Conclusions

The X-ray analyses of protopine and cryptopine have shown conclusively their molecular structures in the crystalline form. In both molecules, the ten-membered ring is severely buckled, with the nitrogen atom N(7) well buried within it, and is held very close to the C(14) atom which lies across the ring from it. The distance N(7)···C(14) is only 2·57 ± 0·01 Å, which is much shorter than the sum of the van der Waals radii of these two atoms. The three C–N bonds and the C(14)···N(7) distance across the ring are very nearly tetrahedrally arranged around the nitrogen atom. Therefore, in forming derivatives of protopine and cryptopine in which the nitrogen atom is tetravalent, it would be necessary to invert the nitrogen atom so that a fourth atom other than C(14) may be attached to N(7). This inversion would also be accompanied by a considerable increase in the N(7)···C(14) distance. On the other hand, no inversion would be required if the fourth bond is formed between N(7) and C(14) thus transforming the ten-membered ring into two six-membered rings with N(7)–C(14) shared between them.

The carbon–oxygen double bond has ketonic character, makes about 39° ± 2° with the plane of the aromatic six-membered ring nearest to it, and about 34° ± 1° with the other. Each six-membered ring has a very slight boat form, and the angle between them is 152·2° in protopine and 149·9° in cryptopine. The atoms C(19) and O(5) are separated by a distance of 3·18 ± 0·01 Å which is just about the sum of the van der Waals radii of these two atoms.

The authors take great pleasure in acknowledging the receipt of some unpublished data on cryptopine from Dr W. H. Barnes. All computations have been carried out with the IBM 360 computer using programs by Ahmed, Hall, Pippy & Huber (1966). The assistance of Mrs M. E. Pippy in the computations involved, and the cooperation of the staff of the NRC Computation Centre, are deeply appreciated.

References

Ahmed, F. R. & Cruickshank, D. W. J. (1953). *Acta Cryst.* **6**, 385.

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1966). *NRC Crystallographic Programs for the IBM/360 System, World List of Crystallographic Computer Programs*. 2nd Edition, Appendix page 52.

Barnes, W. H. (1967). Private communication.

Blow, D. M. (1960). *Acta Cryst.* **13**, 168.

Hall, S. R. & Ahmed, F. R. (1968). *Acta Cryst.* B**24**, 337.

International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.

Karle, I. L., Hauptman, H., Karle, J. & Wing, A. B. (1958). *Acta Cryst.* **11**, 257.

Manske, R. H. F. & Holmes, H. L. (1954). *The Alkaloids. Chemistry and Physiology*. Vol. IV. New York: Academic Press.

Sutton, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Atoms*. Supplement 1956–1959. London: The Chemical Society.

Thomas, A. F., Marion, L. & Manske, R. H. F. (1955). *Canad. J. Chem.* **33**, 570.

Acta Cryst. (1968). B**24**, 355

Al-O and Si-O Tetrahedral Distances in Aluminosilicate Framework Structures

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A new determinative curve has been derived for estimating tetrahedral aluminum from the observed tetrahedral bond lengths in aluminosilicate framework structures. The end values of Si–O, 1·603 Å, and Al–O, 1·761 Å, derived from 13 feldspar analyses only, do not differ significantly from those obtained by considering an additional 19 other framework structures.

Introduction

Smith & Bailey (1963) in their second review of aluminum and silicon to oxygen tetrahedral distances, after examining the available information for framework structures, recommended the use of a straight line relationship of aluminum content *versus* tetrahedral distance. Their actual line based on accurately determined feldspar structures extended from 1·606 Å for Si–O to 1·757 Å for Al–O, but because of various uncertainties they recommended the use of the rounded off figures 1·61 and 1·75.

In the case of the feldspars this rounding off has the effect of placing the line above the majority of the mean T–O distances for frameworks of composition $AlSi_3O_8$ and below the means for those with compositions close to $Al_2Si_2O_8$. Since Smith & Bailey's review four new feldspar determinations have become available and the structures of a number of other frameworks have been completed.

Examination of the above working line seemed worth while to see if Smith & Bailey's more precise figures could be confirmed or new ones obtained.

Data and accuracy

In Table 1 are set out the data used in deducing the lines below. Eighteen of the thirty-two structures used in the present study were also used by Smith & Bailey, but all are listed here as in some cases the values, particularly of aluminum content, are different from those previously used.

The various factors affecting the accuracy of determined tetrahedral bond lengths have been very adequately discussed by Smith & Bailey (1963) and the difficulties inherent in the chemical determination of silicon and aluminum are well known. All that need be added is that the aluminum:silicon ratio has in a number of cases been adjusted to allow for the presence of small amounts of cation carrying a charge different from that of the major cation(s). One danger in this procedure is that a small amount of unmixed material may account for some or all of the differentially charged cation. However, the adjustments with two exceptions are so small that the effect will be negligible.

