bond distances.

WARING, J. R. S. (1961). Ph.D. thesis, University of Cambridge.

WALLMARK, S. & WESTGREN, A. (1937). *Ark. Kemi Min. Geol.* **12**, No. 35.

YOUNG, R. A. & POST, B. (1962). *Acta Cryst.* **15**, 337.

ZOLTAI, T. (1961). Private Communication.

ZOLTAI, T. & BUERGER, M. J. (1959). *Z. Kristallogr.* **111**, 129.

The Crystal Structure of Acenaphthenequinone

By T. C. W. MAK AND J. TROTTER

Department of Chemistry, The University of British Columbia, Vancouver, Canada

The crystal structure of acenaphthenequinone has been determined by two-dimensional Fourier methods. There are four molecules in the orthorhombic unit cell, which has dimensions

$$a = 7 \cdot 81, \quad b = 27 \cdot 0, \quad c = 3 \cdot 851 \text{ Å}.$$

The space group is $P2_12_12_1$. The molecule is planar, and the molecular dimensions and intermolecular distances are normal for this type of structure.

Introduction

Study of the crystal structure of acenaphthenequinone was undertaken as part of an investigation of a series of acenaphthene derivatives.

Experimental

A crystalline sample of acenaphthenequinone was kindly made available to us by Mr I. G. Csizmadia and Dr L. D. Hayward. It consisted of orange-yellow needles elongated along the c-axis, with the (010) face well developed. The cell dimensions were determined from Weissenberg and precession photographs of a crystal mounted about the c-axis. The density was measured by flotation in aqueous potassium iodide.

Crystal data

Acenaphthenequinone (1,2-acenaphthenedione), $C_{10}H_6(CO)_2$; $M = 182 \cdot 2$; m.p. 273–274 °C.

Orthorhombic, $a = 7 \cdot 81 \pm 0 \cdot 01$, $b = 27 \cdot 0 \pm 0 \cdot 05$, $c = 3 \cdot 851 \pm 0 \cdot 005$ Å.

Volume of the unit cell $= 812$ Å^3.

Density, calculated (with $Z = 4$) $= 1 \cdot 49$, measured $= 1 \cdot 48$ g.cm^{-3}.

Absorption coefficients for X-rays, $\lambda = 1 \cdot 5418$ Å, $\mu = 9 \cdot 83$ cm^{-1}; $\lambda = 0 \cdot 7107$ Å, $\mu = 1 \cdot 24$ cm^{-1}.

Total number of electrons per unit cell $= F(000) = 376$.

Absent spectra: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd.

Space group is $P2_12_12_1$–D_2^4, as confirmed later in the analysis.

For intensity purposes the $hk0$ reflexions were recorded on multiple-film Weissenberg photographs, using unfiltered Cu $K\alpha$ radiation. The $0kl$ data were collected on precession films with related time exposures, Mo $K\alpha$ radiation being used. The intensities were estimated visually. The relative values of the structure amplitudes were derived by applying the usual Lorentz and polarization factors, the absolute scale being established later by correlation with the calculated structure factors.

Absorption correction was considered unnecessary since the crystal used had a mean diameter of 0·06 mm. 152 independent $hk0$ reflexions were observed (excluding the 020 reflexion, which was cut off by the beam trap), representing 54% of the total number theoretically observable with Cu $K\alpha$ radiation. Only 33 $0kl$ reflexions were recorded, representing about 20% of the total number observable.

Structure analysis

Space group $P2_12_12_1$ is non-centrosymmetric, but it has centrosymmetric projections (plane group pgg) in all three principal directions. The relations between space group and our projection coordinates are those formulated in Table 1.