structure. Both Ba and Sn retain the same coordination polyhedron which they have in their corresponding monosulfides. Ba is in sixfold coordination with Ba–S distances ranging from 3·13 Å to 3·21 Å forming a distorted octahedron. The Sn atom is also in a distorted octahedral void, but instead of being in the center of the octahedron it moves very close to one of the triangular faces so as to become bonded to 3 S atoms, Sn–S distances of 2·52, 2·58 and 2·61 Å, and is very far from the other 3 S atoms, Sn–S distances of 3·59, 3·68 and 3·79 Å. This kind of polar environment is usually expected for ions with s^2 configuration (Jellinek, 1968) in which one of the sp^3 hybrid orbitals is occupied by the lone pair and the other three are filled by electrons donated by the sulfur ions. Thus the Sn polyhedron can be described as a tetrahedron with one corner occupied by a lone pair of electrons.

As previously mentioned, the structure can be considered as a distortion of the NaCl structure if one considers both metal sites as equivalent. The cations are ordered in slightly puckered layers parallel to (100) in such a way that Ba layers alternate with Sn layers following the overall architecture of the NaCl structure.

Our observed powder pattern does not match HPH's except in a qualitative manner, Table 4. There is substantial agreement for the six strongest lines, but the line we observe at 2·93 Å is not present in HPH's pattern or else it corresponds to the one at 2·88 Å. For the weaker reflections there is qualitative agreement in

intensity between our pattern and theirs, but the positions of the lines do not agree very well. We thought that a monoclinic polymorph of BaSnS₂ exists and that HPH had synthesized an orthorhombic one. However, they report the same phase at 800 °C and at 650 °C and the existence of a different modification at 750 °C seems improbable. We repeated HPH's preparation of BaSnS₂ by heating BaS:SnS at 800 °C for three days and obtained the same powder pattern that we found in the first preparation at 750 °C which had been heated for two weeks. The possibility that there is, indeed, an orthorhombic polymorph seems remote.

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The Crystal Structure of an Anorthoclase: an Intermediate Alkali Feldspar

BY R. DE PIERI AND S. QUARENI

Istituto di Mineralogia e Petrologia, Università di Padova, Padova, Italy

The results of a structure analysis of an anorthoclase (Or 29%, Ab 65%, An 6%) are reported. By use of three-dimensional difference Fourier and least-squares techniques, parameters have been refined to give $R = 7·7\%$. The structure appears to be completely disordered with respect to Al and Si distribution. The anisotropy of the electron densities for the Na/K atom is discussed.

Introduction

Potassium feldspars display a number of different crystal structures which have been studied by many authors. We may mention, in this connexion, the determination and refinement of two sanidine structures obtained by heating orthoclase (Cole, Sörum & Kennard, 1949; Ribbe, 1963), of natural sanidine (Onorato, Penta & Sgarlata, 1963), of an orthoclase (Jones & Taylor, 1961; Colville & Ribbe, 1968), of an adularia (Colville & Ribbe, 1968), of an intermediate microcline (Bailey & Taylor, 1955), and of two maximum microclines (Brown & Bailey, 1964; Finney & Bailey, 1964). In addition, the high and low albite structures are well known (Ferguson, Traill & Taylor, 1958; Ribbe, Megaw & Taylor, 1969). It would appear, therefore, that apart from some as yet unresolved details the end-members of the alkali feldspar series are well determined. On the other hand, absolutely nothing is known about the structures of the intermediate members.

In this paper we wish to report the results of a structure analysis of one of these intermediate members, a natural anorthoclase (Or 29%, Ab 65% An 6%). The

Al/Si distribution in the non-equivalent tetrahedral sites is discussed. It is worth noting that the determination of a natural feldspar structure can give information about its thermal history, a fact that is important in the study of the petrogenesis of the rocks in which it is found. Moreover, the results of structural refinements of alkali feldspars are indispensable in order to establish the correlation between structure and physical property, as for example in the relationships between lattice parameters, optic axial angle, extinction angles and refractive indices.

The present accurate structure analysis has enabled us to interpret the mechanism for the reversible triclinic–monoclinic phase transition which in anorthoclase occurs at moderate temperatures (De Pieri & Quareni, 1972).

Experimental

The anorthoclase sample studied here was obtained from a group of large feldspar crystals found in a camptonitic dyke in Posina (Vicenza, Italy), and has been examined chemically, optically and crystallographically by De Pieri, De Vecchi & Quareni (1970). Table 1 gives the results of the chemical analysis.

