

The Structure of Maximum Microcline

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The structure of an igneous maximum microcline of nearly pure KAlSi_3O_8 composition has been refined by a full matrix least squares program utilizing 2341 observed reflections. The final R is 10.4%. Tetrahedral site $T_1(0)$ is significantly larger than the other three sites and contains 0.94 atoms of Al according to new standard values for tetrahedral Si-O and Al-O distances. The K atom is slightly anisotropic and has seven (or eight) closest neighbors. Deviations from local electrostatic charge balance are comparable to those in low albite, in agreement with the geologic evidence that maximum microcline is the stable low temperature K-feldspar.

Introduction

The crystal structures of the potassium feldspars high sanidine (Cole, Sörum & Kennard, 1949; Ribbe, 1963*a*), orthoclase (Jones & Taylor, 1961), and intermediate microcline (Bailey & Taylor, 1955) have been carefully refined. The structures differ primarily in the relative sizes of the non-equivalent tetrahedra, which leads to the conclusion that the polymorphism of these minerals is due to varying degrees of ordering of the tetrahedral cations (12Si+4Al) over the 16 available sites. The values of Smith (1954) for the standard distances for Si-O and Al-O tetrahedra were used in these investigations as criteria to indicate that high sanidine is completely disordered and that orthoclase has a small preferential segregation of Al into the eight sites composing the T_1 set of tetrahedra (Table 1). Further ordering produces a lowering of symmetry from $C2/m$ to $C\bar{1}$ and a distortion of the unit-cell shape. In particular, the reciprocal angle γ^* is found to range in different triclinic specimens from a value very close to 90° to a maximum value of $92^\circ 20'$. A microcline of intermediate obliquity was found to have a substantial, but not complete,

segregation of Al into the four sites comprising the $T_1(0)$ set of tetrahedra.†

The relative degrees of tetrahedral order found in the three specimens so far investigated are in accord with our knowledge of the variations in the optical properties of potassic feldspars in general and with the geologic evidence regarding their thermal histories. Thus, quenched or rapidly cooled specimens from volcanic rocks or small plutonic bodies tend to be monoclinic with small optic angles, either in a plane parallel to (010) or in a plane normal to (010). Such specimens show small degrees of order, as typified by the two crystals of high sanidine and orthoclase whose structures have been determined. Specimens from larger, more slowly cooled igneous or metamorphic rock bodies, or from rocks with a higher content of volatiles, are usually triclinic with larger optic angles in a plane nearly normal to (010). An intermediate microcline of this type has been shown to have a degree of Si-Al order consistent with its observed obliquity and optical properties. In line with this reasoning, Bailey & Taylor (1955) predicted

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† The original notation of $\text{Si}_1' = T_1(m)$ of Bailey & Taylor has been changed to $\text{Si}_1 = T_1(0)$ as a consequence of changing axial directions according to the recommendation of Laves (1951).

Table 1. *Tetrahedral distances in potassic feldspars*

	Space group	γ^*	Tetrahedral set	Mean T-O distance	% Al (Smith, 1954)
High sanidine (Cole <i>et al.</i> , 1949)	$C2/m$	90°	8 T_1 8 T_2	1.642 Å 1.642	0.25 0.25
Orthoclase (Jones & Taylor, 1961)	$C2/m$	90°	8 T_1 8 T_2	1.652 1.633	0.30 0.19
Intermediate microcline (Bailey & Taylor, 1955)	$C\bar{1}$	$90^\circ 50'$	4 $T_1(0)$ 4 $T_1(m)$ 4 $T_2(0)$ 4 $T_2(m)$	1.700 1.645 1.614 1.611	0.56 0.25 0.08 0.07

Table 2. *Cell dimensions and optical properties of Pellotsalo microcline*

Direct cell		Reciprocal cell		Optical parameters	
a	$8.560 \pm 4 \text{ \AA}$	a^*	0.1299 \AA^{-1}	Refractive indices	$\left\{ \begin{array}{l} \alpha \ 1.5178 \\ \beta \ 1.5207 \\ \gamma \ 1.5247 \end{array} \right.$
b	12.964 ± 7	b^*	0.0772		
c	7.215 ± 3	c^*	0.1540		
α	$90^\circ 39' \pm 5'$	α^*	$90^\circ 23'$	Birefringence ($\gamma - \alpha$)	0.0069
β	$115^\circ 50' \pm 5'$	β^*	$64^\circ 10'$	Optic angle $\left\{ \begin{array}{l} 2V_{\text{meas.}} \\ 2V_{\text{calc.}} \end{array} \right.$	$\left. \begin{array}{l} 82.5^\circ \\ 81.0^\circ \end{array} \right\}$
γ	$87^\circ 42' \pm 5'$	γ^*	$92^\circ 14'$		
V	720.0 \AA^3	V^*	1.3889×10^{-3}	Extinction on (001)	17°
D_x	2.568 g.cm^{-3}			Extinction on (010)	5°

that the microcline showing the greatest deviation from monoclinic symmetry, *i.e.* maximum microcline, should be completely ordered and have all of the Al concentrated in the four sites of the $T_1(0)$ set of tetrahedra. This opinion tacitly assumes that maximum microcline is the potassic feldspar that has the lowest free energy and is most stable under the P - T conditions at the lower end of the cooling range of igneous rocks. Similar views as to the stability of maximum microcline have been expressed by Goldsmith & Laves (1954*a, b*).