The exceptions are the two anorthite structures which play a critical role in determining the midpoint of the line and hence the extrapolated value for pure Al–O. In both analyses there is some doubt as to the exact composition of the crystal used. Primitive anorthite from Monte Somma, Vesuvius, is described (Kempster, Megaw & Radoslovitch, 1962) as 'in the range 95–100% An' from optical examination; an arbitrary figure of 97·5% An, or 0·494 Al has been used. Transitional anorthite from Miyaké, Japan, varies in composition from 94–99% An (Gay, 1953; Laves & Goldsmith, 1954) but the sample from which the crystal was selected yielded a value of 99·1% An (Gay, 1953) or ~0·497 Al which has been used. Although these two structures are critical when feldspars alone are

Table 1. Al, Si–O *tetrahedral distances**

	$\frac{\text{Al}}{(\text{Al}+\text{Si})}$	Overall tetrahedral mean	Reference
Transitional anorthite	0·497	1·6815	Ribbe (1963*b*)
Primitive anorthite	0·494	1·6805	Kempster (1966)
Celsian	0·460	1·676	Newnham & Megaw (1960)
Bytownite	0·450	1·6742	Fleet, Chandrasekhar & Megaw (1966)
Low albite	0·255	1·646	Ribbe, Megaw & Taylor (in preparation); Taylor (1966)
High albite	0·254	1·6435	Ribbe, Megaw & Taylor (in preparation); Taylor (1966)
Microcline (Pellotsalo)	0·250	1·6445	Brown & Bailey (1964)
Microcline (Pontiskalk)	0·250	1·644	Finney & Bailey (1964)
Orthoclase (Spencer C)	0·252	1·643	Jones & Taylor (1961); refinement 1966
Microcline (Spencer U)	0·253	1·642†	Bailey & Taylor (1955)
Adularia (Spencer B)	0·254	1·643	Ribbe (1966)
Adularia (St. Gotthard)	0·255	1·642	Jones & Taylor (in preparation)
Sanidine (Spencer C heat treated)	0·252	1·641	Cole, Sörum & Kennard (1949); Ribbe (1963*a*); Jones (in preparation)
Cancrinite	0·500	1·685	Jarchow (1965)
Kalsilite	0·500	1·677	Perrotta & Smith (1965)
Nepheline	0·500	1·687	Hahn & Buerger (1955)
Tugtupite	0·200	1·633	Danø (1966)
Brewsterite	0·250	1·642	Perrotta & Smith (1964)
Chabazite	0·333	1·657	Smith, Rinaldi & Dent Glasser (1963)
Erionite	0·245	1·635	Staples & Gard (1959)
Gismondine	0·500	1·678	Fischer (1962)
Natrolite	0·400	1·670	Meier (1960)
Mizzonite	0·420	1·669	Papike & Stephenson (1966)
Marialite	0·305	1·646	Papike & Zoltai (1965)
Cordierite	0·444	1·673	Gibbs (1966)
Petalite	0·200	1·631	Liebau (1961)
α-Quartz	0·000	1·609	Zachariasen & Plettinger (1965)
α-Quartz	0·000	1·607	Young & Post (1962)
α-Quartz	0·000	1·607	Smith & Alexander (1963)
α-Cristobalite	0·000	1·6045	Dollase (1965)
Coesite	0·000	1·613‡	Zoltai & Buerger (1959)
Keatite	0·000	1·594§	Shropshire, Keat & Vaughan (1959)

* No attempt has been made to obtain a fully complete table. In particular, several structures of doubtful accuracy have been omitted, particularly if other substances of similar Al/(Al+Si) are available.

† Some mistakes are present in the Lp corrections applied to the Spencer U intensities (Bailey, private communication 1966). It is unlikely that these will significantly affect the average bond length.

‡ This determination may be inaccurate since the calculated and observed specific gravities are not in agreement.

§ This determination is unlikely to be accurate since the only crystals which were available yielded poor photographs.

considered, they are much less influential when the remaining frameworks are included.

Two less critical structures (andesine from Linosa and oligoclase from Bakersville) have been omitted from the calculation because of uncertain composition. The accuracy of the determined bond lengths varies from structure to structure, but since the quoted standard deviations are calculated on different bases it is difficult to select a rational weighting scheme for the least-squares fit. Several schemes were tried but yielded results less than one standard deviation from the unweighted calculation finally used.

