

The Crystal Structures of Orthoclase and Sanidinized Orthoclase

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Orthoclase upon heating for long periods at about 1000° C. is transformed irreversibly into sanidine. Explanations for the phenomenon have been sought in structural changes, but have never been confirmed by X-ray analysis, although work by Chao, Hargreaves & Taylor on the structure of unheated orthoclase suggested that disordering of Al atoms might be responsible for the transformation. In the present paper an account is given of a highly accurate structure determination of the structure of an orthoclase after sanidinization, the sample examined being the same as that investigated as orthoclase by the above-mentioned authors.

A change from an ordered distribution of aluminium atoms in orthoclase to a disordered distribution in sanidine should produce, as one observable effect, changes in the size of the tetrahedral groups around (Si, Al) in the structure. The present examination of sanidine indicates uniformity in the size of these groups, as would be expected from a random arrangement of atoms of either kind in the (Si, Al) positions. A re-examination of the earlier determination of orthoclase, however, shows that its accuracy was not sufficient to establish significant differences in the size of the tetrahedral groups, and so establish an ordered arrangement of Al atoms for that material. A redetermination of its structure, of the same accuracy as the present work, would be required to settle this point finally. Available evidence indicates that the position of the cation does not change during sanidinization.

1. Previous structural work

The structure of sanidine was described by Taylor (1933) and later work by Taylor, Darbyshire & Strunz (1934) included investigations of the structures of potash-barium feldspars, and of some plagioclases (in particular albite), and it was shown that all these feldspars have essentially the same structure as that of the sanidine originally examined. Chao, Smare & Taylor (1939), and Chao & Taylor (1939, 1940) extended the investigations to include the structural arrangement of the lamellae in micropertthitic potash-soda feldspars, and the superlattice structures in the plagioclases. The work of Ito & Inuzuka (1936) and of Ito (1938) was in partial agreement with the observational data of Taylor and his co-workers. Finally Chao, Hargreaves & Taylor (1940) carried out an accurate determination of the structure of orthoclase by quantitative X-ray methods on material for which complete optical and chemical data were available.

2. Thermal transformations in the potash-soda feldspars

If micropertthitic soda-rich potash feldspars are heated for some time to 750–800° C. the micropertthite, which is of the exsolution type, is taken into solid solution, but can be partially reprecipitated by cooling slowly (Spencer, 1930, 1937). During this process the refractive indices and other physical properties change

but the optic axial angle remains unaltered. This reversible effect has been shown by Taylor and his co-workers to be due to migration of the cation through the structure.

On the other hand, if the heating is carried out for prolonged periods at a temperature in the region of 1000° C., the optic axial angle is affected and the material is transformed irreversibly (in laboratory cooling times) into a form which has the optical properties of a sanidine. The effect is observed with all potash-soda feldspars with less than 40% of the soda component (including triclinic as well as monoclinic forms) and was first observed by Des Cloizeaux (1861) and has since been extensively studied by Kôzu & Suzuki (1923), and Spencer (1930, 1937). For orthoclase with a low soda content the optic axial angle changes from about 40° in the plane perpendicular to (010) to about 55° in the symmetry plane, during sanidinization. This change in optic axial angle corresponds to a transposition of the refractive indices γ and β and a relative change in their values of about 0.0010. The present paper is concerned with the structural changes associated with the irreversible transformation of such an orthoclase.

3. Structural changes during sanidinization

For a general description of the feldspar structure reference should be made to the early work by Taylor (1933). It should be pointed out that in all structure determinations so far made on the monoclinic potash feldspars it is assumed that the symmetry is holohedral,

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and this is possible only if Al and Si in the formula $K(AlSi_3)O_8$ are treated as equivalent. The 16 (Al+Si) atoms in the unit cell are divided into two groups of 8 Si_1 and 8 Si_2 , so as to satisfy the holohedral symmetry of the space group $C2/m$ in which the operation of the symmetry elements converts an atom in a general position into a group of eight equivalent atoms. It is possible for the Al atoms to be randomly distributed among both Si_1 and Si_2 groups, or in only one of them, and the symmetry still remains statistically holohedral. The process of sanidinization may be due to a transformation from one type of distribution to the other. It would be expected that in the case of Al segregation the average bond lengths in the tetrahedral groups would be 1.62 Å. for the pure silicon group and 1.66 Å. for the (Si, Al) group. Where Al is randomly distributed in both Si_1 and Si_2 the average bond length for each group would be expected to be 1.64 Å.

It is also possible for the four Al atoms to segregate into definite positions in either of the silicon groups so as to occupy either one fourfold or two twofold equivalent points. If this should happen then the symmetry must be reduced to either monoclinic hemihedral or to triclinic with a symmetry centre, respectively. (Adularia and microcline may have these structural arrangements, but these are matters for future investigations.) In the former case the Al-O distance would be expected to be 1.70 Å., whereas the other three tetrahedral groups would have Si-O distances of 1.62 Å. However, it is not possible by X-ray methods to distinguish between hemihedral and holohedral forms and, although adularia has been reported as being pyro-electric (Hankel, 1877), the results of other tests for polarity in orthoclase and sanidine are negative, so that in these structures the symmetry is assumed to be holohedral.