Ferguson, Traill & Taylor (1958, 1959) and Ferguson (1960) have disputed both the view that maximum microcline is the stable low temperature K-feldspar and the view that it is completely ordered. They contend that the most stable structure is the one that has the best local electrostatic charge balance, rather than the highest degree of Si-Al order. For a K-feldspar they compute the best charge balance to be an 'ideal orthoclase' that has only a slightly larger concentration of Al in the T_1 sites than in the T_2 sites. Maximum microcline was considered unstable and its great abundance in nature was explained as a result of unmixing from an original solid solution containing a large excess of Na over K. They state that with such an origin microcline could not be expected to have a greater degree of Si-Al order than that in the host Na-feldspar, albite, for which the tetrahedral bond length graph of Smith (1954) indicated about 75% of the Al to be in the $T_1(0)$ sites. According to their calculations an albite with this degree of Si-Al order has the best local charge balance and should be considered the stable low temperature Na-feldspar.

The structure of maximum microcline, reported in this paper, was undertaken in an attempt to determine unequivocally its degree of Si-Al order and to provide further data from a structural point of view with regard to its stability.

Crystal data

The microcline used is No. SM4709 in the Helsinki collection. It comes from a granitic body on Pellotsalo, an island in Lake Ladoga that has changed from Finnish to Russian control since the original sampling (Eskola, 1951). The material is coarsely perthitic and has only a few areas of cross-hatch twinning in the

microcline phase. Photomicrographs of this material have been published by Goldsmith & Laves (1954*b*). A single crystal $0.15 \times 0.20 \times 0.25$ mm was easily cut from the untwinned microcline portion. The X-ray reflections are sharp and show no diffuse streaks of the type found in some orthoclase and adularia specimens.

Table 2 contains the unit-cell dimensions and optical properties of the particular crystal used for the structure determination. The cell constants were obtained by the θ method (Weisz, Cochran & Cole, 1948). The refractive indices were measured using the double variation technique and a spindle mount (Wilcox, 1959) on a five-axis universal stage. The γ^* value of $92^\circ 14'$, the triclinicity value ($\Delta = 12.5[d(131) - d(\bar{1}\bar{3}1)]$) of 0.95, the extinction angle on (001) of 17° , the $2V$ of 82° , and the total birefringence of 0.0069 all indicate that the crystal is very close to a maximum microcline, although all of these figures are slightly lower than the maximum values possible. Spectrochemical analysis of the bulk sample gives $\text{Or}_{74}\text{Ab}_{25}\text{An}_1$ (Goldsmith & Laves, 1961). Although we do not have a chemical analysis of the microcline portion of the sample, the $d(400)$ value of 1.925 \AA applied to the graph of Goldsmith & Laves (1961) indicates only 1-2% Na-feldspar in solid solution in the microcline. The $d(\bar{2}01)$ value of 4.213 \AA , after correction for the obliquity, indicates about 5% Na-feldspar. The crystal may be regarded, therefore, as a maximum microcline that is close to the end member KAlSi_3O_8 composition.

Experimental

Intensity data were collected for 2341 observed reflections, using the Weissenberg equi-inclination technique, Mo $K\alpha$ radiation, and multiple film packs. Four levels normal to both the X and the Z axes and seven levels normal to the Y axis were recorded. This distribution includes approximately equal portions of reciprocal space along each axis. All intensities were measured by visual comparison with a multiple set of standard scales.

The intensities have been adjusted for upper level extension-contraction effects by an empirical approach similar to that of Bailey & Taylor (1955), but using the harmonic mean rather than the arithmetic mean. Correction for the progressive α_1 - α_2 doublet separation was applied by assuming that the effect of the un-

Table 3. *Atomic coordinates, Pellotsalo microcline*

Atom*	Starting model			Initial refinement				Final refinement			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	<i>y</i>	<i>x</i>	<i>z</i>	<i>B</i>
K	0.2842	-0.0033	0.1386	0.2821	-0.0069	0.1349	1.44	0.2827	-0.0072	0.1365	1.410†
<i>T</i> ₁ (0)	0.0095	0.1864	0.2221	0.0096	0.1876	0.2164	0.72	0.0104	0.1875	0.2169	0.693
<i>T</i> ₁ (<i>m</i>)	0.0092	0.8164	0.2779	0.0093	0.8199	0.2316	0.49	0.0097	0.8198	0.2327	0.351
<i>T</i> ₂ (0)	0.7089	0.1180	0.3427	0.7107	0.1199	0.3404	0.44	0.7110	0.1202	0.3399	0.341
<i>T</i> ₂ (<i>m</i>)	0.7068	0.8841	0.3461	0.7058	0.8858	0.3500	0.45	0.7059	0.8856	0.3507	0.313
<i>O</i> _A (1)	0.0003	0.1452	-0.0066	0.0004	0.1466	-0.0168	1.10	0.0007	0.1448	-0.0169	0.759
<i>O</i> _A (2)	0.6289	0.0014	0.2861	0.6360	0.0060	0.2862	0.89	0.6366	0.0058	0.2853	0.667
<i>O</i> _B (0)	0.8228	0.1448	0.2226	0.8230	0.1462	0.2206	1.14	0.8202	0.1476	0.2205	1.030
<i>O</i> _B (<i>m</i>)	0.8285	0.8554	0.2353	0.8381	0.8580	0.2415	1.18	0.8316	0.8570	0.2416	1.020
<i>O</i> _C (0)	0.0339	0.3161	0.2548	0.0334	0.3192	0.2545	1.00	0.0352	0.3203	0.2514	0.770
<i>O</i> _C (<i>m</i>)	0.0374	0.6910	0.2630	0.0368	0.6952	0.2724	0.80	0.0366	0.6953	0.2689	0.736
<i>O</i> _D (0)	0.1839	0.1229	0.4063	0.1933	0.1214	0.4040	1.17	0.1911	0.1229	0.4053	0.973
<i>O</i> _D (<i>m</i>)	0.1767	0.8736	0.4106	0.1751	0.8737	0.4101	1.25	0.1753	0.8742	0.4127	0.933

