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The Crystal Structure of Celsian (Barium Felspar)

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Celsian, $BaAl_2Si_2O_8$, is a felspar with a 14 Å *c*-axis and a body-centred lattice. The structure was determined by X-ray analysis, using Fourier difference maps and least-squares methods. The atomic parameters were obtained as the sum of *average parameters*, appropriate to a 7 Å structure and derived from the main (*a*-type) reflections, and *difference parameters*, with opposite signs in the two sub-cells, derived from the difference (*b*-type) reflections. The structure shows a good approximation to an ordered arrangement with alternating Si and Al atoms. The Ba atom occupies identical positions in the two sub-cells but has an anisotropic 'temperature' factor. Discussion of the structure includes comparison with anorthite ($CaAl_2Si_2O_8$) and with potash felspars, with regard both to the behaviour of the large cation and to the nature of the network, the 14 Å repeat being seen as a necessary consequence of the Si, Al alternation.

Introduction

The present study is one of a series of detailed structure analyses of felspar minerals initiated in the Cavendish Laboratory during the past ten years by Dr W. H. Taylor. The principal aim of this long-term investigation is the determination of the structural variations found amongst various key members of the felspar family. Some of the crystal structures examined prior to the present work include sanidine (Cole, Sörum & Kennard, 1949), microcline (Bailey & Taylor, 1955), high and low albite (Ferguson, Traill & Taylor, 1958), primitive anorthite (Radoslovich, 1955, and Kempster, 1957), body-centred anorthite (Sörum, 1953, and Chandrasekhar, 1957), and several others. The structure of celsian is of some interest in a study of this complex series of minerals since it possesses different symmetry from any of the others, and contains the heaviest cation normally found in felspars.

The earliest X-ray investigation of celsian (Taylor, Darbyshire & Strunz, 1934) established the structure as at least approximately isomorphous with that of orthoclase, $KAlSi_3O_8$. Subsequent research (Gay, 1956) revealed a group of extremely weak difference ('superlattice') reflections indicating a doubled unit cell in the *c*-direction with body-centred symmetry.

Material

The specimens of celsian selected for analysis were collected by E. R. Segnit (1946) at Broken Hill, New South Wales, Australia. The crystals were perfectly clear and untwinned, and commonly showed two excellent cleavages at 90°. The results of Segnit's research on the physical and optical properties and the probable chemical composition of this material are listed in Table 1. The chemical formula calculated with respect to O = 8 is

$$Ba_{0\cdot 84}K_{0\cdot 18}Al_{1\cdot 90}Si_{2\cdot 11}O_8\,.$$

This particular variety of celsian thus contains an appreciable substitution of K for Ba and Si for Al, so that the structure reported in this paper may differ to some extent from that of pure celsian.

Table 1. *Physical properties and approximate chemical composition of celsian from Broken Hill, N. S. W.* (Segnit, 1946)

(*a*) Chemical composition (wt.%)

SiO_2	35·1
Al_2O_3	26·8
BaO	35·8
K_2O	2·3
	100·0

(*b*) Crystal optics

$\alpha = 1\cdot 579$

$\beta = 1\cdot 583$

$\gamma = 1\cdot 588$

Sign negative

$2V = 88°$

$\beta = b$, γ: $a = 28°$ in obtuse interaxial angle

(*c*) Specific gravity

3·1 to 3·2

Lattice parameters

Lattice parameters were obtained from oscillation photographs taken about the three major axes with the film in the van Arkel mounting. Measurements of *d* values were made for a number of reflections in the region $\theta > 75°$, and the results were extrapolated graphically to $\theta = 90°$. The values obtained for the lattice parameters were:

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$$a = 8{\cdot}627 \pm 0{\cdot}002,\ b = 13{\cdot}045 \pm 0{\cdot}003,$$
$$c = 14{\cdot}408 \pm 0{\cdot}004\ \text{Å};\ \beta = 115^\circ\ 13' \pm 3'.$$

(Estimated limits of error are given, not standard deviations). The cell volume is 1467 Å^3 and the calculated density 3·26 g.cm.$^{-3}$.

Experimental X-ray work

Zero-layer Weissenberg photographs using Mo $K\alpha$ radiation were taken about the five zone axes [100], [010], [001], [110], and [111]. For classifying the observed reflections, the conventional notation for 14 Å felspars introduced by Laves & Goldsmith (1954) and Gay (1953) will be used, as follows:

'*a*' type, $h+k$ even, l even; '*b*' type, $h+k$ odd, l odd
'*c*' type, $h+k$ even, l odd; '*d*' type, $h+k$ odd, l even.

About 1400 reflections of '*a*' type were obtained, and about 90 reflections of '*b*' type, the latter being systematically absent from the [010] zone. Intensities were measured visually by comparison with a calibrated scale. Absorption corrections were applied to those in the photographs about [110] and [111], for which the crystal cross-sections were markedly elongated.

Symmetry

The X-ray diffraction patterns of celsian are similar to those of 'body-centred anorthite'. The strong reflections are those of '*a*' type; absence of '*c*' and '*d*' type reflections confirm the body-centring, while '*b*' type reflections are systematically weak. Further, $h0l$ reflections are absent for h odd and l odd. This leads at once to the deduction of the space group as either Ic (No. 9, $\{Cc\}$) or $I2/c$ (No. 15, $\{C2/c\}$). The unconventional naming of the space group causes much less inconvenience than would result from a change of axial directions; the present choice is that used for the whole felspar series, according to which the space groups of orthoclase, albite, and body-centred anorthite are $C2/m$, $C\bar{1}$ and $I\bar{1}$ respectively.

There is no evidence to suggest that celsian lacks a centre of symmetry; hence the space group $I2/c$ has been adopted.

Since there are 8 formula units per cell, and the general position is eightfold, all atoms can lie in general positions. Whether atoms of type O_{A1}, which lie on the diad axis in sanidine, remain in this special position in celsian is considered below. With this possible exception it is necessary to determine three independent parameters for each atom in the formula unit, i.e. 39 parameters in all.

In changing from the sanidine structure with space group $C2/m$ to the celsian structure with space group $I2/c$, half the centres of symmetry have been destroyed. The question now arises, which half? Thus, if the same origin is retained as in sanidine, either (0, 0, 0) or (0, 0, ¼) will be a centre of symmetry in celsian, but not both; and the two choices are structurally different. The coordinates of equivalent general positions in the two cases are set out in Table 2, in the usual felspar notation (Megaw, 1956). Atomic sites whose symbols differ only by i in the third place, or by m and z in the first two places, are exactly equivalent because of the body-centring and c-glide symmetry operations. It can be seen that the atom O_{A1}, which in sanidine has coordinates $(0, y, 0)$, is in a general position in the first case but in a special position on the diad axis in the second case, since sites (0000) and (m00c), related by a diad axis through the origin, are occupied by atoms with different subscripts in the first case, with the same subscript in the second case.