The proof of such small changes involves the determination of atomic parameters with very high accuracy and in §§ 4, 5 and 6 of the present paper an account is given of an analysis of the structure of sanidine fulfilling these requirements. It is shown that there is so small a variation in the bond lengths around the two tetrahedral groups that Al atoms must be completely disordered in this material.

The earlier work of Chao *et al.* (1940) on orthoclase seemed to show a significant difference in the bond

lengths around the two tetrahedral groups, and it was this result that made the present work on sanidine of interest. However, re-examination of their data, as discussed in § 7, has shown that the accuracy is not adequate to justify this conclusion regarding the distribution of Al atoms. A further investigation of orthoclase, of the same accuracy as the present analysis of sanidine, is necessary if definite evidence is to be obtained on this point.

4. Experimental details

The material examined here is the heat-treated form of the same material as was examined by Chao *et al.* (1940). It is a specimen of Spencer's from the ruby mines of Mogok in Upper Burma, hereafter designated specimen *C*, which was optically homogeneous and which probably held its small amount of soda feldspar in solid solution. It can be considered as containing 92.2% (by weight) of potash feldspar, 6.8% of soda feldspar and 2.5% of lime feldspar, and thus represents a typical orthoclase, having the structure of pure potash feldspar. It could be sanidinized by heating (Spencer, 1930; 1937) without the process being complicated by the presence of soda-rich lamellae in the unheated material. The physical properties of specimen *C* have also been determined by Spencer and are set out in Table 1. In preparing fragments of this material for X-ray and optical examination we have used the cutting and grinding apparatus described by Thomas & Campbell-Smith (1913-16). Plates were ground normal to the *a* and *b* axes and elongated in the *b* and *a* directions respectively. By splitting along the (001) cleavages, needle-shaped fragments of uniform cross-section were obtained parallel to the *b* and *a* axes. Small equi-dimensional fragments could be obtained by splitting the former along (010) cleavages. One such crystal approximately 0.2 mm. on edge was used for most of the work described in this paper. Examination of crystal plates ground normal to the *a* axis confirmed that the optic axial angle of specimen *C* had been reversed during sanidinization.

Previous X-ray work by Chao *et al.* (1939) showed that specimen *C*, before and after heating, has monoclinic symmetry with the space group $C2/m$, and measurements of cell dimensions and density showed that the unit cell contains four molecules of $KAlSi_3O_8$.

Table 1. *Physical properties of specimen C before and after heating to 1075° C. for 300 hr.*

	Refractive indices			Axial angle		Optical orientation	$\gamma - \alpha$	Specific gravity
	α	β	γ	Meas.	Calc.			
Unheated	1.5188	1.5230	1.5236	43.6°	41.5°	$x \wedge a = 5.3^\circ$ $y \wedge c \approx 21^\circ$ $z = b$	0.0048	2.563
Heat-treated	1.5187	1.5227	1.5233	4.4° R.	—	$x \wedge a = 5.3^\circ$ $y = b$ $z \wedge c \approx 21^\circ$	0.0046	2.555

In comparing refractive indices in this table it must be remembered that for the heat-treated material the optic axial angle is reversed and the values of β and γ are transposed.

Table 2. Cell dimensions of specimen C before and after heating to 1075° C. for 300 hr.

	(Results in parentheses are taken from Chao <i>et al.</i> (1939).)				
	<i>a</i> (Å.)	<i>b</i> (Å.)	<i>c</i> (Å.)	β (°)	Volume (Å. ³)
Unheated	8.5616 ± 0.0002 (8.60)	12.9962 ± 0.0004 (13.02)	7.1934 ± 0.0002 (7.22)	116.015 ± 0.005	719.294
Heat-treated	8.5642 ± 0.0002 (8.60)	13.0300 ± 0.0004 (13.03)	7.1749 ± 0.0002 (7.16)	115.994 ± 0.005	719.654
Difference	+0.0026	+0.0338	-0.0185	-0.021	+0.360

The cell dimensions of Chao *et al.* (1940) were from layer-line spacings and were consequently not of high accuracy. We have redetermined these constants for both unheated and heat-treated crystals, with very high accuracy, by a graphical extrapolation method previously described (Weisz, Cochran & Cole, 1948). A small equi-dimensional crystal 0.2 mm. on edge was used for each series. The results (Table 2) show that as a result of heat treatment *a* is almost unchanged, *c* and β are slightly reduced, and *b* and the volume are slightly increased. These changes in axial lengths are in the same direction as those reported in the earlier work.

