Acta Cryst. (1978). B**34**, 1757–1764

Anorthite Quenched from 1530°C. II. Discussion

BY G. CHIARI, A. FACCHINELLI AND E. BRUNO

Istituto di Mineralogia, Cristallografia e Geochimica dell'Università di Torino, Via San Massimo 24, I-10123 *Torino, Italy*

(*Received* 26 *July* 1977; *accepted* 25 *October* 1977)

A comparison is made between the structure of anorthite quenched from 1530°C and a low-temperature anorthite. The $P\bar{1}$ model of quenched anorthite shows a slightly less pronounced deviation from the $C\bar{1}$ (7 Å) symmetry. In quenched anorthite the values of Al occupancies of the T sites indicate a partial Al–Si disorder. Average Al occupancies are $t_1(0) = 0{\cdot}56$, $t_1(m) = 0{\cdot}46$, $t_2(0) = 0{\cdot}51$, $t_2(m) = 0{\cdot}47$. This result is discussed in terms of the two main hypotheses proposed to explain the Al–Si distribution in feldspars, one involving charge balance and the other involving π bonding. To test the first hypothesis a series of linear regression analyses is carried out to verify in which way the different Ca—O bond-strength sums on the O atoms of each tetrahedron are balanced by the variation in the T—O bond-strength sums. In the two structures this balance takes place in two different ways. In untreated anorthite the balance is obtained by different bond-strength contributions from the T atoms of neighbouring tetrahedra, while the bond-strength sums from internal T atoms of the tetrahedra are constant. In this way no departure from the perfect Al–Si alternation occurs. In quenched anorthite the balance is preferentially obtained by different contributions of the bond-strength sums from the internal T atoms. This implies a variation of the Al occupancy that is highly inversely correlated with the Ca—O bond-strength sums. The Al–Si distribution at room temperature is a consequence of the quenching of the dynamic equilibrium occurring at temperatures near to the melting point. In this equilibrium the length of stay of Al and Si in each T site is controlled by the Ca—O bond-strength sums. The second hypothesis, which implies a correlation between the average T—O—T angles of a tetrahedron and its Al occupancy, is also verified, but only approximately. This correlation, however, might be only a consequence of the correlation between the average T—O—T angles and the Ca—O bond-strength sums.

Introduction

The most important results of the structure refinement of anorthite quenched from 1530°C (AnQ hereinafter) already reported in a previous paper (Bruno, Chiari & Facchinelli, 1976) can be summarized as follows: thermal treatment near to the melting point and subsequent quenching at room temperature causes in anorthite the disappearance of '*c*' and '*d*' reflections and significant modifications of the unit-cell parameters. In spite of the diffractometric evidence the most probable space group is $P\bar{1}$; '*c*' antiphase domains at high temperature are small enough to render undetectable '*c*' and '*d*' reflections. With respect to the untreated anorthite (Wainwright & Starkey, 1971; AnWS hereinafter) the Ca atoms show large differences in thermal parameters, and only minor modifications in the coordination polyhedra. The Al–Si distribution, perfectly ordered in AnWS, presents a small but significant degree of disorder in AnQ. The aim of this paper is to discuss the crystallochemical aspects of the structural modifications induced in anorthite by the thermal treatment at very high temperature.

Chemical composition

In the previous paper the chemical composition of the sample was indirectly determined from the refractive index of the glass obtained by melting, and confirmed from cell dimensions obtained from a powder spectrum. The resulting chemical composition was An_{100}. To verify this result, electron microprobe analyses, before

Table 1. *Chemical composition*

A: untreated, *B*: quenched from 1530°C. The analysts were R. Rinaldi and G. Vezzalini.

Chemical analyses (wt %)			Atomic proportions (O = 8)		
	A	*B*		*A*	*B*
CaO	19·63	19·61	Ca	0·98	0·98
Na_2O	0·20	0·22	Na	0·02	0·02
K_2O	0·05	0·03	K	–	–
FeO*	0·09	–	Fe	–	–
MgO	–	0·03	Mg	–	–
Al_2O_3	36·22	36·18	Al	1·98	1·99
SiO_2	43·65	43·06	Si	2·03	2·01
Total	99·84	99·13			

* All Fe as FeO.

and after the thermal treatment, were carried out in the wavelength-dispersive mode on a fully automated ARL-SEMQ instrument operated at 15 kV, 0·15 μA beam current and a defocused beam (spot size ≃50 μm). Under these conditions no appreciable loss of Na counts was detected during three successive analyses on the same specimen point. Counting times were 2, 20, 2 s for high background, peak and low background respectively. On-line data reduction was based on the Ziebold & Ogilvie (1964) method by the use of Albee & Ray (1970) correction factors. Synthetic plagioclase glasses and natural microcline were used as standards for Si, Al, Ca, Na and K; natural olivine for Fe and Mg. The results shown in Table 1 confirm that the thermal treatment did not produce modifications in the chemical composition, which is An_{98}.