Table 2. *Possible equivalent points in celsian*

Symbol of site	$I2/c$	
	Centre at (0, 0, 0)	Centre at (0, 0, ¼)
0000	x_1, y_1, z_1	x_1, y_1, z_1
000*c*	$\bar{x}_1, \bar{y}_1, \bar{z}_1$	$\bar{x}_2, \bar{y}_2, \bar{z}_2$
00*i*0	$\frac{1}{2}+x_1, \frac{1}{2}+y_1, \frac{1}{2}+z_1$	$\frac{1}{2}+x_1, \frac{1}{2}+y_1, \frac{1}{2}+z_1$
00*ic*	$\frac{1}{2}-x_1, \frac{1}{2}-y_1, \frac{1}{2}-z_1$	$\frac{1}{2}-x_2, \frac{1}{2}-y_2, \frac{1}{2}-z_2$
0*z*00	$x_2, y_2, \frac{1}{2}+z_2$	$x_2, y_2, \frac{1}{2}+z_2$
0*z*0*c*	$\bar{x}_2, \bar{y}_2, \frac{1}{2}-z_2$	$\bar{x}_1, \bar{y}_1, \frac{1}{2}-z_1$
0*zi*0	$\frac{1}{2}+x_2, \frac{1}{2}+y_2, z_2$	$\frac{1}{2}+x_2, \frac{1}{2}+y_2, z_2$
0*zic*	$\frac{1}{2}-x_2, \frac{1}{2}-y_2, \bar{z}_2$	$\frac{1}{2}-x_1, \frac{1}{2}-y_1, \bar{z}_1$
*m*000	$x_2, \bar{y}_2, z_2$	$x_2, \bar{y}_2, z_2$
*m*00*c*	$\bar{x}_2, y_2, \bar{z}_2$	$\bar{x}_1, y_1, \bar{z}_1$
*m*0*i*0	$\frac{1}{2}+x_2, \frac{1}{2}-y_2, \frac{1}{2}+z_2$	$\frac{1}{2}+x_2, \frac{1}{2}-y_2, \frac{1}{2}+z_2$
*m*0*ic*	$\frac{1}{2}-x_2, \frac{1}{2}+y_2, \frac{1}{2}-z_2$	$\frac{1}{2}-x_1, \frac{1}{2}+y_1, \frac{1}{2}-z_1$
*mz*00	$x_1, \bar{y}_1, \frac{1}{2}+z_1$	$x_1, \bar{y}_1, \frac{1}{2}+z_1$
*mz*0*c*	$\bar{x}_1, y_1, \frac{1}{2}-z_1$	$\bar{x}_2, y_2, \frac{1}{2}-z_2$
*mzi*0	$\frac{1}{2}+x_1, \frac{1}{2}-y_1, z_1$	$\frac{1}{2}+x_1, \frac{1}{2}-y_1, z_1$
mzic	$\frac{1}{2}-x_1, \frac{1}{2}+y_1, \bar{z}_1$	$\frac{1}{2}-x_2, \frac{1}{2}+y_2, \bar{z}_2$

Both sets of coordinates in the space group $I2/c$ were used for trial structures; it will be shown below that only the first led to satisfactory agreement with experiment. The non-centrosymmetric space group Ic was not examined.

Outline of procedure

It is assumed that the structure of celsian is closely similar to that of orthoclase or sanidine, but that the two sub-cells (halves of the unit cell) in celsian may differ in two ways, each with a possible effect on its diffraction: (i) in the different distribution of Si and Al among the B sites, (ii) in the detailed coordinates of all the atoms—which can conveniently be described as opposite displacements from a mean position, of a kind consistent with the symmetry. Of these, (i) is necessarily accompanied by (ii), but it cannot be assumed *a priori* that the contribution of the atomic displacements to the intensities will be large compared with that of the differences of atomic scattering factor; on the other hand, it must be emphasised that (ii) can occur independently of (i). It can be shown for celsian that the difference of atomic scattering factor between Si and Al is insufficient to account for the magnitude of the observed intensities; hence we must look for differences in coordinates, leaving completely open for the present the question whether they arise as a consequence of differences in (Si, Al) distribution. In what follows, both Si and Al atoms will be referred to as B atoms until it becomes necessary (and possible) to distinguish between them; an average scattering factor between those of Si and Al is used throughout.

The contributions of the sub-cells to *a*-type reflections are in phase, giving strong reflections; to the *b*-type reflections they are exactly out of phase, giving difference reflections. A synthesis using only *a*-type reflections treats the sub-cells as if they were identical, and thus gives an electron-density map in which they are superposed. In principle, all peaks in this are doubled; in practice, the splitting may be too small to be easily detected, if the sub-cells are very nearly identical. This is the case for celsian; the difference reflections are an order of magnitude weaker than the corresponding reflections in primitive anorthite, and very weak indeed compared with the *a*-type reflections. The following procedure was therefore adopted.

(i) A set of average coordinates was obtained by using the *a*-type reflections to construct two-dimensional difference syntheses for the five projections.
(ii) The *b*-type reflections were considered independently to obtain a set of difference parameters between nearly equivalent atoms.
(iii) The average coordinates and the difference parameters were combined in the final step to give the refined structure.

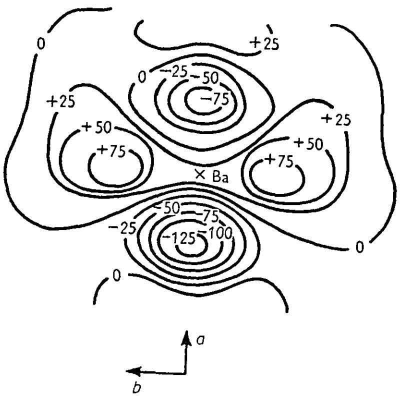
Scattering factors

Thomas–Fermi scattering factor curves were used for barium and potassium, and those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for the lighter atoms. Weighted mean values were calculated in accordance with the chemical composition so that no distinction was made between either Ba and K or Si and Al.

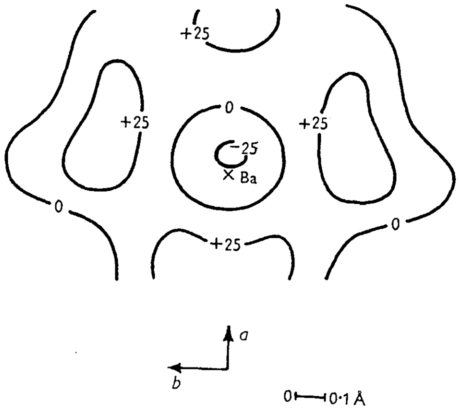
Determination of average structure

For the first trial structure, the coordinates of sanidinised orthoclase (Cole, Sörum & Kennard, 1949) were used. Since these gave initial agreement factors of 0·25 or less for the *a*-type reflections, there was little difficulty in determining the signs of these reflections. The initial temperature factors were taken as 1·0, 0·4 and 1·5 Å^2 for Ba, Si and O respectively, these values being suggested as plausible by other felspar work in progress in the laboratory.