Measurements of X-ray intensities for the determination of the structure of specimen C, after heat treatment, were made on the same small crystal as was used in the determination of cell dimensions. For such a crystal the maximum variation in absorption for reflexions with Mo *K* α radiation in different directions was not greater than 10%, and for most reflexions the error in the measured intensity due to this factor did not exceed $\pm 3\%$. General (*hkl*) reflexions were recorded on equi-inclination Weissenberg photographs with the crystal rotated about the *a*, *b* and *c* axes. *a*-axis photographs were taken up to the (*8kl*) level, *b*-axis photographs up to (*h*.12.*l*), and *c*-axis photographs up to (*hk*3). In all, 26 levels were recorded covering data for 737 reflexions, nearly all of which were recorded three times. Intensities were measured and corrected for Lorentz and polarization factors as described in a previous publication (Kaan & Cole, 1949). We have obtained the integrated intensity for each reflexion by a photometric method which gives for most reflexions an accuracy within $\pm 10\%$. No experimentally determined corrections were made for extinction, but, as will be seen in a later section, account was taken of this factor.

The integrated intensities of reflexion, which were measured on an arbitrary scale, were converted to absolute units by comparison with structure amplitudes calculated from the atomic parameters published by Chao *et al.* (1940) for the unheated material. In the calculation of the structure amplitudes use was made of the empirical atomic *f* curves of Bragg & West (1928), and it was assumed that the Al and Si atoms were indistinguishable. A constant multiplying factor, converting the arbitrary to the absolute scale of intensities, was obtained by taking a mean for all those reflexions with calculated *F* values between 30 and 105. The

only temperature factor introduced into the calculated structure amplitudes in this paper is that embodied in the atomic *f* curves of Bragg & West.

5. Determination of atomic parameters

In determining atomic parameters the electron density was first calculated for three-dimensional Fourier sections parallel to the *xOz* symmetry plane at heights *y* equal to the atomic co-ordinates published by Chao *et al.* (1940) for the unheated material. The *x* and *z* parameters so determined were then used to define a series of three-dimensional line syntheses normal to the symmetry plane from which new *y* parameters were obtained. In the space group *C2/m* the electron density at any point *x*, *y*, *z* is given by (Lonsdale, 1936)

$$\rho_{xyz} = \frac{4}{V} \sum_0^{\infty} \sum_0^{\infty} \sum_0^{\infty} \left\{ F(hkl) \cos 2\pi \left(\frac{hx}{a} + \frac{lz}{c} \right) + F(\bar{h}kl) \cos 2\pi \left(-\frac{hx}{a} + \frac{lz}{c} \right) \right\} \cos 2\pi \frac{ky}{b},$$

and this expression can be put into a form suitable for the use of Lipson and Beever's strips (Goodwin & Hardy, 1938) in calculating the required sections and lines. In these calculations the phases are either 0° or 180° and the appropriate sign (+ or -) for each reflexion was taken from the structure-amplitude calculations mentioned in the previous section. The calculations for the Fourier syntheses were done manually, using two-figure Lipson and Beever's strips and two-decimal multiplying tables, and rounding off to the nearest whole number. The results of these syntheses are not published, but they showed that the only significant difference in parameters between the unheated and heat-treated materials was in the *x* and *z* co-ordinates of an oxygen atom in the symmetry plane (*O*₄₂), that all the Si-O distances were almost identical, and that all atoms were accompanied by diffraction rings.

In order to remove these diffraction effects new syntheses were made after introducing an artificial temperature factor of the form $\exp[-B(\sin \theta/\lambda)^2]$, where $B=5 \text{ \AA.}^2$, which reduced the terms of highest $\sin \theta/\lambda$ to about 1/30 of their observed value. In addition the observed *F* value was replaced by the calculated *F* value for all planes with *F*_{calc.} above 100 so as to make allowance for extinction effects. Furthermore all changes in sign resulting from the new set of parameters were corrected before starting the new syn-

Table 3. Co-ordinates of atoms in the unit cell of specimen C, heat-treated, compared with those for the unheated material published by Chao *et al.* (1940)

Atom	No. in cell	Unheated			Heat-treated		
		θ_1	θ_2	θ_3	θ_1	θ_2	θ_3
O _{A1}	4	0	55	0	0	53.0	0
O _{A2}	4	240	0	109	228.5	0	102.9
O _B	8	295	55	82	298.0	52.9	80.8
O _C	8	15	114	94	12.3	111.6	92.7
O _D	8	62	46	150	64.5	45.7	144.9
Si ₁	8	3.5	67.5	81	3.5	66.6	80.4
Si ₂	8	255.5	42	125	255.2	42.4	124.0
K	4	105	0	50	102.85	0	49.65

In the above table θ_1 , θ_2 , θ_3 are the angular co-ordinates defined by the expression $\theta_1 = 360 x/a^\circ$, $\theta_2 = 360 y/b^\circ$, $\theta_3 = 360 z/c^\circ$, where x , y , z are the atomic co-ordinates in Ångström units and a , b , c are the axial lengths as given in Table 2. 1° in θ_1 , θ_2 , θ_3 equals 0.0238, 0.0362, 0.0199 Å, respectively. Silicon and aluminium atoms are not distinguished.