* Atoms listed are prototypes with full symbols (0000) or (*m*000) in the notation of Megaw (1956).

† Anisotropic *B* for K atom listed in Table 9.

resolved doublet is to cause a linear decrease of the measured intensity relative to the true intensity as the spot width increases. Correction for the Lorentz-polarization factor was made, but no absorption correction was attempted because of the small, uniform size of the crystal and the low linear absorption coefficient of 14 cm⁻¹.

Space group *C* $\bar{1}$, the same as that for intermediate microcline, was confirmed by the extinctions and by the *N*(*z*) test for a center of symmetry (Howells, Phillips & Rogers, 1950).

Refinement

The atomic coordinates for intermediate microcline, transformed to the orientation of Laves (1951), were used as the starting point. The refinement was carried out in two stages because of the types of computing facilities available. The scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and isotropic temperature factors were used, except for the last refinement cycle in which the anisotropic temperature factor of potassium was determined.

The first stage of the refinement utilized only 600 selected reflections having $F_o > 6$ and $\sin^2 \theta > 0.16$. The Least Squares II program of Senko & Templeton for the IBM 650 computer, slightly modified to include triclinic crystals, was used in this stage. The diagonal approximation used by this program required ten cycles to reduce the reliability index from an initial value of 0.25 to a minimum of 0.085. Following the initial stage of the refinement three more cycles were run with all 2341 observed reflections. For these cycles the full matrix least squares program of Busing & Levy for the IBM 704 computer was used. The final minimum *R* for all reflections is 0.104.

The atomic coordinates of the initial model and those at the completion of the two refinement stages are catalogued in Table 3. The shifts of atomic parameters from those of the intermediate microcline model are

all small, the maximum shift being 0.07 Å for atom *O*_A(1). It should be noted that some change in the parameters is introduced automatically by the decrease in the γ angle from intermediate to maximum microcline. The second stage of the refinement shifted many parameters by apparently significant amounts, despite the use of three-dimensional data in both stages. For example, atom *O*_B(0) was shifted by 0.024 Å, which is equivalent to five standard deviations as calculated by the Senko-Templeton program. The average shift is about 0.011 Å. The individual *T*-O bond lengths derived from the two refinement stages are also significantly different in some cases, although the agreement for the average *T*-O distances is quite good. Table 4 lists the standard deviations of the final atomic coordinates and temperature factors. Table 5 lists the interatomic bond distances and angles.

Table 4. *Standard deviations of atomic coordinates and temperature factors*

	$\sigma(x)$	$\sigma(B)$
K	0.001 ₆ Å	0.02 ₆
<i>T</i> ₁ (0)	0.001 ₈	0.02 ₇
<i>T</i> ₁ (<i>m</i>)	0.001 ₆	0.02 ₄
<i>T</i> ₂ (0)	0.001 ₆	0.02 ₄
<i>T</i> ₂ (<i>m</i>)	0.001 ₆	0.02 ₄
<i>O</i> _A (1)	0.004 ₅	0.06 ₈
<i>O</i> _A (2)	0.004 ₃	0.06 ₅
<i>O</i> _B (0)	0.004 ₆	0.07 ₀
<i>O</i> _B (<i>m</i>)	0.004 ₇	0.07 ₁
<i>O</i> _C (0)	0.004 ₄	0.06 ₈
<i>O</i> _C (<i>m</i>)	0.004 ₅	0.06 ₀
<i>O</i> _D (0)	0.004 ₅	0.07 ₂
<i>O</i> _D (<i>m</i>)	0.004 ₆	0.07 ₂

Accuracy of results

The positional standard deviations $\sigma(x)$ listed in Table 4 were calculated by the Busing & Levy least squares program. The bond length errors in Table 5 were derived from these standard deviations from the relation $\sigma^2(d_{1-2}) = \sigma^2(x_1) + \sigma^2(x_2)$. For comparing aver-

Table 6. Degree Si-Al order of potassic feldspars

	Maximum microcline		Intermediate microcline		Orthoclase		Sanidine	
	Mean T-O	% Al	Mean T-O	% Al	Mean T-O	% Al	Mean T-O	% Al
$T_1(0)$	1.741 Å	0.94	1.700 Å	0.64	1.652 Å	0.30 × 2	1.642 Å	0.23 × 2
$T_1(m)$	1.614	0.03	1.645	0.25				
$T_2(0)$	1.611	0.01	1.614	0.03	1.633	0.17 × 2	1.642	0.23 × 2
$T_2(m)$	1.612	0.02	1.611	0.01				
Σ Al		1.00		0.93		0.94		0.92
Degree order*		92%		61%		19%		0%