The atomic coordinates were refined by means of $F_o - F_c$ syntheses on all five projections. Though improved agreement between F_o and F_c was obtained, it quickly became obvious that alterations in temperature factors would also be necessary if the structure were to be refined to the limit of reliability of the experimental data. In particular, the barium atom appeared ellipsoidal, requiring anisotropic temperature factor corrections; these were calculated on a digital computer using Cochran's (1954) distorted-reciprocal-lattice method. Fig. 1 illustrates the appearance of the barium atom in difference maps before and after the application of the anisotropic temperature factor. For the other atoms, isotropic temperature factors were adequate, but their values were modified slightly, adjustments being made empirically from inspection of the $F_o - F_c$ synthesis after each cycle of refinement.



(*a*) Initial



(*b*) Final

Fig. 1. Portions of the [001] difference synthesis, illustrating the appearance of the barium atom, (*a*) initial, (*b*) final. Contour heights marked are in units of 10^{-2} e.Å^{-2}.

After reasonably correct temperature factors had been obtained the atomic coordinates were again adjusted. Each projection was treated independently during the final stages of refinement. Altogether at least five cycles of refinement were performed on each projection.

Table 3. *Final status of the five projections*

Zone axis	Zone condition	*Number of reflections	*Reliability index R
[100]	$h=0$	173	0·052
[010]	$k=0$	210	0·082
[001]	$l=0$	242	0·054
[110]	$h+k=0$	570	0·071
[111]	$h+k+l=0$	244	0·078

* Unobservable reflections and all b-type reflections have been excluded.

The final R-factors are given in Table 3, along with the number of reflections included in each zone. The weighted mean of the R-factors is 0·069, a figure comparable to the internal consistency of the experimental data. The overall agreement factor between observed structure amplitudes common to two or more projections is 0·065. A list of the observed and final calculated structure factors is filed in the Cavendish Laboratory.

The temperature factors for the five projections were combined by the method of least-squares. In view of the fact that the F_o's from which they have been determined (those of a-type reflections) can give information only about the *average* of the two sub-cells, one must ask whether these temperature factors have a real meaning. Only if it can be shown that the position of any atom is identical in the two sub-cells, within limits which are considerably less than the r.m.s. amplitude of the thermal vibration, shall we be able to say that the temperature factor derived from the average projection is real and not an artefact. For the barium atom such a claim can be made, as shown below, but not for the others; refinement of the structure after inclusion of the difference parameters might have given an answer, but it is doubtful if the accuracy of the data would have justified such an attempt. From the average projection, the B values found for silicon/aluminium and oxygen were 0·6 and 1·2 Å^2 respectively; these correspond to r.m.s. displacements of 0·09 and 0·12 Å, which are of the order of magnitude of the difference parameters. The results for the barium atom are given in Table 4.

Table 4. *Thermal vibration parameters of* Ba *atom*

Temperature factors (Å^2)	r.m.s. displacement (Å)
$B_X = 0·5$	0·08
$B_Y = 1·0$	0·11
$B_Z = 1·2$	0·12

$Y=b$; X: $a=16°$ in obtuse interaxial angle β.

Standard deviations estimated from combination of five difference projections: 0·12 Å^2 in magnitude and 5° in orientation.

Table 5. *Final average coordinates (in fractions of cell edges)*

Atom	x	y	z
Ba	0·28261	0	0·06526
Si_1	0·0082	0·1830	0·1118
Si_2	0·7031	0·1185	0·1734
O_{A1}	0	0·1382	0
O_{A2}	0·6238	0	0·1429
O_B	0·8272	0·1378	0·1122
O_C	0·0262	0·3101	0·1277
O_D	0·1865	0·1265	0·1983

The mean average coordinates for celsian are given in Table 5. The accuracy of these coordinates was determined from the final difference syntheses using Cochran's method (Cochran, 1951; Lipson & Cochran, 1953, p. 308). The experimental data used were the slopes $\partial D/\partial x$ of the difference map averaged over the whole area of the unit cell, and the curvatures at the peaks, C_n, estimated from the F_o map for the average structure. The resulting standard deviations are given in Table 6.

Table 6. *Standard deviations in atomic positions*

$\sigma(r)$ is in Å.; $\sigma(z)$ is defined as $\sigma(r)/c$, and $\frac{1}{2}\sigma(x) \simeq \sigma(y) \simeq \sigma(z)$

	Average parameters		Difference parameters		Final positions
	$\sigma(z)$	$\sigma(r)$	$\sigma(z)$	$\sigma(r)$	$\sigma(r)$
Ba	0·00007	0·001	(< 0·0001)	—	0·001
(Si, Al)	0·00030	0·004	0·00015	0·0021	0·005
O	0·00070	0·010	0·00040	0·0056	0·011

Table 7. *Silicon–oxygen distances calculated from the average coordinates*

B_1–O_{A1}	1·687 Å	B_2–O_{A2}	1·671 Å
–O_B	1·671	–O_B	1·672
–O_C	1·671	–O_C	1·665
–O_D	1·681	–O_D	1·684
Mean	1·678 ± 0·004	Mean	1·673 ± 0·004

Table 7 lists the B–O bond lengths calculated using the average coordinates. Each of these interatomic distances represents an average over two independent B_1 or B_2 tetrahedra; the fact that their means for B_1 and B_2 do not differ significantly indicates that the Al atoms are divided nearly equally between the atomic sites B_1 and B_2.

Difference structure

The difference parameters, i.e. the small but important structural variations indicating a true unit cell larger than the prototype, are obtained through consideration of the b-type reflections occurring in the [100] and [111] zones. Essentially this is accomplished as follows. Suppose that x_1 and x_2 are the atomic coordinates of two nearly equivalent atoms, such that x_1 is approximately equal to x_2, but not quite. The structure factor $F(h)$ will of course be some trigonometric function of x_1 and x_2. It is then possible to replace the variables x_1 and x_2 by two others, x and δx, defined by the relations

$$x=(x_1+x_2)/2 \quad \text{and} \quad \delta x=(x_1-x_2)/2 \ ,$$

and rewrite the structure factor as a function of these new variables. The resulting expression can be rearranged to separate the angular arguments involving the average coordinate x from those containing the difference parameter δx. In the case of celsian, we wish to obtain values for the difference parameters in terms of the known average coordinates and observed structure factor amplitudes. The calculation is greatly facilitated if it can be assumed that δx is suffficiently small to justify the approximations

$$\sin 2\pi h\delta x=2\pi h\delta x \quad \text{and} \quad \cos 2\pi h\delta x=1 \ .$$

The structure factor formulae for the b-type difference reflections can then be written as linear functions of the difference parameters, with numerical coefficients depending on the average coordinates. The a-type reflections, on the other hand, are very nearly independent of the difference parameters since they involve only second order terms in δx.* Thus in so far as the above approximation is valid, the a-type reflections depend only on the average coordinates while the amplitudes of the b-type reflections are linearly proportional to the difference parameters. There are at least three reasons to suppose the approximation to hold good: (1) the extreme faintness of the b-reflections predicts very small departures from the prototype structure, (2) it was possible to obtain a highly consistent set of average coordinates from five different projections, in good agreement with experiment and without regard to the b-reflections, and (3) none of the final difference parameters calculated by the use of the approximation turned out to be greater than 0·05 Å.