Table 4. Interatomic distances for specimen C, heat-treated, compared with those for the unheated material published by Chao *et al.* (1940)

(All results expressed in Ångström units)

	Unheated		Heat-treated	
	Si ₁ (O _{A1})	Si ₂ (O _{A2})	Si ₁ (O _{A1})	Si ₂ (O _{A2})
Si-O _A	1.66	1.57	1.642	1.644
Si-O _B	1.70	1.60	1.640	1.640
Si-O _C	1.69	1.57	1.647	1.642
Si-O _D	1.67	1.57	1.640	1.644
Mean	1.68	1.58	1.642	1.642
O _A -O _B	2.72	2.59	2.618	2.689
O _A -O _C	2.77	2.59	2.743	2.600
O _A -O _D	2.72	2.51	2.623	2.674
O _B -O _C	2.79	2.54	2.707	2.686
O _B -O _D	2.74	2.55	2.718	2.716
O _C -O _D	2.73	2.65	2.680	2.721
Mean	2.74	2.57	2.682	2.681
K-O _{A1}	3.00		2.919	
K-O _{A2}	2.90		2.698	
K-O _B	3.12		3.026	
K-O _C	3.09		3.129	
K-O _D	3.11		2.948	

Table 5. Interatomic angles for specimen C, heat-treated, compared with those for the unheated material published by Chao *et al.* (1940)

	Unheated		Heat-treated	
	Si ₁ (O _{A1})	Si ₂ (O _{A2})	Si ₁ (O _{A1})	Si ₂ (O _{A2})
O _A -Si-O _B	Not calculated		105° 45'	109° 57'
O _A -Si-O _C			113° 1'	104° 38'
O _A -Si-O _D			106° 5'	108° 52'
O _B -Si-O _C			110° 52'	109° 51'
O _B -Si-O _D			111° 52'	111° 33'
O _C -Si-O _D			109° 14'	111° 47'
Mean			109° 28'	109° 26'
Si ₁ -O _{A1} -Si ₁	147°		145° 6'	
Si ₂ -O _{A2} -Si ₂		152°		138° 3'
Si ₁ -O _B -Si ₂	152°		152° 7'	
Si ₁ -O _C -Si ₂	133°		131° 6'	
Si ₁ -O _D -Si ₂	148°		141° 51'	

theses. They were made firstly by lines through the new x and z co-ordinates, and then by sections through these last-determined y co-ordinates. All manual calculations were made by two workers independently using three-decimal multiplying tables and rounding

off to the first decimal place, except where the numbers were rounded off to the nearest whole number so as to make use of the Lipson and Beevers strip method of summation. This latter work was carried out on a commercial Hollerith machine with cards of three-figure accuracy as described by Hodgson, Clews & Cochran (1949). In all the lines electron densities were calculated at 3° , and in all the sections at 6° intervals. The parameters for all atoms agreed with those of the previous syntheses except for the x and z co-ordinates of O_{A2}, K and O_D which differed by as much as $1\frac{1}{2}^\circ$. These differences must be due to the elimination of diffraction effects, and consequent finite-summation error, by the use of the artificial temperature factor. In order to find out how effective the method has been in reducing this error, structure amplitudes were re-calculated for all 737 planes with the last set of co-ordinates, and syntheses with calculated F values (Booth, 1946) were made for a section through O_D and one through O_{A2} and K. This back-synthesis method showed that the finite-summation errors had been corrected in O_D, but that for O_{A2} and K the correction was in the right direction but not of the right amount.

Our final parameters are set out in Table 3 alongside those of the unheated material published by Chao *et al.* (1940). The values for the x and z co-ordinates of atoms O_B, O_C, Si and Si₂ may be in error by $\pm 0.1^\circ$ (≈ 0.002 Å.) because, after the syntheses had been completed, three computational errors were found and these were corrected only in the lines. In Tables 4 and 5 are given the corresponding interatomic distances and angles for the parameters set out in Table 3. The results are also illustrated by Figs. 1 and 2.

6. Accuracy of results

The accuracy attained can be seen in a general manner from the fact that the ratio

$$\frac{\sum |F_{\text{obs.}}|}{\sum |F_{\text{calc.}}|} \div \sum |F_{\text{obs.}}|$$

is 0.20 when $F_{\text{calc.}}$ is evaluated for the co-ordinates published by Chao *et al.* (1940), and 0.14 when it is evaluated for the co-ordinates presented here.