Table 1. *Chemical composition of the anorthoclase*

SiO_2	65·32 wt.%		(1)		(2)
Al_2O_3	21·23	Or	25·2 mol.%	Or	29 mol.%
Fe_2O_3	0·23	Ab	67·9	Ab	65
CaO	1·32	An	6·5	An	6
Na_2O	7·66	Cn	0·4		
K_2O	4·60				
BaO	0·24				
Total	100·30				

(1) Bulk composition of the megacrystal by the chemical analysis.
(2) Composition extimated by α^* and γ^* values.

From the α^* and γ^* angles (De Pieri, De Vecchi & Quareni, 1970) it was possible to distinguish slight differences in composition between fragments of the same crystal; in particular, α^* and γ^* for the present sample indicated that its composition was as given in Table 1.

The sample used was $0·21 \times 0·24 \times 0·46$ mm with its longest dimension along [100] and showed no twinning or unmixing phenomena. The axes of reference chosen here are the conventional ones for feldspars and on this basis the space-group symbol is $C\bar{1}$.

Table 2 shows the lattice constants measured with a precession camera calibrated with quartz and NaCl using Cu $K\alpha$ ($\lambda = 1·5418$) radiation. The density was determined by suspension in liquid according to the technique suggested by Straumanis (1953). The refractive indices were obtained by the λ variation method and the optic angle was measured on a universal stage.

Equi-inclination Weissenberg photographs of all layers between $0kl$ and $7kl$ were taken using multiple-

Table 2. *Crystal data*

a_0	$8·300 \pm 0·005$ Å	α	$91°18' \pm 5'$
b_0	$12·953 \pm 0·008$ Å	β	$116°25' \pm 5'$
c_0	$7·149 \pm 0·005$ Å	γ	$90°19' \pm 5'$
$F(000)$	532	$n\alpha$	1·5275
Z	4	$n\beta$	1·5324
D_4^{22}	2·602	$n\gamma$	1·5337
		$2V\alpha$	56°

Estimated limits of error are given, not standard deviations.

film techniques (Mo $K\alpha$ radiation). The strong and medium intensities were measured with a Flying Spot Microdensitometer (Joyce–Loebl); only spots with optical density less than 1 were considered. The weak reflexions were estimated visually by comparison with an intensity scale made with a reflexion from the same crystal.

The intensities after correction for Lorentz–polarization factors were scaled together using common reflexions on $hk0$ and $hk1$ layers, taken with the same crystal and using the same technique.

No absorption corrections were applied since, on surveying the intensities, we felt that errors in measurement were not small enough to justify such correction.

Some very strong reflexions occurring at low angle showed extinction effects and were discarded during the refinement procedure, which was carried out on a total of 1353 independent observed reflexions.

Refinement

Atomic scattering factors for Na^+, K^+, Ca^{2+}, Al^{3+} and Si^{4+} were taken from *International Tables for X-ray Crystallography* (1962). An average scattering factor of $\frac{3}{4}Si^{4+}$ plus $\frac{1}{4}Al^{3+}$ was calculated for all atoms in tetrahedral sites on the assumption of complete disorder of Al and Si.

Similarly, average values were estimated for Na, K and Ca according to the composition as estimated from the angles α^* and γ^*. Using these scattering factors the Forsyth & Wells (1958) constants were computed. In the case of oxygen (O^{2-}) the constants given by Tokonami (1965) were employed. All calculations were carried out on the TITAN computer of the Mathematical Laboratory, Cambridge (England).

The structure was refined starting with the atomic coordinates for high albite given by Ribbe, Megaw & Taylor (1969), at first using a difference Fourier program written by J. Matthewman and then using a full-matrix least-squares program, written by the same author. In the least-squares refinement the weighting scheme of Cruickshank (1965) was used and gave a rapid convergence.

The refinement was conducted in two stages: at first the Na and K atoms, which occupy the same sites in the structure, were treated as if they were a single atom with atomic scattering factor weighted according to chemical composition; then individual scattering fac-

tors for the Na and K atoms were assigned according to the relative amounts present.

The atomic coordinates obtained with refinement of isotropic temperature factors ($R = 10\cdot1\%$) do not present any significant differences with respect to those obtained with anisotropic thermal parameters ($R = 7\cdot7\%$).