The appropriate structure factor formulae were first derived for the $I2/c$ structure with symmetry centre at (0, 0, 0). This was the easiest case to consider initially since the b-type structure factors are real with phase angles of either 0 or π. The b-type structure factors took the form

$$F(hkl)=\sum_i f_i C(hkl,\, x_i y_i z_i)[h\delta x_i+k\delta y_i+l\delta z_i] \ ,$$

where the summation is carried out over all the atoms in the asymmetric unit of the prototype structure. Obviously the contribution of any one of these is large only if $C(hkl,\, x_i y_i z_i)$ *and* at least one difference parameter is relatively large. Hence by listing the coefficients $C(hkl,\, x_i y_i z_i)$ for a large number of b-type reciprocal lattice points hkl (in practice, 200 points in the [100] and [111] zones) and comparing them with $F_o(hkl)$, it is possible by systematic trial and error to find out which of the parameters δx_i, δy_i and δz_i are significant and to estimate their magnitude.

An arbitrary choice of sign must be made for the first difference parameter to be determined; this is equivalent to choosing the origin on one or other of the two sub-cells, which makes no difference to the structure. The choice actually made was that allowing easiest comparison of the structure with that of primitive anorthite; this will be explained more fully later.

The atoms Ba, O_{A1} and O_{A2}, which we may call 'special atoms' because they are in special positions in the ideal 7 Å structure, need separate comment. In the 14 Å structure, atoms Ba, O_{A2}, which were on a mirror plane, are now on or near a glide plane, so that a pair of atoms whose (small) y parameters are equal in magnitude but opposite in sign have z parameters differing by exactly $\frac{1}{2}$ and equal x parameters; hence the y parameter is itself the y difference parameter, and the x and y difference parameters are zero. Similarly, atoms O_{A1}, which were on a rotation diad, are now, since the centre of symmetry is at (0, 0, 0), on or near a screw diad, and have therefore y parameters differing by exactly $\frac{1}{2}$; hence the x and z parameters are difference parameters, and the y difference parameter is zero. If the centre of symmetry had been at (0, 0, $\frac{1}{4}$) there would have been two independent O_{A1} atoms in special positions on a rotation diad; then the x and z difference parameters would have been zero, and the y difference parameter non-zero.

Contributions to the intensities from the barium atom were first examined, because the large value of f_{Ba} would make these predominant if the difference parameter y_{Ba} were appreciable. No correlation between calculated and observed intensities was found, even at high values of the reciprocal radius where the predominance of barium would be particularly marked. Hence the y-parameter of Ba is small.

Next the B (i.e. (Si, Al)) contributions were considered. It was assumed that for the outer reflections the O contributions would be small. In the $0kl$ zone the observed b-reflections in this region could be explained satisfactorily by assuming that δz of B_1 and δy of B_2 contributed fairly appreciably, and were approximately equal in magnitude and opposite in sign. The remaining parameters, δy of B_1 and δz of B_2, were still taken as zero because no correlation with observed intensities could be found at this stage.

The inner reflections of the $0kl$ zone were next considered. Here the contributions from oxygen are appreciable, and can be used to estimate the oxygen difference parameters now that the B difference parameters are known. In this region, accidentally absent b-reflections were often as useful and informative as their more intense neighbours. The parameters determined in this way served to determine the signs of the great majority of b-reflections in the $0kl$ zone.

Forty of the non-zero F_o's were then used in a linear least-squares analysis to obtain the most probable

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* Using the difference parameters derived later, it can be estimated that their neglect would alter a-type intensities by at most about 4% if they all cooperated in direction.

values of δy and δz for each atom. The 'special' atoms were included in this analysis; for Ba and O_{A2}, the difference parameters have components (0, y, 0), while for O_{A1} they are (x, 0, z). In the [100] projection there are therefore 13 parameters in all to be determined. The first cycle showed that the difference parameters of the three 'special' atoms were small, and they were thereafter taken as zero. The structure factors calculated from the remaining parameters gave quite good agreement with the observed.

Table 8. *Final difference parameters (in fractions of cell edges)*

Atom	δx	δy	δz
Ba	—	0·0000	—
B_1	+0·0009	−0·0002	−0·0024
B_2	+0·0027	+0·0020	−0·0001
O_{A1}	−0·0004	—	+0·0003
O_{A2}	—	+0·0001	—
O_B	+0·0051	+0·0010	−0·0011
O_C	−0·0038	−0·0029	−0·0044
O_D	−0·0039	+0·0033	−0·0036

Table 9. *Observed and calculated structure factors for 'b'-reflections*

(*a*) [100] zone

h,k,l	F_o	F_c
0,1,1	<0·2	−0·1
0,1,3	2·3	1·8
0,1,5	1·8	1·2
0,1,7	1·3	−0·6
0,1,9	3·1	−3·1
0,1,11	<1·0	0·4
0,1.13	3·2	3·5
0,1,15	<1·2	−0·7
0,1,17	1·8	−1·7
0,3,1	2·0	−1·5
0,3,3	0·6	−0·1
0,3,5	<0·8	−0·7
0,3,7	<0·9	0·9
0,3,9	1·1	0·8
0,3,11	<1·0	−1·0
0,3,13	<1·1	−0·2
0,3,15	<1·2	−0·1
0,3,17	<1·3	0·8
0,5,1	0·8	−0·8
0,5,3	<0·7	0·0
0,5,5	0·8	−0·1
0,5,7	0·9	−1·4
0,5,9	2·5	2·5
0,5,11	<1·0	0·4
0,5,13	2·8	−2·7
0,5,15	<1·3	0·6
0,5,17	<1·3	0·8
0 7,1	1·3	1·2
0,7,3	<0·8	−0·2
0,7,5	1·9	1·7
0,7,7	1·4	−0·5
0,7,9	2·9	−2·9
0,7,11	<1·0	0·9
0,7,13	2·5	2·0
0,7,15	<1·2	0·2
0,7,17	2·1	−2·0
0,7,19	1·5	−0·3
0,9,1	2·4	2·1
0,9,3	0·9	−0·9
0,9,5	2·1	−2·4
0,9,7	2·6	2·8
0,9,9	<1·0	0·4
0,9,11	<1·1	−1·1
0,9,13	<1·2	−0·2
0,9,15	<1·2	−0·8
0,9,17	1·5	1·5
0,11,1	1·3	−1·1
0,11,3	0·9	1·0
0,11,5	<1·0	0·0
0,11,7	1·1	−1·0
0,11,9	0·9	0·7
0,11,11	<1·1	−0·1
0,11,13	<1·2	0·2
0,11,15	<1·3	−0·4
0,11,17	<1·4	0·1
0,13,1	2·6	−2·6
0,13,3	<1·2	0·1
0,13,5	2·5	2·5
0,13,7	2·0	−1·8
0,13,9	<1·2	−0·2
0,13,11	<1·2	0·3
0,13,13	<1·3	−0·2
0,13,15	<1·4	1·3
0,13,17	<1·5	−1·1
0,15,1	1·9	1·6
0,15,3	<1·1	−0·3
0,15,5	1·3	−1·1
0,15,7	<1·2	0·5
0,15,9	1·0	0·8
0,15,11	<1·3	0·5
0,15,13	<1·5	−1·7
0,15,17	<1·6	−0·2
0,17,1	1·8	1·6
0,17,3	<1·3	−0·2
0,17,5	<1·3	−0·8
0,17,7	1·3	1·5
0,17,9	1·5	−1·7
0,17,11	<1·4	−0·4
0,17,15	2·4	2·0