* Using equation of MacKenzie & Smith (1961) with Σ Al adjusted to 1.00.

age T-O distances for different tetrahedra, the standard error of the mean was calculated from $\sigma_n = \sigma(T-O)/\sqrt{n}$. For maximum microcline $\sigma_n = 0.0024$ Å for all four tetrahedra. Cruickshank (1949) suggests that two bond lengths should differ by more than three standard deviation units in order to be considered real. For Cruickshank's tests the standard deviation unit to be used for comparing two tetrahedral means is $\sigma = \{[\sigma_n(T_1)]^2 + [\sigma_n(T_2)]^2\}^{1/2}$. Because σ_n is the same for all four tetrahedra we can use $\sigma = \sigma_n \cdot 1/2$ in the present case. The 3σ value is therefore $3(0.0034)$, or about 0.01 Å. The differences between the mean $T_1(0)$ distance and the other three tetrahedral means are all close to 0.13 Å, a difference of about 13σ . Therefore $T_1(0)$ is significantly larger than the other tetrahedra. The differences between the three small tetrahedra are all non-significant. It is interesting to note that the significance level of three standard deviation units would correspond to a difference in tetrahedral Al content of about 7% in this case.

A similar analysis applied to the temperature factors for the tetrahedral cations reveals that the $T_1(0)$ cation has a significantly higher temperature factor than do cations of the other tetrahedra, a difference of 10σ . This difference is apparently due to the use of a Si scattering factor in an Al-rich site, because the scattering factor for Si was used for all four tetrahedra to avoid the assumption of ordering.

Si-Al order

The structures of 12 feldspars have now been determined. In addition to the K- and Na-varieties these include oligoclase, andesine, bytownite, anorthite, celsian, and reedmergnerite, the boron analogue of albite. If the T-O distances in each structure are averaged over the entire unit cell, without regard to possible Si or Al content, and plotted with respect to bulk tetrahedral composition, a line of best fit predicts pure Si-O and Al-O values of 1.61 Å and 1.75 Å respectively (Smith & Bailey, 1963). The maximum deviation of any point from the line of best fit is only 0.003 Å, which indicates that the mean T-O distances represent tetrahedral composition quite accurately.

Comparison of the new standard values for Si-O and Al-O with previously determined T-O distances

shows that the slowly-cooled feldspars are more ordered than was previously believed. Table 6 lists the tetrahedral Al-content derived for maximum microcline and for other potassic feldspars by linear extrapolation between the new standard figures.

Tetrahedral site $T_1(0)$ of maximum microcline contains, on the average, $Al_{0.94}Si_{0.06}$. According to the equation of MacKenzie & Smith (1961), the crystal is 92% ordered. The accuracy of the results suggests that the deviation from 100% order is significant, although not highly significant. This finding is in accord with the observation that the crystal is not quite a maximum microcline, *i.e.* all of its geometrical and optical parameters that are sensitive to degree of order are slightly smaller than the maximum values possible. However, the influence of external bonds on individual T-O distances must also be considered in explaining the apparent deviation from 100% order. Smith & Bailey (1963) have suggested, for example, that the influence of the local environment around each tetrahedron may lead to errors of $\pm 5\%$ Al, in addition to any experimental error.

It is interesting to note that the tetrahedral temperature factors could also be used as indicators of degree of order. The final isotropic temperature factor for site $T_1(0)$ is twice as large as those for the other three tetrahedra when Si scattering factors are used for all four sites (Table 3). A fourth least squares refinement cycle was run to test the effect on the temperature factors of assuming complete order and of using f_{Al} for site $T_1(0)$. There were no significant changes in the positional parameters, but the tetrahedral temperature factors adjusted to the same order of magnitude (Table 7). The slightly smaller value of B for $T_1(0)$ relative to the other T sites can be interpreted either as an indication that ordering is not complete or as an expression of the differences in the local environments of the tetrahedra due to the different sizes and charges of the cations contained.

Table 7. Final tetrahedral temperature factors

	B	$\sigma(B)$
$T_1(0)$	0.29	0.02 ₈
$T_1(m)$	0.38	0.02 ₂
$T_2(0)$	0.38	0.02 ₄
$T_2(m)$	0.35	0.02 ₃

Table 8. Charge balance of alkali feldspars

Tetrahedral Al contents from graph of Smith & Bailey (1963), adjusted to 1.00 Al where necessary. Charge imbalance is measured by deviation from +8.00 of bonds leading to each tetrahedral anion group, assuming coordination about the large cation as indicated. For low and high albite the total charge imbalance is obtained by combining the columns for Na(1) and Na(2)

	Maximum microcline (this paper)		Intermediate microcline (Bailey & Taylor, 1955)			Orthoclase (Jones & Taylor, 1961)	Sanidine (Cole <i>et al.</i> , 1949)			
	K		K			K	K			
	C.N.=7	C.N.=8	C.N.=8	C.N.=9		C.N.=9	C.N.=9			
$T_1(0)$	0.94 Al	7.75	7.67	0.69 Al	7.86	7.79	} 2×0.32 Al	8.02	} 2×0.25 Al	8.06
$T_1(m)$	0.03	8.16	8.22	0.27	8.04	8.10				
$T_2(0)$	0.01	8.16	8.11	0.03	8.03	8.10	} 2×0.18	7.98	} 2×0.25	7.94
$T_2(m)$	0.02	7.93	8.00	0.01	8.07	8.01				
$\Sigma \Delta $		0.64	0.66		0.28	0.42		0.08		0.24