The atomic coordinates, interatomic distances and bond angles taken from the first stage of refinement are given in Tables 3, 4 and 5 respectively.

The root mean square displacements and the directions of the thermal ellipsoid axes, calculated from the anisotropic thermal parameters using a program written by J. K. Brandon (private communication) are given in Table 6.

Table 3. Atomic coordinates, in fractions of the cell edges, and isotropic thermal parameters

	x	y	z	B (Å²)
Na, K	0·2748 (1)	0·0020 (1)	0·1355 (2)	2·9
$T_1(0)$	0·0082 (1)	0·1739 (1)	0·2205 (1)	0·7
$T_1(m)$	0·0065 (1)	0·8178 (1)	0·2257 (1)	0·7
$T_2(0)$	0·6942 (1)	0·1133 (1)	0·3334 (1)	0·7
$T_2(m)$	0·6929 (1)	0·8810 (1)	0·3469 (1)	0·7
$O_A(1)$	0·0028 (3)	0·1379 (1)	0·9934 (3)	1·6
$O_A(2)$	0·6048 (3)	0·9966 (1)	0·2840 (3)	1·4
$O_B(0)$	0·8250 (3)	0·1253 (2)	0·2172 (3)	1·9
$O_B(m)$	0·8229 (3)	0·8567 (2)	0·2340 (3)	1·9
$O_C(0)$	0·0226 (3)	0·3004 (1)	0·2629 (3)	1·5
$O_C(m)$	0·0225 (3)	0·6907 (1)	0·2385 (3)	1·4
$O_D(0)$	0·1900 (3)	0·1195 (1)	0·3974 (3)	1·5
$O_D(m)$	0·1872 (3)	0·8717 (1)	0·4129 (3)	1·5

Standard errors $\times 10^{-4}$ are in parentheses.

Table 4. Interatomic distances in Å

$T_1(0)-O_A(1)$	1·660	$T_2(0)-O_A(2)$	1·641
$T_1(0)-O_B(0)$	1·634	$T_2(0)-O_B(0)$	1·644
$T_1(0)-O_C(0)$	1·653	$T_2(0)-O_C(m)$	1·637
$T_1(0)-O_D(0)$	1·651	$T_2(0)-O_D(m)$	1·640
Mean	1·649	Mean	1·640
$T_1(m)-O_A(1)$	1·650	$T_2(m)-O_A(2)$	1·651
$T_1(m)-O_B(m)$	1·632	$T_2(m)-O_B(m)$	1·637
$T_1(m)-O_C(m)$	1·655	$T_2(m)-O_C(0)$	1·630
$T_1(m)-O_D(m)$	1·641	$T_2(m)-O_D(0)$	1·645
Mean	1·644	Mean	1·641

Table 5. Interatomic angles in degrees

$O_A(1)-T_1(0)-O_B(0)$	105·4	$O_A(2)-T_2(0)-O_B(0)$	108·9
$O_A(1)-T_1(0)-O_C(0)$	113·8	$O_A(2)-T_2(0)-O_C(m)$	104·8
$O_A(1)-T_1(0)-O_D(0)$	104·5	$O_A(2)-T_2(0)-O_D(m)$	108·3
$O_B(0)-T_1(0)-O_C(0)$	111·7	$O_B(0)-T_2(0)-O_C(m)$	112·0
$O_B(0)-T_1(0)-O_D(0)$	111·6	$O_B(0)-T_2(0)-O_D(m)$	110·0
$O_C(0)-T_1(0)-O_D(0)$	109·5	$O_C(m)-T_2(0)-O_D(m)$	112·6
$O_A(1)-T_1(m)-O_B(m)$	105·6	$O_A(2)-T_2(m)-O_B(m)$	110·0
$O_A(1)-T_1(m)-O_C(m)$	111·1	$O_A(2)-T_2(m)-O_C(0)$	105·6
$O_A(1)-T_1(m)-O_D(m)$	105·4	$O_A(2)-T_2(m)-O_D(0)$	107·6
$O_B(m)-T_1(m)-O_C(m)$	111·1	$O_B(m)-T_2(m)-O_C(0)$	110·9
$O_B(m)-T_1(m)-O_D(m)$	112·2	$O_B(m)-T_2(m)-O_D(0)$	110·4
$O_C(m)-T_1(m)-O_D(m)$	109·6	$O_C(0)-T_2(m)-O_D(0)$	112·1