(*b*) [111] zone

h,k,l	F_o	F_c
0,1,$\bar{1}$	<0·3	0·1
0,3,$\bar{3}$	<0·4	0·1
0,5,$\bar{5}$	<0·6	0·1
0,7,$\bar{7}$	<0·8	0·5
0,9,$\bar{9}$	<0·9	−0·4
0,11,$\overline{11}$	<1·0	0·1
0,13,$\overline{13}$	<1·1	0·2
0,15,$\overline{15}$	<1·2	0·2
$\bar{1}$,10,$\bar{9}$	<0·9	−0·3
$\bar{1}$,8,$\bar{7}$	1·6	1·6
$\bar{1}$,6,$\bar{5}$	<0·7	−1·4
$\bar{1}$,4,$\bar{3}$	<0·5	−0·4
$\bar{1}$,2,$\bar{1}$	1·6	−1·7
$\bar{1}$,0,1	<0·3	0·0
$\bar{1}$,$\bar{2}$,3	1·5	−1·5
$\bar{1}$,$\bar{4}$,5	<0·5	0·1
$\bar{1}$,$\bar{6}$,7	1·2	−1·3
$\bar{1}$,$\bar{8}$,9	1·6	1·1
$\bar{1}$,$\overline{10}$,11	<0·9	0·1
$\bar{1}$,$\overline{12}$.13	<1·1	−0·5
$\bar{1}$,$\overline{14}$,15	<1·3	0·5
$\bar{2}$,11,$\bar{9}$	<1·0	0·0
$\bar{2}$,9,$\bar{7}$	<0·9	0·4
$\bar{2}$,7,$\bar{5}$	2·1	−2·2
$\bar{2}$,5,$\bar{3}$	0·7	−0·3
$\bar{2}$,3,$\bar{1}$	<0·5	−0·4
$\bar{2}$,1,1	0·5	0·4
$\bar{2}$,$\bar{1}$,3	1·0	−1·0
$\bar{2}$,$\bar{3}$,5	<0·5	−0·1
$\bar{2}$,$\bar{5}$,7	1·5	−1·7
$\bar{2}$,$\bar{7}$,9	1·8	2·0
$\bar{2}$,$\bar{9}$,11	<0·9	0·4
$\bar{2}$,$\overline{11}$,13	<1·1	−0·1
$\bar{2}$,$\overline{13}$,15	<1·2	0·2
$\bar{3}$,12,$\bar{9}$	<1·1	0·1
$\bar{3}$,10,$\bar{7}$	<0·9	0·7
$\bar{3}$,8,$\bar{5}$	0·8	0·8
$\bar{3}$,6,$\bar{3}$	<0·7	−0·2
$\bar{3}$,4,$\bar{1}$	<0·6	0·1
$\bar{3}$,2,$\bar{1}$	<0·5	−1·0
$\bar{3}$,0,3	<0·5	0·0
$\bar{3}$,$\bar{2}$,5	<0·5	0·2
$\bar{3}$,$\bar{4}$,7	0·7	0·5
$\bar{3}$,$\bar{6}$,9	1·6	1·9
$\bar{3}$,$\bar{8}$,11	<0·9	1·0
$\bar{3}$,$\overline{10}$,13	1·5	1·4
$\bar{4}$,13,$\bar{9}$	1·6	1·9
$\bar{4}$,11,$\bar{7}$	<1·1	0·7
$\bar{4}$,9,$\bar{5}$	1·4	1·5
$\bar{4}$,7,$\bar{3}$	2·0	−1·8
$\bar{4}$,5,$\bar{1}$	<0·8	−1·4
$\bar{4}$,3,1	0·6	−0·4
$\bar{4}$ 1,3	<0·6	−0·5
$\bar{4}$,$\bar{1}$,5	1·2	−1·3
$\bar{4}$,$\bar{3}$,7	1·7	−1·9
$\bar{4}$,$\bar{5}$,9	2·2	−2·1
$\bar{4}$,$\bar{7}$,11	<0·9	−0·1
$\bar{4}$,$\bar{9}$,13	1·9	2·3
$\bar{4}$,$\overline{11}$,15	<1·3	0·5
$\bar{5}$,12,$\bar{7}$	<1·2	−0·6
$\bar{5}$,10,$\bar{5}$	<1·0	0·6
$\bar{5}$,8,$\bar{3}$	<0·9	−0·1
$\bar{5}$,6,$\bar{1}$	<0·8	−0·8
$\bar{5}$,4,1	1·5	1·6
$\bar{5}$,2,3	1·9	1·7
$\bar{5}$,0,5	<0·7	0·0
$\bar{5}$,$\bar{2}$,7	1·0	−1·4
$\bar{5}$,$\bar{4}$,9	1·6	−1·7
$\bar{5}$,$\bar{6}$,11	<0·9	1·0
$\bar{5}$,$\bar{8}$,13	<1·0	0·6
$\bar{5}$,$\overline{10}$,15	1·5	1·1
$\bar{6}$,11,$\bar{5}$	<1·1	−0·5
$\bar{6}$,9,$\bar{3}$	1·4	1·9
$\bar{6}$,7,$\bar{1}$	<0·9	−1·3
$\bar{6}$,5,$\bar{1}$	0·8	0·8
$\bar{6}$,3,3	<0·8	−0·3
$\bar{6}$,1,5	2·5	2·8
$\bar{6}$,$\bar{1}$,7	1·6	1·2
$\bar{6}$,$\bar{3}$,9	<0·8	−0·9
$\bar{6}$,$\bar{5}$,11	<0·9	−1·2
$\bar{6}$,$\bar{7}$,13	2·9	−2·8
$\bar{6}$,$\bar{9}$,15	<1·1	0·6
$\bar{7}$,12,$\bar{5}$	<1·2	−0·9
$\bar{7}$,10,$\bar{3}$	<1·1	0·5
$\bar{7}$,8,$\bar{1}$	1·0	−1·1
$\bar{7}$,6,1	<0·9	−1·4
$\bar{7}$,4,3	<0·8	−0·2
$\bar{7}$,2,5	<0·8	−0·4
$\bar{7}$,0,7	<0·8	0·0
$\bar{7}$,$\bar{2}$,9	<0·8	0·6
$\bar{7}$,$\bar{4}$,11	<0·8	−0·4
$\bar{7}$,$\bar{6}$,13	<1·0	0·7
$\bar{8}$,11,$\bar{3}$	<1·2	0·2
$\bar{8}$,9,$\bar{1}$	<1·1	0·9
$\bar{8}$,7,1	1·4	−1·6
$\bar{8}$,5,3	<0·9	0·4
$\bar{8}$,3,5	1·8	−1·4
$\bar{8}$,1,7	<0·9	0·7
$\bar{8}$,$\bar{1}$,9	2·1	2·0
$\bar{8}$,$\bar{3}$,11	<0·9	−0·9
$\bar{8}$,$\bar{5}$,13	<1·0	0·8
$\bar{8}$,$\bar{7}$,15	1·5	−2·5
$\bar{9}$,10,$\bar{1}$	1·6	1·5
$\bar{9}$,8,1	<1·1	−0·7
$\bar{9}$,6,3	<1·0	0·1
$\bar{9}$,4,5	<1·0	−1·0
$\bar{9}$,2,7	<0·9	0·4
$\bar{9}$,0,9	<0·9	0·0
$\bar{9}$,$\bar{2}$,11	<1·0	−0·6
$\bar{9}$,$\bar{4}$,13	<1·1	0·6
$\bar{9}$,$\bar{6}$,15	1·1	−0·7
$\overline{10}$,9,1	<1·2	0·1
$\overline{10}$,7,3	<1·1	−0·7
$\overline{10}$,5,5	<1·1	−1·0
$\overline{10}$,3,7	<1·1	−0·2
$\overline{10}$,1,9	<1·1	−0·2
$\overline{10}$,$\bar{1}$,11	2·6	2·4
$\overline{10}$,$\bar{3}$,13	1·5	1·0
$\overline{10}$,$\bar{5}$,15	1·6	1·9
$\overline{11}$,8,3	<1·2	−0·4
$\overline{11}$,6,5	<1·1	0·2
$\overline{11}$,4,7	<1·1	−0·6
$\overline{11}$,2,9	2·6	−2·3
$\overline{11}$,0,11	<1·1	0·0
$\overline{11}$,$\bar{2}$,13	2·8	−2·5
$\overline{11}$,$\bar{4}$,15	<1·2	1·2
$\overline{12}$,9,3	<1·3	0·1
$\overline{12}$,7,5	<1·2	−0·5
$\overline{12}$,5,7	<1·2	0·4
$\overline{12}$,3,9	<1·2	−1·0
$\overline{12}$,1,11	<1·2	0·3
$\overline{12}$,$\bar{1}$,13	1·7	−1·2
$\overline{13}$,6,7	1·5	1·6