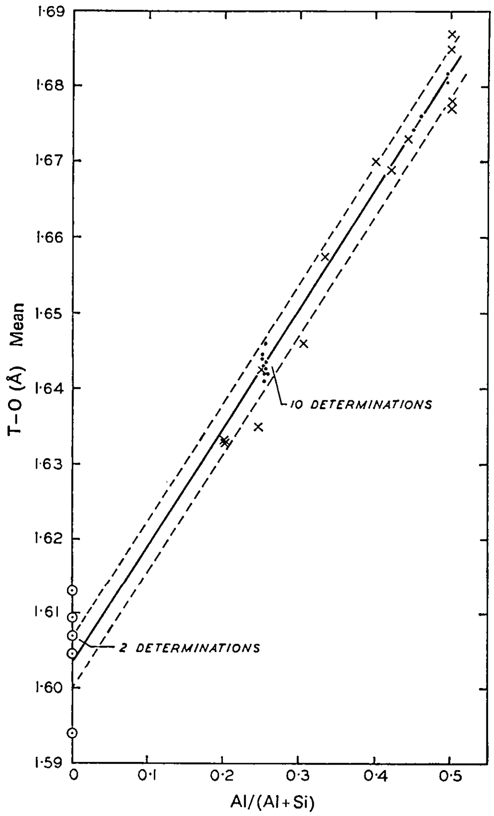

Fig. 1. Plot of average tetrahedral distance against aluminum content for framework structures. The line of best fit is that calculated for feldspar structures alone. The dashed lines are at one standard deviation from it as calculated for the full 32 structures. Black dots: feldspars; crosses: other aluminosilicate frameworks; dots with circles: silica polymorphs.

Results

Table 2 gives the equation for the line of best fit for the thirteen feldspars used in this study with the correlation coefficient, standard deviation between fitted and observed values and the calculated points for 0, 0·25, 0·5 and 1·0 Al. Since all these structures have an average Al/(Al+Si) value between 0·25 and 0·5, the end points of 0 and 1·0 Al, which must be used for the examination of individual tetrahedra, represent considerable extrapolations which will only be justified if the line is strictly straight.

There do not appear to be any data of sufficient accuracy available for structures with Al/(Al+Si) greater than 0·5 but there are framework structures which are in many respects similar to feldspars with ratios right down to a value of 0. These can be used both to test whether the line does appear to be straight below 0·25 Al and also whether the feldspar line is compatible with data from other framework structures. The equations for these structures alone and also that obtained from combining the data from these and the feldspars are included in Table 2.

The small differences between the equations are statistically quite insignificant and the scatter diagram shown in Fig. 1 indicates a random distribution of points about the line of best fit. The only real difference is an increase in the standard deviation when the second set of structures is included.

Application

Although this comparison constitutes some evidence that a linear relation exists between average T–O distance and tetrahedral aluminum content over the whole range from 0 to 1·0 Al, caution should still be used in applying it to the determination of the aluminum content of individual tetrahedra. It is not possible, at present, to make any quantitative allowance for local tetrahedral environment. Evidence of the qualitative importance of this will be presented elsewhere (Jones & Taylor, in preparation) and this is the reason for the conspicuous omission in the present study of the feldspar-like reedmergnerite $NaBSi_3O_8$.

Table 2. *Equation for determining tetrahedral aluminum content*

	Equation of fitted line	Correlation Coefficient	Standard deviation	T–O distance for O–Al	0·25 Al	0·5 Al	1·0 Al
Feldspars	$y=6{\cdot}3481x-10{\cdot}178$	0·997	0·008 Al =0·001 Å	$1{\cdot}603_3$	$1{\cdot}642_6$	$1{\cdot}682_0$	$1{\cdot}760_8$
Other similar frameworks	$y=6{\cdot}4334x-10{\cdot}337$	0·987	0·03 Al =0·005 Å	$1{\cdot}603_6$	$1{\cdot}642_5$	$1{\cdot}681_3$	$1{\cdot}759_1$
Combined data	$y=6{\cdot}4116x-10{\cdot}282$	0·989	0·02 Al =0·003 Å	$1{\cdot}603_6$	$1{\cdot}642_6$	$1{\cdot}681_6$	$1{\cdot}759_6$

$y=\text{Al}$, $x=\text{T–O}$ (Å)

The end points of 1·603 and 1·761 may be compared with the values for individual tetrahedra in some structures which appear to be nearly or completely ordered (Table 3). The value of 1·616 given by Zachariasen & Plettinger (1965) for one of the tetrahedra of quartz would yield an aluminum content of 0·12. This may be in part the lack of any aluminum present which is likely to lengthen the Si–O distance slightly (Jones & Taylor, in preparation) but is presumably mainly the result of local environment.