	Low albite (Ribbe, 1963b)				High albite (Ferguson <i>et al.</i> , 1958)			
	Na(1)		Na(2)		Na(1)		Na(2)	
	C.N.=7	C.N.=5	C.N.=5	C.N.=9	C.N.=7	C.N.=6	C.N.=7	
$T_1(0)$	0.94 Al	7.75	7.84	7.60	0.30 Al	8.03	8.13	8.17
$T_1(m)$	0.00	8.17	8.14	8.30	0.21	8.11	8.03	7.96
$T_2(0)$	0.04	8.15	8.12	8.16	0.23	7.95	8.03	7.96
$T_2(m)$	0.02	7.93	7.90	7.94	0.26	7.91	7.81	7.91
$\Sigma \Delta $		0.64	0.52	0.92		0.28	0.38	0.34

Stability

The validity of the charge balance hypothesis of Ferguson *et al.* (1958, 1959) and of Ferguson (1960) depends on the correctness of their conclusion that low albite is only partly ordered. The particular degree of order determined by these investigators by comparison with Smith's 1954 bond length graph, 75% Al in site $T_1(0)$, is the distribution that gives the best possible balance of charges for albite. This conclusion then led to the hypothesis that maximum microcline, which was considered to have poor charge balance, must be an unstable structure that originates only by unmixing from a very soda-rich host.

The original two-dimensional data of Ferguson *et al.* (1958) for low albite have been supplemented by three-dimensional data (Ribbe, 1963b). Both the two-dimensional and the three-dimensional results indicate about 92% ordering according to the new standard values of Smith & Bailey (1963) for tetrahedral Si-O and Al-O distances. The mean T-O distances in low albite are almost identical with those reported here for maximum microcline. The effect of this high degree of Si-Al order in low albite is to create a local imbalance of electrostatic charges that is comparable to that in maximum microcline, but is greater than that present in orthoclase, intermediate microcline, and even in accepted high temperature forms, such as high albite and sanidine (Table 8).

One of the problems in computing the electrostatic charge distribution in a feldspar is to decide on the strengths of the bonds leading from the large cation (K, Na, Ca, Ba) to its immediate neighbors. For ease in comparing results, we have followed the procedure of Ferguson *et al.* (1958) of assigning equal strengths

to all bonds leading to oxygen atoms in the primary coordination group. We agree with the suggestion of Jones & Taylor (1961), however, that the bond strengths should be scaled according to the varying distances of the nearest neighbors.

Because of the irregular configuration around the large cation, it is difficult to decide which neighbors to include in the primary coordination group. For example, Table 5 shows that for maximum microcline there are seven K-O contacts under 3.0 Å. Atom $O_C(m)$ and one of the $O_A(2)$ atoms, which have K-O distances of 3.34 and 3.40 Å respectively, are probably outside the primary coordination group, but atom $O_B(m)$ at a distance of 3.14 Å is in an intermediate position. The coordination could reasonably be chosen either as sevenfold or eightfold, and both possibilities have been considered in the charge balance computations in Table 8. In high and low albite the additional complication is met that electron density maps and anisotropic temperature factor calculations indicate that the Na position is a superposition of two atoms, Na(1) and Na(2), that have different coordinations. In low albite the separation of the two sodium atoms is 0.35 Å (Ribbe, 1963b). Atom Na(1) has seven oxygen neighbors that have Na-O distances under 2.85 Å, but Na(2) has only five such closest neighbors plus another group of four neighbors having Na-O distances between 3.09 and 3.29 Å. We have assumed in the results quoted in Table 8 that sites Na(1) and Na(2) are occupied equally, and we have used the coordinations appropriate to each, citing separate results for the different coordinations possible around Na(2) in both low albite and high albite.

We conclude from Table 8 that there is no valid basis for using charge balance computations of this

Table 9. *Anisotropic thermal parameters for potassium*

Ellipsoid axis	r.m.s.	<i>B</i>	Angles to crystal axes (°)					
			<i>X</i>	Δ	<i>Y</i>	Δ	<i>Z</i>	Δ
1	0.112	0.99	28.6	3.2	103.1	3.3	91.3	3.8
2	0.142	1.60	95.2	5.2	43.5	10.3	49.1	10.4
3	0.154	1.88	118.1	3.5	130.5	10.3	40.9	10.5

particular type to judge the relative stabilities of different structures. The resulting values bear no relation to accepted equilibrium or non-equilibrium phases. MacKenzie & Smith (1959) have pointed out that the use of an average tetrahedral composition in computing charge balance, as used by Ferguson *et al.* and followed in this paper, assumes that electrostatic charges are effective over several unit cell edges. They state that it is probably more correct to assume only a short range effectiveness of charge and to compute the total charge imbalance in terms of the actual distribution of the tetrahedral cations rather than the physically impossible, average distribution. They compute on this basis that a fully ordered maximum microcline has a better charge balance than partly ordered orthoclase or disordered sanidine.