The *b*-reflections in the [111] zone were treated in much the same way as those in [100]. Here the intensities are functions of all three difference parameters (δx, δy, and δz); since approximate values of δy and δz were known, they could be substituted in the linear equations for the structure factors, and δx chosen so as to reduce the discrepancy between F_o and F_c as much as possible. The signs of a good proportion of the reflections were thus established. Forty of the strongest *b*-reflections of this zone were then used in another least-squares calculation to give improved values of the parameters. Here again the three 'special' atoms were at first included, making 19 parameters in all to be determined; but again their difference parameters were small at the end of the first cycle, and were thereafter taken as zero.

Finally, two more combined least-squares cycles were carried out using forty reflections from each zone (15 remaining parameters).

The final difference parameters are listed in Table 8. For the 'special' atoms the difference parameters found in the first cycle have been included in order to avoid possible confusion, though they are less than the standard deviations shown in Table 6. These were estimated, for B and O, from the residuals of the least-squares calculation. For Ba, this method is not applicable, but it is sufficient to note that the observed value of y was less than 0·0001, or 0·0013 Å. This justifies the conclusion of the last section that the anisotropy of the barium atom observed in the average projection represents a true 'temperature' factor and not an artefact of the averaging process. (In calling it a temperature factor, however, according to conventional usage, we are not attempting to decide whether the spread of electron density described by it is in fact due to temperature-dependent atomic vibrations or to some other cause.)

Table 9 gives the observed and calculated structure factors for all *b*-reflections within the region of reciprocal space where their magnitude was appreciable. The R-factors are 0·16 and 0·17 for non-zero reflections in [100] and [111] respectively. Perhaps even more convincing evidence for the correctness of these parameters is the fact that all but a very few of the F_c's for accidentally absent reflections were below the limit of observability.

Table 10. *Final atomic coordinates (in fractions of cell edges)*

Atom	x	y	z
Ba(0000)	0·2826	0·0000	0·0653
$B_1(0000)$	0·0091	0·1828	0·1096
$B_1(0z00)$	0·0073	0·1832	0·6142
$B_2(0000)$	0·7058	0·1205	0·1733
$B_2(0z00)$	0·7004	0·1165	0·6735
$O_{A1}(0000)$	0·9996	0·1382	0·0003
$O_{A2}(0000)$	0·6238	0·0001	0·1429
$O_B(0000)$	0·8323	0·1388	0·1111
$O_B(0z00)$	0·8221	0·1368	0·6133
$O_C(0000)$	0·0224	0·3072	0·1233
$O_C(0z00)$	0·0300	0·3130	0·6321
$O_D(0000)$	0·1826	0·1298	0·1947
$O_D(0z00)$	0·1904	0·1232	0·7019

(Symmetry-related atoms are at $\pm(x, y, z)$; $\pm(x, \bar{y}, \frac{1}{2}+z)$: $\pm(\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z)$; $\pm(\frac{1}{2}+x, \frac{1}{2}-y, z)$).

Table 11. *Final interatomic distances (in Å) and angles (in degrees)*

(*a*) (Silicon, aluminium)–oxygen distances: $\sigma(d) = 0·012$

	$B_1(0000)$		$B_1(0z00)$
$O_{A1}(0000)$	1·651	$O_{A1}(mz0c)$	1·722
$O_B(0000)$	1·640	$O_B(0z00)$	1·703
$O_C(0000)$	1·633	$O_C(0z00)$	1·711
$O_D(0000)$	1·630	$O_D(0z00)$	1·733
Mean	1·639	Mean	1·717
	±0·004		±0·004

	$B_2(0000)$		$B_2(0z00)$
$O_{A2}(0000)$	1·702	$O_{A2}(mz00)$	1·640
$O_B(0000)$	1·698	$O_B(0z00)$	1·645
$O_C(mzi0)$	1·714	$O_C(m0i0)$	1·617
$O_D(mz0c)$	1·733	$O_D(m00c)$	1·637
Mean	1·712	Mean	1·635
	±0·006		±0·006

(*b*) Barium–oxygen distances: $\sigma(d) = 0·011$

	Ba(0000)		Ba(0000)
$O_{A1}(0000)$	2·850	$O_B(m00c)$	2·939
$O_{A1}(000c)$	2·850	$O_C(0zi0)$	3·112
$O_{A2}(0000)$	2·667	$O_C(mzi0)$	3·135
$O_{A2}(000c)$	3·421	$O_D(0000)$	2·909
$O_B(000c)$	2·927	$O_D(m000)$	2·902

(*e*) Oxygen–oxygen distances in tetrahedra: $\sigma(d) = 0·015$

	$B_1(0)$	$B_1(z)$	$B_2(0)$	$B_2(z)$
O_A–O_B	2·575	2·674	2·725	2·630
O_A–O_C	2·786	2·911	2·638	2·554
O_A–O_D	2·568	2·669	2·794	2·665
O_B–O_C	2·702	2·856	2·842	2·727
O_B–O_D	2·737	2·880	2·858	2·718
O_C–O_D	2·666	2·805	2·888	2·705
Mean	2·672	2·799	2·791	2·667