Calcium environment and charge balance

Table 2 shows, for both AnQ and AnWS, the Ca–O distances up to 4 Å as well as the bond strengths calculated following Brown & Kang Kun Wu (1976). In AnQ, the first seven neighbours of Ca(0*i*0), Ca(*z*00) and Ca(*zi*0) are the same as in AnWS; the Ca(000)–O_C(*mzi*0) distance is much shorter than in AnWS, while the Ca(000)–O_C(0*zi*0) distance is longer, which results in the entry of the former O into and the exit of the latter from the seven-coordination sphere. It is worth noting that for these two atoms the T–O–T angles also change from 131·0 to 124·7° for O_C(*mzi*0) and from 130·4 to 132·3° for O_C(0*zi*0) in AnWS and AnQ respectively. This is a substantial change, considering that the T–O_C–T angles are fairly constant in all feldspar structures. A narrower T–O–T angle corresponds to a shorter Ca–O distance and *vice versa*. It seems that the variations of the two Ca–O distances are related to a tilt of the tetrahedra bonded by these O_C atoms. The exchange of these two atoms in the coordination polyhedron of Ca(000) makes its environment more similar to the environment of the other three independent Ca atoms in the unit cell, and could be ascribed to the general phenomenon of the increase of symmetry with heating. This phenomenon can also be verified by the decrease in AnQ of the average departure from 'true' symmetry (splits) reported in Table 3 [see Foit & Peacor (1973) for calculation details].

Table 2. Ca–O *distances and corresponding bond strengths in* AnQ *and* AnWS

Ca–O in Å and *s*(Ca–O) in valence units.

Ca(000)

	AnQ		AnWS	
O	Ca–O	*s*(Ca–O)	Ca–O	*s*(Ca–O)
A(1000)	2·625	0·18	2·607	0·19
A(100*c*)	2·601	0·19	2·514	0·23
A(2000)	2·318	0·35	2·292	0·37
A(200*c*)	(3·812)	(0·02)	(4·010)	(0·02)
A(2*z*0*c*)	(3·509)	(0·04)	(3·521)	(0·04)
B(000*c*)	2·368	0·31	2·377	0·31
B(*m*00*c*)	(3·653)	(0·03)	(3·763)	(0·03)
C(0*zi*0)	(3·215)	(0·06)	3·106	0·07
C(*mzi*0)	3·059	0·08	(3·269)	(0·05)
D(0000)	2·360	0·32	2·389	0·30
D(*m*000)	2·686	0·16	2·538	0·21
⟨Ca^{VII}–O⟩	2·574		2·546	
∑ *s*(Ca^{VII}–O)		1·59		1·68

Ca(0*i*0)

	AnQ		AnWS	
O	Ca–O	*s*(Ca–O)	Ca–O	*s*(Ca–O)
A(10*i*0)	2·395	0·29	2·447	0·26
A(10*ic*)	2·877	0·11	2·816	0·12
A(20*i*0)	2·339	0·33	2·337	0·34
A(20*ic*)	(3·385)	(0·05)	(3·254)	(0·06)
B(00*ic*)	2·417	0·28	2·425	0·27
B(*m*0*ic*)	2·487	0·24	2·492	0·24
C(0*z*00)	(3·754)	(0·03)	(3·797)	(0·02)
C(*mz*00)	2·620	0·18	2·562	0·20
D(00*i*0)	2·479	0·24	2·432	0·27
D(*m*0*i*0)	(3·876)	(0·02)	(3·885)	(0·02)
	2·516		2·502	
		1·68		1·71

Ca(*z*00)

	AnQ		AnWS	
A(1*z*00)	2·466	0·25	2·496	0·23
A(1*z*0*c*)	2·753	0·14	2·732	0·14
A(2*z*00)	2·331	0·34	2·333	0·34
A(2*z*0*c*)	(3·428)	(0·04)	(3·349)	(0·05)
B(0*z*0*c*)	2·436	0·27	2·443	0·26
B(*mz*0*c*)	2·499	0·23	2·493	0·24
C(00*i*0)	(3·793)	(0·02)	(3·841)	(0·02)
C(*m*0*i*0)	2·606	0·19	2·560	0·21
D(0*z*00)	2·427	0·27	2·371	0·31
D(*mz*00)	(3·744)	(0·03)	(3·771)	(0·03)
⟨Ca^{VII}–O⟩	2·503		2·490	
∑ *s*(Ca^{VII}–O)		1·69		1·73