Because the deviation from local electrostatic charge balance in maximum microcline is comparable to that in low albite, whichever method of computation is used, the original reason for considering microcline to be unstable no longer holds. We believe that the vast majority of the geologic evidence as well as this structural evidence indicates that maximum microcline is the stable low temperature K-feldspar. There is no need, therefore, to evoke a special mode of origin for microcline by unmixing from an extremely Na-rich host. Laves & Goldsmith (1961) have summarized other evidence against the charge balance hypothesis of Ferguson *et al.*

Thermal anisotropy of potassium

The potassium atom has measurable anisotropy in all of the potassic feldspars so far studied. The ellipsoid of vibration has been determined in detail only for orthoclase, in which the ellipsoid major axis was deduced from difference maps as being parallel to *Y*, the median axis parallel to *Z*, and the minor axis parallel to *X** (Jones & Taylor, 1961). The root mean square displacements, *B* values, and ellipsoid axis directions were refined for the Pellotsalo microcline during the last cycles of the least square analysis (Table 9). The triaxial ellipsoid is slightly disk shaped with two long axes and one short axis. The ellipsoid can be described to a first approximation as oriented with the minor axis parallel to *X** and the median and major axes lying in (100) and symmetrically disposed about the *Z* axis (Fig. 2). In actuality the ellipsoid is rotated from this approximate orientation by 10° clockwise about the direction [203].

The anisotropy can be explained satisfactorily as

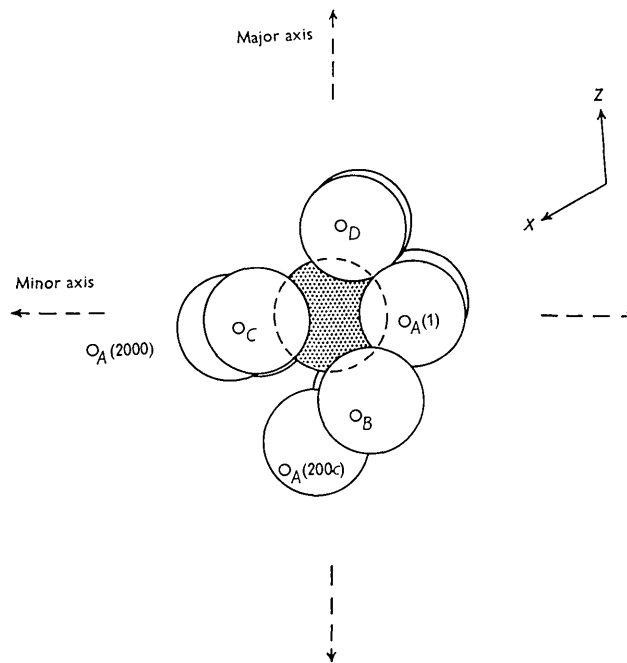


Fig. 1. Projection along Y^* of coordination group around potassium in relation to the major and minor axes of its thermal ellipsoid. At the top the major axis plunges 40° below the plane of the diagram and at the left the minor axis plunges 15°. Arbitrary radii of 1.4 and 1.5 Å, respectively, have been used for oxygen and potassium.

thermal vibration within an irregular coordination group. Figs. 1–3 illustrate views from different directions of the coordination group around the potassium atom. Viewed along Y^* in Fig. 1 the potassium atom has a nearly coplanar group of four oxygen neighbors above the (010) plane and a similar group of four neighbors below (010). In addition, there are two $O_A(2)$ atoms at about the same *y* level as the potassium. Of these 10 neighbors, atoms $O_A(200c)$, $O_C(m)$, and probably, $O_B(m)$ are not in direct contact with K. The major axis of the ellipsoid, oriented 41° from *Z*, points between these three atoms on one side of the potassium and toward $O_D(m)$ on the other side (Fig. 2). These four oxygen atoms are, respectively, 0.51, 0.44, 0.24, and 0.10 Å farther from the potassium than the average K–O contact of 2.894 Å for the seven closest neighbors. This spatial relationship accounts satisfactorily for the observed direction of maximum vibration. The minor axis of the ellipsoid is 12° off parallelism with X^* . Oscillation in this direction is restricted by four close oxygen neighbors and also by repulsion from an adjacent K atom (Fig. 3).

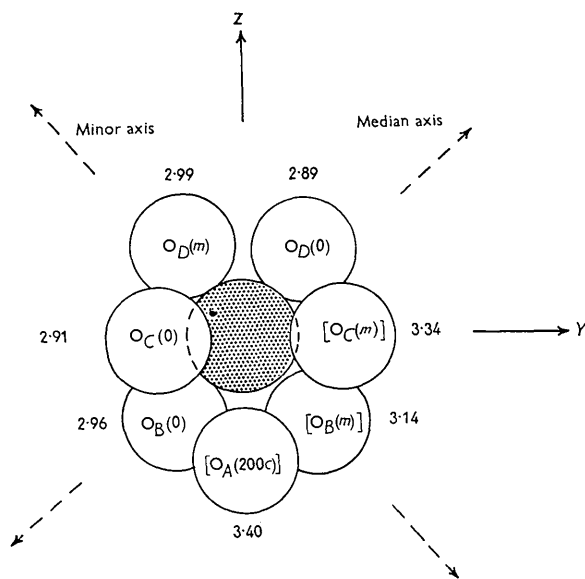


Fig. 2. Potassium coordination group viewed approximately in the plane of the major and median axes of the thermal ellipsoid. Two $O_A(1)$ atoms, located below the two O_C atoms, and atom $O_A(2000)$, directly above K, have been omitted for clarity. The K-O distances are listed beside each oxygen. Symbols in brackets refer to oxygen atoms not in direct contact with potassium.