(*d*) Oxygen–silicon–oxygen bond angles: $\sigma(\psi) = 0·6°$

O_{A1}–$B_1(0)$–O_B	103·0	O_{A1}–$B_1(z)$–O_B	102·6
O_{A1}–$B_1(0)$–O_C	116·2	O_{A1}–$B_1(z)$–O_C	115·9
O_{A1}–$B_1(0)$–O_D	103·0	O_{A1}–$B_1(z)$–O_D	101·1
O_B–$B_1(0)$–O_C	111·3	O_B–$B_1(z)$–O_C	113·6
O_B–$B_1(0)$–O_D	113·7	O_B–$B_1(z)$–O_D	113·8
O_C–$B_1(0)$–O_D	109·6	O_C–$B_1(z)$–O_D	109·0
Mean	109·5	Mean	109·3
O_{A2}–$B_2(0)$–O_B	106·5	O_{A2}–$B_2(z)$–O_B	106·4
O_{A2}–$B_2(0)$–O_C	101·1	O_{A2}–$B_2(z)$–O_C	103·3
O_{A2}–$B_2(0)$–O_D	108·9	O_{A2}–$B_2(z)$–O_D	108·9
O_B–$B_2(0)$–O_C	112·8	O_B–$B_2(z)$–O_C	113·5
O_B–$B_2(0)$–O_D	112·8	O_B–$B_2(z)$–O_D	111·8
O_C–$B_2(0)$–O_D	113·8	O_C–$B_2(z)$–O_D	112·4
Mean	109·3	Mean	109·4

(*e*) Silicon–oxygen–silicon bond angles: $\sigma(\psi) = 0·8°$

B_1–O_{A1}–B_1	139·4	B_1–$O_C(0)$–B_2	127·0
B_2–O_{A2}–B_2	135·2	B_1–$O_C(z)$–B_2	130·2
B_1–$O_B(0)$–B_2	150·2	B_1–$O_D(0)$–B_2	139·4
B_1–$O_B(z)$–B_2	149·6	B_1–$O_D(z)$–B_2	138·1

The difference parameters of Table 8 were combined with the average coordinates of Table 5 to give the final atomic coordinates in Table 10; the standard deviations are given in Table 6. The bond lengths and bond angles calculated from them are given in Table 11, together with standard deviations calculated from those of atomic coordinates recorded in Table 6.

An independent estimate of the standard deviation of the Si–O bond can be made if it is assumed that the four bonds of the same tetrahedron are equal; the standard deviations of the mean bond length of each tetrahedron, calculated in this way, are recorded in Table 11. Since the standard deviation of an individual bond length is double that of the mean of four observations the agreement between the independent estimates is very satisfactory.

The structure described above was deduced using the assumption that there was a centre of symmetry at the origin. It is necessary to examine the alternative possibility, that the centre of symmetry is at $(0,0,\frac{1}{4})$. This can be done by the same method, though the structure factors are now imaginary with phase angles $\pm\pi/2$. No set of difference parameters could be found which could account for the observed intensities of the *b*-reflections. In view of the success of the solution with the original postulate, there can be no reasonable doubt that the centre of symmetry remains at (0,0,0). This result agrees with what is found in primitive anorthite.

The possibility that centres of symmetry were lacking altogether was not examined further, in view of the fact that agreement between F_o and F_c for the centrosymmetric structure was as close as could be expected from the limits of experimental error.

Discussion

The two primary points of interest in the structure determination are the distribution of silicon and aluminium atoms amongst the tetrahedral sites and the nature of the heavy barium atom and its influence on the surrounding silicate framework.

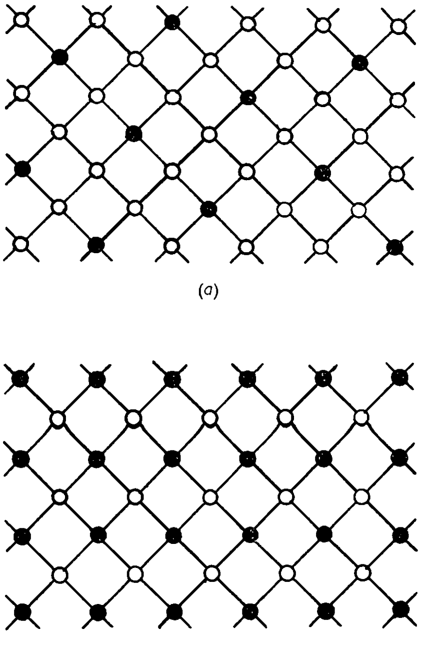
The silicon–oxygen bond lengths given in Table 11 suggest that the Si–Al arrangement is at least partially ordered. The mean Si–O bond lengths can be used to estimate the relative aluminium content of each tetrahedron (Smith, 1954). The results (Table 12) are consistent with the chemical analysis of 47% Al substitution for Si. Relative to a completely disordered state, about half of the aluminium atoms have migrated out of the $B_1(0)$ and $B_2(z)$ tetrahedra into the $B_1(z)$ and and $B_2(0)$ sites. The minor differences between tetrahedra $B_1(0)$ and $B_2(z)$ and between $B_1(z)$ and $B_2(0)$ are not significant. The ordered distribution is of a different type from that found in either microcline or low-albite, where the majority of Al atoms are segregated into one of the two B_1 tetrahedra; it was evident even from the average structure (see Table 7) that such was not the case in celsian.

Table 12. *Aluminium content of each tetrahedron*

Tetrahedron	Mean bond length	Al-content*
$B_1(0)$	1·639 ± 0·006 Å	22 ± 4%
$B_1(z)$	1·717 ± 0·006	65 ± 4
$B_2(0)$	1·712 ± 0·006	62 ± 4
$B_2(z)$	1·635 ± 0·006	20 ± 4

* Standard deviations quoted are those due to standard deviations in the mean bond lengths. Any error in the conversion scale relating bond lengths to Al content would introduce a further, systematic, error. It should also be observed that any incompleteness of refinement would have the effect of a systematic error giving an underestimate of the degree of order. While we believe that refinement is complete or very nearly so, we cannot assert that there is no residual error of this kind. The figures thus set a lower but not an upper limit to the actual degree of order.

The network representing the kind of order in celsian is extremely simple: each predominantly aluminium tetrahedron is surrounded by four predominantly silicon tetrahedra, and vice versa. In comparison, the triclinic felspars microcline and low albite have a more complicated arrangement, with only one-quarter of the tetrahedra predominantly aluminium; the Al tetrahedra are again surrounded by four Si tetrahedra, but two-thirds of the Si tetrahedra have one Al and three Si neighbours while the remaining one-third of the Si tetrahedra have two Al and two Si tetrahedra as neighbours. The difference between these two types of distribution can be illustrated by means of the two-dimensional networks shown in Fig. 2, where the solid circles represent tetrahedra of


(*a*)

(*b*)

Fig. 2. Two-dimensional networks illustrating the nature of ordered Si, Al distribution in (*a*) microcline, (*b*) celsian.

high Al-content and the open circles those which are primarily silicon. Though the analogy between the drawing and the three-dimensional felspar structure has obvious limitations it nevertheless serves to illustrate nearest-neighbour configurations. It also brings out a further point of interest, namely that transformation of the Si-poor type of network, (*b*), into the Si-rich type, (*a*), involves more than a simple replacement of Al by Si; there must simultaneously be replacement of Si by Al at other sites. This rearrangement of atoms means that materials of intermediate Si content cannot be described as solid solutions of one network in the other.