In particular we have evaluated the standard deviation of errors in atomic parameters and Si-O

distances according to the statistical methods developed by Cruickshank (1949). Only experimental and computational errors have been considered, as the results set out in Table 3 should be free from finite-summation errors. Considering experimental errors for a monoclinic cell in the y direction,

$$\sigma(y) = \sigma(A_k) / A_{hh},$$

where $\sigma(y)$ is the standard deviation of the r.m.s. peak error in position, $\sigma(A_k)$ is the standard deviation of the

where ρ is the electron density at a distance r from the centre of the atom. The expressions for $\sigma(x)$ and $\sigma(z)$ are similar to that for $\sigma(y)$ for the orthorhombic system but slightly more complex for the monoclinic (Cruickshank, 1949). For A_{hh} we have evaluated the curvature over the three highest values of the electron density ρ_1, ρ_2 and ρ_3 , along the line syntheses, from

$$\partial^2 \rho / \partial r^2 = -\{(\rho_2 - \rho_3) + (\rho_2 - \rho_1)\} / n^2,$$

where n is the summation interval of 3° , and we have

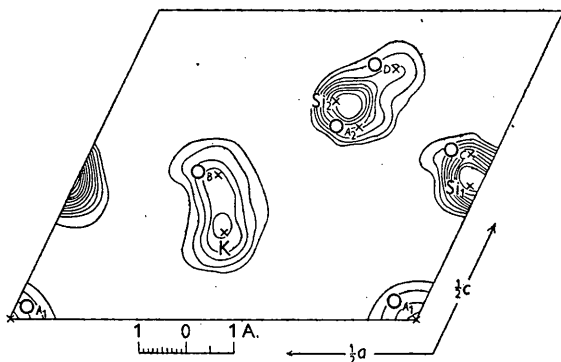


Fig. 1. Electron density for specimen *C*, heat-treated, projected along the b axis. The electron-density contours are drawn to an arbitrary scale.

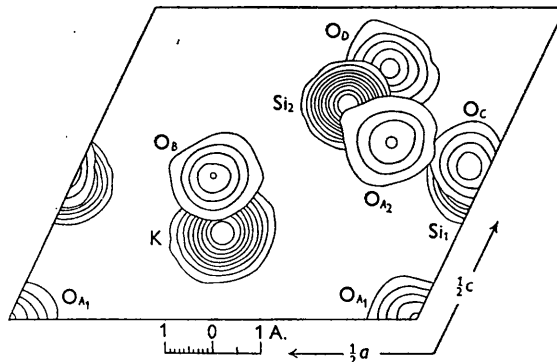


Fig. 2. Superposition of all three-dimensional Fourier sections for specimen *C*, heat-treated, so that atoms all fall into the same quadrant of the unit cell. The electron-density contours are drawn to an arbitrary scale.

r.m.s. slope error and A_{hh} is the central curvature of a peak.

$$\sigma(A_k) = \frac{2\pi}{bV} \left\{ \sum_3 k^2 \Delta F^2 \right\}^{\frac{1}{2}},$$

where ΔF is the difference between $F_{obs.}$ and $F_{calc.}$ in which due account is taken of multiplicity of planes, and the other symbols have their usual significance.

$$A_{hh} = \partial^2 \rho / \partial r^2,$$

taken the mean for the O atoms and the mean for the Si atoms. A_{hh} for the K atom was evaluated from the section through the symmetry plane and a mean was taken of the curvature in the x and z directions. $\sigma(x)$, $\sigma(y)$, $\sigma(z)$ and $\sigma(\rho)$ were calculated for the syntheses made with and without the temperature factor, and the results are set out in Table 6.

Table 6. Analysis of experimental and computational errors in the Fourier syntheses for specimen *C*, heat-treated

		Details of atom peaks			Experimental errors				Computational errors				Total errors (approx.) $\sigma(\text{Si-O})$ (A.) $\times 10^{-4}$					
		$\rho(\text{peak})$ (e.A. ⁻³)	$-A_{hh}$ (e.A. ⁻⁵)	$-A_{hh}$ (mean) (e.A. ⁻⁵)	$\sigma(\rho)$ (e.A. ⁻³) $\times 10^{-3}$	$\sigma(x)$ (A.) $\times 10^{-4}$	$\sigma(y)$ (A.) $\times 10^{-4}$	$\sigma(z)$ (A.) $\times 10^{-4}$	$\sigma(\rho)$ (e.A. ⁻³)		$\sigma(q)$ (A.)							
									Sections $\times 10^{-3}$	Lines $\times 10^{-3}$	Sections $\times 10^{-4}$	Lines $\times 10^{-4}$						
					90				3.9	2.8								
With temperature factor	O _{A1}	2.39	17.6	17.3	280	80	75	85	12.2	11.8	85							
	O _{A2}	2.32	17.2															
	O _B	2.29	16.6															
	O _C	2.37	18.5															
	O _D	2.33	16.7															
	Si ₁	5.48	50.0	50.1									28	26	30	4.2	4.0	
	Si ₂	5.46	50.2															
K	5.85	47.7	47.7		29	27	31	4.7	4.6									
Without temperature factor	O _{A1}	6.47	86.3	84.6	280	80	75	85	12.2	11.8	85							
	O _{A2}	6.32	78.5															
	O _B	6.11	79.6															
	O _C	6.48	104.5															
	O _D	5.96	74.0															
	Si ₁	17.28	260.8										257.8	23	23	23	23	23
	Si ₂	16.89	254.8															
K	16.53	219.2	219.2	27	27	27	27	27										

Although the data in the above table are self-consistent, the absolute values of $\rho(\text{peak})$, A_{hh} and $\sigma(\rho)$ are not correct. This arises because the data were taken from Fourier syntheses in which the effect of multiplicity of planes was taken into account by appropriately weighting the F values so that F_{hkl} occurred only once.