Table 3. Si–O *and* Al–O *distances* (Å) *in some completely ordered or nearly completely ordered structures*

	Si–O	Al–O
Silica polymorphs	1·594 – 1·617 Av. 1·606 ± ~0·005	
Tugtupite	1·601 ± 0·008	1·762 ± 0·014
Low albite	1·610, 1·612, 1·615 Av. 1·612 ± 0·002	1·746 ± 0·008
Microcline (Pellotsalo)	1·611, 1·612, 1·614 Av. 1·612 ± 0·001	1·741 ± 0·002
Anorthite	1·600 – 1·625 Av. 1·612 ± < 0·0015	1·714 – 1·775 Av. 1·749 ± < 0·0015

The remaining structures in Table 3 are complicated by the additional factor of the degree of order present – any departure from complete order will result in an increase in Si–O and corresponding decrease in Al–O. For the microcline there is independent optical and geometrical evidence that order is less than complete (Brown & Bailey, 1964).

Another factor which will affect individual bond lengths, perhaps differentially, is thermal vibration. It is unlikely that any meaningful estimate of the effects of this can be made for the present structures, since the quoted temperature factors are likely to be reflecting errors of numerous types and unknown magnitudes absorbed during the process of refinement.

Although the calculated line should yield the average aluminum content of a feldspar to better than about ±0·02, it would appear best to retain Smith & Bailey's (1963) figure of ±0·05 when examining individual tetrahedra.

Note added in proof: – After submission of this paper a note on this subject by Ribbe & Gibbs (1967) appeared. Our independent conclusions are in substantial agreement.

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References

Bailey, S. W. & Taylor, W. H. (1955). *Acta Cryst.* **8**, 621.

Brown, B. E. & Bailey, S. W. (1964). *Acta Cryst.* **17**, 1391.

Cole, W. F., Sörum, H. & Kennard, O. (1949). *Acta Cryst.* **2**, 280.

Danø, M. (1966). *Acta Cryst.* **20**, 812.

Dollase, W. A. (1965). *Z. Kristallogr.* **121**, 369.

Finney, J. J. & Bailey, S. W. (1964). *Z. Kristallogr.* **119**, 413.

Fischer, K. (1962). Private communication to Smith & Bailey (1963).

Fleet, S. G., Chandrasekhar, S. & Megaw, H. D. (1966). *Acta Cryst.* **21**, 782.

Gay, P. (1953). *Miner. Mag.* **30**, 169.

Gibbs, G. V. (1966). *Amer. Min.* **51**, 1068.

Hahn, J. & Buerger, M. J. (1955). *Z. Kristallogr.* **106**, 308.

Jarchow, O. (1965). *Z. Kristallogr.* **122**, 407.

Jones, J. B. & Taylor, W. H. (1961). *Acta Cryst.* **14**, 443.

Kempster, C. J. E., Megaw, H. D. & Radoslovich, E. W. (1962). *Acta Cryst.* **15**, 1005.

Kempster, C. J. E. (1966). Rerefinement, personal communication.

Laves, F. & Goldsmith, J. R. (1954). *Acta Cryst.* **7**, 465.

Liebau, F. (1961). *Acta Cryst.* **14**, 399.

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

Newnham, R. & Megaw, H. D. (1960). *Acta Cryst.* **13**, 303.

Papike, J. J. & Zoltai, T. (1965). *Amer. Min.* **50**, 641.

Papike, J. J. & Stephenson, N. C. (1966). *Amer. Min.* **51**, 1014.

Perrotta, A. J. & Smith, J. V. (1964). *Acta Cryst.* **17**, 857.

Perrotta, A. J. & Smith, J. V. (1965). *Miner. Mag.* **35**, 588.

Ribbe, P. H. (1963*a*). *Acta Cryst.* **16**, 426.

Ribbe, P. H. (1963*b*). Ph.D. Thesis, Cambridge.

Ribbe, P. H. (1966). I.M.A. Meeting, Cambridge, 1966.

Ribbe, P. H. & Gibbs, G. V. (1967). *Trans. Amer. Geophys. Union*, **48**, 229.

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. & Bailey, S. W. (1963). *Acta Cryst.* **16**, 801.

Smith, J. V., Rinaldi, F. & Dent Glasser, L. S. (1963). *Acta Cryst.* **16**, 45.

Staples, L. W. & Gard, J. A. (1959). *Miner. Mag.* **32**, 261.

Taylor, W. H. (1966). Private communication.

Young, R. A. & Post, B. (1962). *Acta Cryst.* **15**, 337.

Zachariasen, W. H. & Plettinger, H. A. (1965). *Acta Cryst.* **18**, 710.

Zoltai, T. & Buerger, M. J. (1959). *Z. Kristallogr.* **111**, 129.