Mean tetrahedral angle 109·36°

$T_1(0)-O_A(1)-T_1(m)$	143·3	$T_1(0)-O_C(0)-T_2(m)$	131·9
$T_2(0)-O_A(2)-T_2(m)$	132·4	$T_1(m)-O_C(m)-T_2(0)$	132·8
$T_1(0)-O_B(0)-T_2(0)$	148·5	$T_1(0)-O_D(0)-T_2(m)$	138·8
$T_1(m)-O_B(m)-T_2(m)$	154·9	$T_1(m)-O_D(m)-T_2(0)$	145·1
	mean		140·9°

Discussion

(a) Si/Al distribution

The average dimensions of the tetrahedra and the corresponding Al contents, calculated with the equation of Ribbe & Gibbs (1969) show that there is no significant difference from a completely disordered Si/Al distribution with one quarter of the Al atoms in each of the four tetrahedral positions (Table 7). It is interesting to note that the tetrahedral dimensions in the anorthoclase are practically equal to those in the high albite studied by Ribbe, Megaw & Taylor (1969), shown for comparison in the Table 7. In both cases tetrahedron $T_1(0)$ is slightly larger than the others. In the case of albite, this can be attributed to incomplete disorder in the Si/Al distribution obtained by prolonged heating of the original low albite. In anorthoclase, however, it might be due to some partial ordering produced by the rapid natural cooling that the crystal underwent in the matrix from which it was extracted. This phenomenon, in agreement with Ribbe et al. (1969), can also be explained in terms of local and periodic stresses which can give rise through their effects on the tetrahedral framework to a completely disordered structure. We prefer this second hypothesis; in fact, if a mechanism of this kind, rather than partial ordering of Si and Al, is responsible for the large size of the $T_1(0)$ tetra-

Table 4 (cont.)

Tetrahedron	O_A-O_B	O_A-O_C	O_A-O_D	O_B-O_C	O_B-O_D	O_C-O_D	Tetrahedral mean
$T_1(0)$	2·621	2·775	2·618	2·721	2·716	2·699	2·692
$T_1(m)$	2·615	2·754	2·618	2·711	2·713	2·693	2·684
$T_2(0)$	2·672	2·597	2·659	2·720	2·690	2·727	2·677
$T_2(m)$	2·694	2·613	2·660	2·691	2·695	2·717	2·678
Bond mean	2·650	2·685	2·639	2·711	2·703	2·709	

Na/K–O_A(1000)	2·70		Na/K–O_B(m00c)	3·05
Na/K–O_A(100c)	2·73		Na/K–O_C(00i0)	3·22
Na/K–O_A(2000)	2·46		Na/K–O_C(m0i0)	3·05
Na/K–O_A(200c)	3·81		Na/K–O_D(0000)	2·71
Na/K–O_B(000c)	2·78		Na/K–O_D(m000)	2·96

Table 6. *Parameters for the thermal ellipsoids*

		(1)	(2)		
			a	b	c
Na, K	1	0·264	114°	135°	45°
	2	0·176	57	134	131
	3	0·124	43	85	74
T₁(0)	1	0·116	68	155	109
	2	0·095	54	86	63
	3	0·065	136	114	34
T₁(m)	1	0·109	58	41	85
	2	0·095	32	117	128
	3	0·075	92	62	141
T₂(0)	1	0·112	24	105	132
	2	0·108	68	75	51
	3	0·062	99	158	67
T₂(m)	1	0·113	13	96	127
	2	0·105	77	67	46
	3	0·065	91	156	67
O_A(1)	1	0·182	22	91	95
	2	0·151	80	150	118
	3	0·110	109	119	28
O_A(2)	1	0·195	17	99	130
	2	0·124	73	60	54
	3	0·106	90	149	61

		(1)	(2)		
			a	b	c
O_B(0)	1	0·180	84°	147°	128°
	2	0·156	108	61	127
	3	0·132	160	105	52
O_B(m)	1	0·179	64	152	108
	2	0·150	49	78	70
	3	0·137	127	114	28
O_C(0)	1	0·153	92	70	147
	2	0·133	58	142	120
	3	0·117	148	120	76
O_C(m)	1	0·150	20	100	133
	2	0·133	96	166	75
	3	0·123	71	80	47
O_D(0)	1	0·173	22	105	130
	2	0·145	68	46	68
	3	0·110	91	47	132
O_D(m)	1	0·187	10	99	120
	2	0·142	96	152	61
	3	0·107	82	64	44

(1) R.m.s. displacement of the principal axes of the ellipsoids in Å.
(2) Directions of the principal axes of the ellipsoids relative to the crystallographic axes *a*, *b* and *c*.

hedron, we can explain why, during the ordering process, the Al atoms concentrate in this site since it is already predisposed to accept the larger Al atom.