Computational errors due to rounding off at various stages of the calculations may be considered as small experimental errors and treated accordingly, except that account should finally be taken of the method of determining the position of the maxima. If this is done by a three-point parabola method from ρ_1 , ρ_2 and ρ_3 , then

$$\sigma(q) = \frac{\sqrt{3}}{2n} \sigma(\rho_1) \left/ \frac{\partial^2 \rho}{\partial r^2} \right.,$$

where $\sigma(q)$ is the standard deviation of the r.m.s. value of the error in position of the maximum from the highest electron density ρ_2 , and $\sigma(\rho_1)$ is the standard deviation of the error in the electron density ρ_1 . $\sigma(q)$ should finally be converted into $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$. The value of $\sigma(\rho_1)$ depends upon the manner in which the summations were performed. The computational errors for the syntheses in which a temperature factor was introduced are set out in Table 6 and it will be seen that they are negligible when compared with the experimental errors. On the other hand, computation of the latter from $\Delta F = F_{\text{obs.}} - F_{\text{calc.}}$ produces an over-estimate of this error, a fact which is obvious from the remarkably good agreement of the Si-O distances.

7. Discussion of results

Perhaps the most interesting feature of the results for the heat-treated material is the fact that all the Si-O distances are the same. This means that Al atoms are randomly distributed among both Si₁ and Si₂ groups. One interesting feature of the work of Chao *et al.* (1940) on the unheated material was the fact that the Si-O distances around Si₁ were larger than those around Si₂, indicating that Al atoms were randomly distributed among Si₁ groups only, and the Si₂ groups were solely occupied by Si atoms. We have re-examined the earlier work in the light of our own more accurate data and have concluded that the features revealed there are not real. Our evidence for this is as follows:

(1) The work of Chao *et al.* (1940) was based on (*h*0*l*) and (*0kl*) reflexions; the experimental data for which are in slightly better agreement with structure amplitudes calculated from the parameters for the heat-treated material than with their own. Thus for the (*h*0*l*) reflexions $\sum ||F_{\text{obs.}}| - |F_{\text{calc.}}|| \div \sum |F_{\text{obs.}}|$ from the earlier work is 0.15, and when the new set of structure amplitudes is used this ratio is reduced to 0.12. For the new observed and new calculated values and the same reflexions, the ratio is 0.12. For (*0kl*) reflexions the ratio for the earlier work is 0.14, and when the new set of structure amplitudes is used it is 0.13. For the new observed and new calculated values and the same reflexions, the ratio is 0.14. The information from which these values have been derived is set out in Table 7.

(2) In Table 7 it will be seen that more terms have been observed for the heat-treated material than for the unheated. From the (*0kl*) reflexions one derives in

projection the *z* co-ordinate of O₄₂, the true position of which is crucial for the differentiation in sizes of the two sets of tetrahedra suggested for the unheated material by Chao *et al.* (1940). A two-dimensional line synthesis with the (*0kl*) reflexions for the unheated material gives the *z* co-ordinate for O₄₂ as 108.9° which agrees with the value quoted in Table 3. The (*0kl*) reflexions for the heat-treated material give the *z* co-ordinate as 102.1° which agrees with the value obtained from three-dimensional data set out in Table 3. This difference results from the inclusion of additional reflexions observed with the heat-treated material which produce a maximum at 99.2°. If these reflexions are omitted from the calculation for the heat-treated material, the maximum occurs at 109.1° showing that, except for the extra planes, there is no real difference in the two sets of data. By considering calculated *F* values it can be shown that if these planes occur in the unheated material then the O₄₂ position of Chao *et al.* (1940) must be inaccurate, because for either set of calculated structure amplitudes the effect of the extra terms is to lower the *z* co-ordinate of O₄₂ by between 6° and 7°. We have found in photographs taken specially for this purpose that reflexions do occur in the unheated material with relative intensities in agreement with the calculated values given in Table 7 and we conclude that the (*0kl*) reflexions in the earlier work are incomplete.

(3) From the (*0kl*) reflexions one can also determine the *y* co-ordinate of O₄₁ (the only variable parameter for this atom) lying on the digonal axis, and we find a state of affairs similar to that in the case of O₄₂.