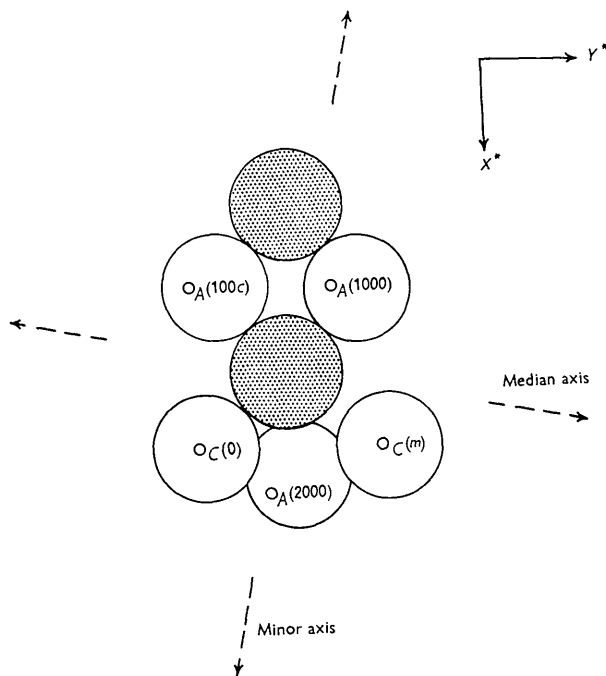


Fig. 3. Section normal to $[001]$ in which all atoms are close to the plane of the section. The potassium ellipsoid minor axis lies in the plane of the section, but the median axis plunges 41° at the left side.

The variable distances of the oxygen atoms from potassium are due in part to the electrostatic charge distribution created by ordering of the tetrahedral

cations. Each of the $O(1)$ or $O(0)$ atoms [$O_A(1)$, $O_B(0)$, $O_C(0)$, and $O_D(0)$] is shared between an Al tetrahedron and a Si tetrahedron, whereas each of the $O(2)$ or $O(m)$ atoms is shared by two Si tetrahedra. The negative charge of each of the latter type of oxygen atom is completely satisfied by its two bonds to Si, assuming complete order. The $O(1)$ or $O(0)$ atoms have excess negative charges and are correspondingly closer to the potassium. The average K-O(0) bond is 2.90 \AA compared to 3.12 \AA for the average K-O(m) bond. Atoms $O_A(200c)$, $O_C(m)$, and $O_B(m)$ are far enough away that they are not considered to be in contact with the potassium. Atom $O_A(2000)$ does not follow the average trend of the other $O(2)$ and $O(m)$ atoms and is actually the closest potassium neighbor, but for steric rather than charge reasons (Bailey & Taylor, 1955; Ferguson *et al.*, 1958; Megaw, Kempster & Radoslovich, 1962).

It is to be expected that the thermal ellipsoid for the large cation in other feldspars will resemble that in microcline because of the overall similarity of all feldspar structures. Differences in details of the ellipsoids will result from differences in symmetry, in the degree of Si-Al order, in the Si-Al ratio, and in the size and charge of the large cation, all of which influence the closeness of approach of individual oxygens to the large cation. The nature of the coordination group suggests that in all feldspars vibration along X^* will be more difficult than along Y or Z . This is verified by the details of the thermal ellipsoids in orthoclase, in the Ba-feldspar, celsian (Newnham & Megaw, 1960), and in the Ca-feldspar, anorthite (Kempster, Megaw & Radoslovich, 1962). The relation of the anisotropic ellipsoid in microcline to the more pronounced atom-splitting in high and low albite and in some of the other plagioclases is uncertain, but there is no evidence from our investigation to support any interpretation of the microcline anisotropy other than by thermal vibration or frozen-in vibration. The B values are reasonable for the weak bonds and the irregular coordination involved, and the spatial distribution of nearest neighbors appears to account for the observed vibration directions.

Transformation twinning

The concentration of Al in the T_1 set of tetrahedral sites rather than in the T_2 set in maximum microcline follows the trend observed in the other low temperature alkali feldspars whose structures are known. Brown (1962) has pointed out that this trend is probably due to a combination of steric and electrostatic charge factors. In passing from the monoclinic to the triclinic state with increase in degree of order, the T_1 tetrahedra are split into two non-equivalent sets, $T_1(0)$ and $T_1(m)$. There is no obvious factor favoring the observed enrichment of the $T_1(0)$ set relative to $T_1(m)$. Because the two sets must be crystallographically and topologically equivalent in

Table 10. *Effect of external bonds on T-O distances*

The numbers of individual bond lengths of each type that have been averaged are given in parentheses. The coordination numbers apply to the large cations, K or Ca

No. of K or Ca neighbors	Maximum microcline Mean bond lengths in Å		Anorthite Mean bond lengths in Å		
	Si-O		Al-O	Si-O	Al-O
	C.N.=7	C.N.=8	C.N.=7 or 8	C.N.=7	C.N.=7
2	1.592 (1)	1.592 (1)	1.738 (1)	1.632 (4)	1.780 (4)
1	1.609 (7)	1.610 (9)	1.742 (3)	1.622 (20)	1.755 (20)
0	1.622 (4)	1.631 (2)	—	1.588 (8)	1.719 (8)

monoclinic symmetry, we assume that the further concentration of Al in $T_1(0)$ or in $T_1(m)$ must depend on random selection.