The celsian type of network, with its alternation of Si and Al, necessarily requires a doubling of the *c* axis, as can be seen from the following argument. Suppose we proceed from a B atom along any B–O–B–O · · · chain, counting the steps between B atoms; then since the Si, Al atoms alternate, an even number of steps brings us to an atom like the starting point, an odd number to an atom of the other species. Now the shortest route between sites related by a 7 Å *c*-axis vector consists of three such steps; hence this vector cannot be a translation identity but must be doubled in order to give one. By contrast, the *a* and *b* vectors of the prototype unit cell can remain translation identities, since they represent four and six steps respectively.

The kind of (Si, Al) order present in celsian has recently also been demonstrated in primitive anorthite (Kempster, 1957). (In fact the choice of origin, or choice of sign for the first difference parameter, in the present work was made so that the same names should apply to Si-rich sites in the two, the criterion suggested by Megaw (1956) being inapplicable here because the δz difference parameter of Ba is zero.) The arrangement is that predicted by Loewenstein (1954) from arguments of crystal chemistry. It is a very reasonable assumption that, where the 1:1 ratio of Si:Al exists, the arrangement with alternating Si and Al will be electrostatically the most stable. Thus the existence of this idealised (Si, Al) network in celsian and primitive anorthite, and of the 14 Å repeat necessitated by it, is a consequence of the charge on the *A* cation and not of its size.

When we consider the degree of order present rather than its kind, conclusions are less obvious. It is an unexpected fact that the proportion of Al in the two Al-rich sites $B_1(z)$ and $B_2(0)$ is the same, within the limits of accuracy of the present work, and similarly for the two Al-poor sites $B_1(0)$ and $B_2(z)$. There is no immediately apparent reason, either from geometry or electrostatics, why this should be. We draw attention to it as an experimental fact without trying to explain it here.

Turning to the barium ion, it can be seen that it has an irregular configuration in celsian very similar to that of potassium in either sanidine or microcline. Each barium has one nearby oxygen neighbour at 2·66 Å, six between 2·85 and 2·95 Å, two more at 3·1 Å and another at 3·4 Å, although the latter is probably not in contact. There is a strong resemblance of this barium–oxygen configuration to those found in paracelsian (Smith, 1953) and sanbornite (Douglass, 1958). Detailed comparison of the Ba–O distances in celsian and the K–O distances in microcline (Table 13) showed, however, that the Ba–O distances were nearly all shorter, (the two exceptions being among the longest bonds in the set). This tightening of the oxygen configuration around barium was particularly striking for oxygens O_{A2} and O_B, and also showed in a pronounced effect on the Si–O–Si bond angles; in every case these angles were smaller than the corresponding angles found in microcline (Table 13(*b*)). The corresponding values for sanidine, which resemble those for microcline, are included for comparison.

Table 13. *Comparison of bond lengths (in Å) and angles (in degrees) in barium and potassium felspars*

(*a*)	Ba–O (celsian)	K–O (microcline)	K–O (sanidine)
O_{A2}	2·667	2·758	2·698
O_{A1}	2·850 2·850	2·882 2·897	2·919
O_D	2·902 2·909	2·920 2·985	2·948
O_B	2·927 2·939	3·096 3·105	3·026
O_C	3·112 3·135	3·054 3·209	3·129
O_{A2}	3·421	3·405	

(*b*)	Angle Si–O–Si Celsian	Microcline	Sanidine
O_{A1}	139·4	144·0	145·1
O_{A2}	135·2	139·8	138·0
O_B	150·2 149·6	155·0 151·6	152·1
O_C	127·0 130·2	132·1 130·3	131·1
O_D	139·4 138·1	144·0 140·5	141·9

The shortening of the Ba–O distances as compared with K–O is rather surprising, in view of the fact that Ba^{2+} is generally thought to have a larger ionic radius than K^+. The contrast is still more marked when one compares the shortest distances, 2·67 Å and 2·76 Å, with the sums of the ionic radii, corrected for 9-coordination, which are 2·86 and 2·78 Å for Ba–O and K–O respectively. Taken in conjunction with the decrease of bond angle at O, it suggests an increase in homopolar character of the Ba compound as compared with the K compound.

The markedly anisotropic character of the apparent thermal motion of the barium atom also calls for comment. Its thermal vibration ellipsoid approximates to an oblate spheroid with the minimum vibration direction along a^*. The anisotropy is much less pronounced than that of Na or Ca in the plagioclase felspars but is quite definite none the less. A possible explanation for the thermal hindrance of barium along a^* is illustrated in Fig. 3. The extremely short Ba–O_{A2} contact lies almost exactly along a^*, and this factor, together with the mutual repulsion of the two barium ions, may force the atom to vibrate chiefly in (100). An alternative explanation is that the very anisotropic homopolar forces indicated by the short bond actually produce a change in electron-density distribution so that the atom can no longer be treated as spherical. It would need a redetermination of the structure at a low temperature to distinguish between these points of view.

An interesting parallel exists between the orientation of the Ba vibration ellipsoid and that of the optical indicatrix (Tables 1(*b*) and 4). Their principal axes coincide approximately in direction. The direction of hardest polarisation (greatest refractive index) is close to a^*, the short axis of the vibration ellipsoid and the direction of the short bond; while the direction of easiest polarisation (least refractive index) is close to c and the longest axis of the vibration ellipsoid, and is a direction of loose Ba–O binding. No quantitative calculation has been attempted in view of the complexity of the felspar structure, but the barium ion might reasonably be expected to make a large contribution to the refractive index because of its large electronic polarisability.

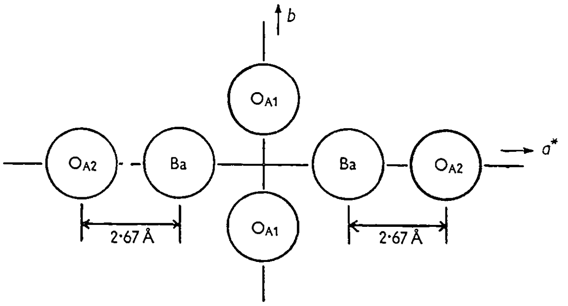


Fig. 3. Part of barium–oxygen configuration, showing short bond.

The zero y-parameter of the Ba atom also deserves comment. This is not a consequence of the space group: the atom is not in a special position. The zero value is therefore in a sense accidental. On the other hand, it has the effect that, if the Ba atoms *alone* were considered, they would lie on a mirror plane which does not operate on the rest of the structure. At least one other example of a similar effect is known: in $CdTiO_3$ (Kay & Miles, 1957) the Cd and Ti atoms lie on planes with $y=0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$, though there is no mirror plane in the structure as a whole. The effect suggests that the stability of a pseudosymmetric crystal structure may require higher symmetry in the arrangement of the heavy atoms than in that of the main framework. This, however, is speculative; at present we only wish to call attention to the fact.

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