(4) For the (*h*0*l*) reflexions twelve extra planes are observed for the heat-treated material, but as the number of common terms is greater than for the (*0kl*) reflexions their effect is not so marked. Re-examination of the (*h*0*l*) reflexions for the unheated material shows that the *x* co-ordinate of the K atom is slightly inaccurate, for it should be 103° instead of 105° as given by Chao *et al.* (1940), a displacement of 0.05 Å. Furthermore, if we subtract the contribution of Si₂ in Fig. 1 we get a peak for the O₄₂ atom at $\hat{x} = 226.6^\circ$ and $\hat{z} = 98.7^\circ$ which is in far better agreement with the new parameters than with the old. Re-examination of the other parameters in this projection does not lead to such definite conclusions, but the general tendency appears to be the same as for the atoms considered.

(5) A survey of the literature shows that in silicates with SiO₄ groups the Si-O distance is usually 1.62 Å. Assuming that this would be the distance in the unheated material between Si₂ and O₄₂, if the Si₂ group were solely Si atoms, we find that the Al-O distance is 1.72 Å. when Al occupies one quarter of the silicon positions in the heat-treated material. This value agrees with the value given for Al in fourfold co-ordination in sillimanite (Hey & Taylor, 1931). If one half the Si₁ positions in the unheated material were occupied by Al atoms, we would expect the distance between Si₁

Table 7. Observed and calculated F 's for specimen C, heat-treated, compared with those for the unheated material published by Chao et al. (1940)

$(\sin \theta/\lambda)^2$	Indices	Heat-treated		Unheated		$(\sin \theta/\lambda)^2$	Indices	Heat-treated		Unheated	
		$F_{obs.}$	$F_{calc.}$	$F_{obs.}$	$F_{calc.}$			$F_{obs.}$	$F_{calc.}$	$F_{obs.}$	$F_{calc.}$
0-006	(001)	24	11	16	23	0-494	(12.0.4)	27	35	0	43
0-014	(201)	119	132	121	137	0-495	(12.0.5)	45	48	0	47
0-017	(200)	41	36	32	48	0-504	(12.0.3)	32	30	0	26
0-023	(202)	148	177	172	167	0-508	(12.0.6)	32	34	0	27
0-024	(002)	166	208	178	198	0-510	(804)	52	66	71	64
0-032	(201)	20	15	17	23	0-514	(10.0.9)	50	48	63	62
0-044	(203)	12	12	0	1	0-529	(606)	54	58	63	51
0-054	(003)	39	24	27	24	0-534	(12.0.7)	26	31	0	17
0-056	(401)	72	71	67	79	0-589	(6.0.11)	49	46	47	49
0-057	(402)	92	83	75	74	0-611	(10.0.3)	37	31	20	19
0-059	(202)	60	60	59	71	0-682	(12.0.10)	35	57	0	54
0-068	(400)	125	135	108	133						
0-069	(403)	98	101	92	93	0-006	(001)	24	11	16	23
0-079	(204)	178	214	191	196	0-006	(020)	37	28	32	33
0-094	(404)	30	34	30	22	0-012	(021)	15	13	0	8
0-097	(004)	31	17	27	20	0-024	(040)	121	126	124	119
0-098	(203)	47	43	51	43	0-024	(002)	166	208	178	198
0-123	(602)	147	155	124	149	0-030	(022)	69	61	64	62
0-124	(205)	41	42	43	45	0-030	(041)	88	87	95	91
0-126	(603)	34	34	27	45	0-053	(060)	171	176	162	187
0-127	(402)	152	162	194	175	0-054	(003)	39	24	27	24
0-130	(405)	112	87	92	81	0-059	(061)	60	62	66	59
0-131	(601)	62	51	73	51	0-077	(062)	102	92	104	96
0-143	(604)	103	101	98	109	0-078	(043)	105	98	101	90
0-149	(204)	115	106	95	108	0-095	(080)	72	71	72	57
0-151	(005)	51	51	52	47	0-097	(004)	31	17	27	20
0-152	(600)	101	103	87	109	0-101	(081)	43	32	48	39
0-170	(605)	71	79	74	67	0-103	(024)	102	95	92	104
0-175	(403)	51	45	51	56	0-107	(063)	59	62	60	53
0-181	(206)	60	61	63	57	0-119	(082)	51	44	53	54
0-185	(601)	50	44	61	42	0-148	(0.10.0)	80	87	83	85
0-212	(205)	48	46	47	39	0-149	(083)	69	54	71	47
0-219	(803)	44	37	48	34	0-150	(064)	64	48	63	54
0-224	(802)	36	42	46	53	0-151	(005)	51	51	52	47
0-226	(804)	26	22	0	9	0-157	(025)	22	55	54	59
0-229	(602)	19	24	20	31	0-172	(0.10.2)	63	61	69	59
0-236	(404)	51	50	52	56	0-175	(045)	50	52	59	49
0-240	(407)	74	68	73	84	0-192	(084)	113	117	108	122
0-242	(801)	48	50	50	52	0-202	(0.10.3)	18	14	0	12
0-245	(805)	64	51	70	71	0-204	(065)	35	24	23	19
0-262	(607)	35	33	40	12	0-213	(0.12.0)	32	11	23	2
0-275	(806)	46	51	50	52	0-219	(0.12.1)	48	54	59	55
0-287	(206)	65	71	72	87	0-223	(026)	41	45	41	51
0-296	(007)	45	36	43	29	0-241	(046)	21	14	0	18
0-308	(405)	19	12	0	11	0-246	(085)	35	32	24	32
0-312	(408)	41	52	45	60	0-267	(0.12.3)	58	62	57	49
0-319	(807)	46	50	51	59	0-270	(066)	38	26	17	25
0-325	(608)	33	44	27	44	0-290	(0.14.0)	33	13	39	20
0-345	(10.0.3)	38	46	37	44	0-296	(007)	45	36	43	29
0-353	(10.0.5)	46	47	53	31	0-296	(0.14.1)	20	29	0	29
0-355	(604)	23	19	0	10	0-302	(027)	41	52	47	47
0-359	(10.0.2)	42	48	51	44	0-310	(0.12.4)	29	15	42	17
0-366	(802)	62	67	65	52	0-312	(086)	61	66	65	65
0-373	(808)	46	43	47	41	0-314	(0.14.2)	38	32	51	33
0-375	(10.0.6)	56	64	63	61	0-320	(047)	50	64	51	54
0-386	(10.0.1)	41	34	25	40	0-349	(067)	24	11	0	16
0-386	(008)	40	41	44	41	0-379	(0.16.0)	83	94	95	86
0-391	(406)	24	27	0	29	0-386	(008)	40	41	44	41
0-397	(409)	58	64	74	67	0-391	(087)	28	30	0	30
0-402	(609)	52	38	53	44	0-403	(0.16.2)	53	50	62	44
0-410	(10.0.7)	37	29	40	37	0-439	(068)	26	29	0	28
0-424	(10.0.0)	52	65	65	68	0-489	(009)	49	53	55	54
0-436	(605)	41	35	40	27	0-509	(0.12.7)	26	35	0	37
0-455	(10.0.8)	34	33	33	24	0-513	(049)	27	28	0	26
0-474	(10.0.1)	30	26	26	20	0-542	(069)	28	17	0	16
0-489	(009)	49	53	55	54	0-576	(0.18.4)	28	45	0	47
0-490	(6.0.10)	25	19	0	7	0-586	(0.14.7)	28	50	0	48