In an untwinned single crystal of microcline there is no way to distinguish $T_1(0)$ from $T_1(m)$ on an absolute basis. Because of the manner of distortion of the structure around the site occupied by Al, be it $T_1(0)$ or $T_1(m)$, the resulting disposition of triclinic axes and angles is such that the Al-rich site must be identified as $T_1(0)$ according to convention. If, however, Al preferentially occupies $T_1(0)$ sites in certain domains of the crystal and $T_1(m)$ sites in other domains during the process of ordering, nuclei of two differently oriented triclinic structures are established within the monoclinic host. As the ordered domains enlarge and grow together, the tendency of the framework to remain as undistorted as possible requires the two structures to join together either in the albite or pericline twin orientations. Laves (1950) shows possible models of the manner of junction of the domains and presents experimental evidence that the (010) albite twin plane is perpendicular to the [010] pericline twin axis.

Microcline grid twinning, in which the twin plane can be shown to be normal to the twin axis, is evidence of the original monoclinic ancestry of the feldspar and is a natural consequence of the random choice of different T_1 sites by Al during the course of ordering and inversion. Untwinned microcline is to be expected only under unusual circumstances in which the Al can segregate in only one set of triclinic tetrahedral sites or in which one domain can grow at the expense of its neighbors to the boundaries of the crystal.

Comparison with other feldspars

Megaw, Kempster & Radoslovich (1962) have pointed out in connection with their analysis of the anorthite structure that in all feldspars so far examined certain bond lengths and angles tend to be consistently larger or smaller than the mean values. This trend is followed closely in maximum microcline also, indicating that its tetrahedral framework is of the same general shape as that in other feldspars. For example, the $T-O-T$ angles involving O_B atoms are about 10° larger than the mean for such angles and those angles involving O_C atoms are about 10° smaller than the

mean. The deviations of individual $O-T-O$ angles from the mean are in the same direction and of approximately the same magnitude as in other alkali feldspars. Likewise certain bond lengths, such as O_A-O_C in T_1 tetrahedra, are consistently longer than the mean of such values and other bonds, such as O_A-O_C in T_2 tetrahedra, are shorter than the mean values. Megaw *et al.* have shown convincingly that this distortion of the feldspar framework is independent of the Si:Al ratio and degree of order and is a consequence primarily of electrostatic repulsion between the large cations (K, Na, Ca, or Ba) across the relatively unshielded $O_A(1)-O_A(1)$ shared edge (Fig. 3).

One feature of the anorthite structure that is not copied in the microcline structure concerns the influence of external bonds from the large cations on individual $T-O$ bonds. In anorthite, oxygen atoms with two close Ca neighbors have appreciably longer $T-O$ bonds than do oxygen atoms with one or zero Ca neighbors. In microcline the trend is just the opposite. Oxygen atoms with two K neighbors have shorter $T-O$ bonds than those oxygen atoms with one or zero K neighbors (Table 10). The trend is consistent whether the K atom is considered to have seven- or eight-fold coordination, although the number of bonds of each type is considerably smaller than for anorthite because of symmetry.

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The Probability Distribution of Bijvoet Differences

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The statistical distribution of the difference in intensities between inverse reflexions (Bijvoet difference) in non-centrosymmetric crystals containing atoms, some of which scatter anomalously, has been investigated theoretically. The theory is worked out for structures containing one, two and many anomalous scatterers (all assumed to be alike) in addition to a large number of non-anomalous scatterers. The theoretical results have been tested with calculations based on hypothetical models and also with the observed data from two known structures. The agreement is found to be good. The results suggest that, for observing large Bijvoet differences, a structure containing a large number of anomalous scatterers with a centric configuration is the least favourable as compared with a structure containing either a small number of atoms (one or two) or a large number with an acentric configuration.

1. Introduction

The use of the anomalous dispersion technique in crystal structure analysis, particularly for the determination of the absolute configuration of a structure, was first pointed out by Bijvoet (1954) and the method has since then proved to be one of the most interesting applications of X-ray methods to the elucidation of chemical structure. The full potentialities of the effect came to be realized soon and methods of applying it to actual structure determination were evolved almost simultaneously, but independently, by two groups of workers, namely, Ramachandran & Raman (1956) and Pepinsky and collaborators (Okaya, Saito & Pepinsky, 1955; Pepinsky & Okaya, 1956).

The approach of Ramachandran & Raman was basically from the Fourier-synthesis point of view, whereby the phase angle of a reflexion could be solved for, but for an inherent ambiguity, from the Bijvoet differences.* Of these two possibilities in the phase angle, the one which is closer to the heavy atom phase is taken to be the correct one and a Fourier synthesis, using these phases, would yield the structure. Pepinsky and co-workers have, however, approached the problem from the point of view of the

* We shall use the term *Bijvoet difference* to denote the difference in intensity between inverse reflexions; that is $I = I(\mathbf{H}) - I(\bar{\mathbf{H}})$. Here \mathbf{H} stands for the reflexion indices hkl and $\bar{\mathbf{H}}$ for $\bar{h}\bar{k}\bar{l}$.