Table 7. Al–Si *distribution in anorthoclase and in high albite*

	Anorthoclase		High albite (Ribbe et al., 1969)	
Tetrahedron	Mean T–O distance	Al content	Mean T–O distance	Al content
T₁(0)	1·649	0·29	1·648	0·29
T₁(m)	1·644	0·26	1·644	0·26
T₂(0)	1·640	0·23	1·639	0·22
T₂(m)	1·641	0·24	1·643	0·25
		Total Al 1·02		Total Al 1·01

Al contents are determined in both cases from the equation given by Ribbe & Gibbs (1969); the same results are obtained using the equation given by Jones (1968).

(b) Anisotropy of Na and K atoms

In both the low and high albite structures the electron density distribution around the Na atom shows a marked anisotropy which makes the atom appear to be noticeably elongated (Ferguson, Traill & Taylor, 1958; Ribbe, Megaw & Taylor 1969). In high albite the anisotropy is particularly pronounced and is probably due to a 'space-average' of the different positions of the Na atom within a cavity of varying shape in different unit cells, rather than to a 'time-average' caused by thermal vibration.

The smaller anisotropy found in low albite is almost certainly due instead to a genuine anisotropy in the thermal motion (Quareni & Taylor, 1969).

The anisotropy of the Na/K atom in our anorthoclase, which as far as the framework of tetrahedra is concerned is practically identical with high albite, is similar to that found in low albite. It would therefore seem logical to suppose that it is due to thermal effects by analogy with the case of low albite.

If, instead, we consider the different anisotropy shown by Na and K in related feldspars, a different conclusion may be reached.

The anisotropy of the K atom gives rise to a slightly squashed ellipsoid of rotation with its minor axis almost along **a***. The anisotropy of Na, however, gives a greatly elongated ellipsoid with its major axis almost parallel to the (100) plane and inclined to [001] by about 45°; its shortest axis is still nearly along **a***.

In the anorthoclase structure the Na/K anisotropy should represent something intermediate between the anisotropies of K and Na in the related feldspars.

In the second stage of refinement we have therefore attributed to the Na and K individual scattering factors according to the relative amounts present. Some cycles of least-squares refinement were used to obtain the position and anisotropic 'thermal' parameters of the Na atom. For this purpose the position of the K atom was fixed using the results from the first stage of refinement, and the anisotropic thermal parameters used were those for K in the adularia of Colville & Ribbe (1968). At the end of this refinement the anisotropic parameters for Na were found to be close to those in high albite. This result therefore seems to support the hypothesis that the resulting anisotropy for the Na/K in this anorthoclase can be explained in terms of a 'space-average'; potassium, because of its size, must occupy the whole of the cavity in which it is

located, whereas the sodium, with its much smaller size, gives rise to cavities of different shape within which it can occupy different positions in the various unit cells.

The R index decreased by only 0·01 % in the second stage and although this small change gave a slight improvement in the difference Fourier maps it was not possible from this to decide whether the anisotropy of the Na/K atom was best explained in terms of a 'space-average' or a 'time-average'.

The model assumed for the second stage of refinement is compatible with the fact that the isotropic temperature factor for Na/K (2·9 Å^2) is intermediate between that obtained in sanidines (2·0 Å^2, Onorato et al., 1963; 2·1 Å^2, Ribbe, 1963) and that in high albite (5·7 Å^2, Ribbe et al., 1969).

Conclusions

The structure analysis of this anorthoclase has shown that there is complete disorder in the Si/Al distribution and that the framework of tetrahedra is perfectly analogous to that in high albite. The large anisotropy of the Na/K atom can be interpreted in terms of a 'space-average' of the Na atoms as in high albite with the K atom, because of its larger size, occupying a single position within the cavity in which it is found. The possibility that this anisotropy may represent a true anisotropy in the thermal vibration ('time-average') cannot however be excluded.

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