and O_{41} to be 1.66 Å. Thus, if Al atoms replaced Si atoms in only one Si group in orthoclase we would expect the average value of the Si-O distance for the tetrahedra containing Al to be 1.66 Å., and for those free from Al, 1.62 Å. The values given by Chao *et al.* (1940) are 1.68 and 1.58 Å. respectively.

The process of sanidinization results in slight changes in the cell dimensions. It will be seen from Table 2 that a is constant, b increases, and c decreases, and from Table 1 that the refractive indices in these directions are unchanged, decreased and increased respectively. The changes in b and c are not sufficiently large to account for all the change one would expect if sanidinization were due to rearrangement of Al atoms in Si positions. However one would expect that if all the Al atoms were in Si_1 positions before heating and only half after heating, then c would decrease because, in every ring of four tetrahedra parallel to the symmetry plane, equivalent Si_1 positions always lie in the direction of the c axis and are bonded to O_{41} in this direction. As a consequence of half of the Al atoms entering Si_2 positions one would expect b to increase because equivalent Si_2 positions are bonded to O_{42} in that direction. All other short bonds involve both Si_1 and Si_2 in closed-ring structures the adjustment of which would probably account for the smallness of the observed changes in cell dimensions.

The environment of the potassium atom in the heat-treated material is essentially the same as in the unheated, but it is noteworthy that the K- O_{41} distance of 2.698 Å. in the former is very short and only a little greater than the sum of the ionic radii of K^+ and O^{2-} ($1.33 + 1.32 = 2.65$ Å.).

Approximate estimates have been made of the number of electrons included under the electron-density peaks for each of the atoms in the structure of the heat-treated material. The numbers for silicon and oxygen are higher when the estimate is taken in the direction of the Si-O bond than when taken normal to it, and this is to be expected in view of the partially homopolar nature of the bond.

8. Conclusions

It must be concluded that the process of sanidinization may be due to the disordering of the Al atoms as was suggested by the earlier work of Chao *et al.* (1940). Such a disordering would produce a difference in bond lengths of only 0.04 Å., and for this difference to be significant one would require to determine Si-O distances having standard deviations equal to or less than 0.017 Å. (Cruikshank, 1949). This could be attained only by a structural determination for the unheated material almost as accurate as that reported here for the heat-treated material. A more profitable investigation would be the determination of the structure of microcline in view of the symmetry change which must take place when this species of potash-soda feldspar is sanidinized. It is improbable

that the process of sanidinization in specimen *C* is due to an alteration in the position of the cation.

Completeness of experimental data is far more important in achieving an accurate structure than accuracy in intensity measurements.

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