Ca(*zi*0)

	AnQ		AnWS	
A(1*zi*0)	2·446	0·26	2·454	0·26
A(1*zic*)	2·688	0·16	2·586	0·19
A(2*zi*0)	2·331	0·34	2·300	0·37
A(2*zic*)	(3·624)	(0·03)	(3·799)	(0·02)
A(20*ic*)	(3·670)	(0·03)	(3·717)	(0·03)
B(0*zic*)	2·392	0·30	2·405	0·29
B(*mzic*)	(3·192)	(0·06)	(3·301)	(0·05)
C(0000)	(3·614)	(0·03)	(3·516)	(0·04)
C(*m*000)	2·719	0·15	2·833	0·12
D(0*zi*0)	2·410	0·28	2·438	0·27
D(*mzi*0)	2·961	0·09	2·715	0·15
	2·564		2·533	
		1·58		1·64

Table 3. *Average deviation* (Å) *from 'true' symmetry for pseudo-symmetrically related atom pairs*

	c/2		(a + b)/2		(a + b + c)/2	
	AnQ	AnWS	AnQ	AnWS	AnQ	AnWS
Ca	0·688	0·769	0·197	0·193	0·689	0·769
T	0·16	0·19	0·13	0·14	0·14	0·14
O	0·29	0·32	0·14	0·18	0·26	0·26

Looking at Table 2 one notices also that, in general, the first seven neighbours have longer distances in AnQ than in AnWS [see Bruno *et al.* (1976), Table 15]. The sites where this difference is largest are (000) and ($zi0$), which are also characterized by much higher thermal parameters than the other two. Simultaneously the second neighbours (*i.e.* those O atoms with distances from Ca between 3 and 4 Å) have shorter distances in AnQ than in AnWS. Averaging the Ca—O distances up to 4 Å over the four sites gives the following values for AnQ and AnWS, respectively: 2·890 (σ = 0·54) and 2·888 (σ = 0·57) Å. The smaller value of σ (square root of the variance) for AnQ indicates that, due to the thermal treatment, the cavity of the non-tetrahedral cation tends to be less distorted. This does not imply a variation in the coordination number, since the distances from Ca of the second neighbours still remain too long for these O atoms to be considered chemically bonded. The values of bond strength for the second-neighbour O atoms (in parentheses in Table 2) are not reliable, because they were calculated by extrapolating the analytical bond length–bond strength curve, which was derived empirically for Ca with distances shorter than $\simeq$3·1 Å. The use of this curve in the range of distances between 3 and 4 Å highly overestimates the calculated bond strength (Brown, 1977).

It is worth noting that, both in AnQ and in AnWS, adding the O bond-strength contributions to the Ca atom gives a value much smaller than two (formal charge of Ca) for each site. The bond-strength sums shown in Table 2 are calculated taking into account only the first seven neighbours for all four sites. Extending the summation of the bond strength to O atoms up to 4 Å away from Ca would not lead to a significantly better agreement with the theoretical expectation, in spite of the overestimation pointed out above. These large discrepancies between the expected and calculated values could be explained by the fact that the Ca atom is too small for the cavity. This cavity could not become smaller because of the rigidity of the Al—Si framework, already collapsed to the upper limit (Bruno & Facchinelli, 1974). Ca—O bond-strength sums smaller than two are not peculiar to the anorthite structure, but are present in many other Ca-containing structures [for example hexagonal (Takéuchi & Donnay, 1959) and pseudo-orthorhombic (Takéuchi, Haga & Ito, 1973) $CaAl_2Si_2O_8$, danburite (Phillips, Gibbs & Ribbe, 1974), hurlbutite (Lindbloom, Gibbs & Ribbe, 1974), bavenite (Cannillo, Coda & Fagnani, 1966), dehydrated offretite (Mortier, Pluth & Smith, 1976), *etc.*]. It can be supposed that in anorthite as well the values of bond strength calculated from Ca—O distances with these curves are underestimated. In spite of this fact, the bond strength–bond length curves are useful for comparison between the relative values of bond strength for different atoms of the same structure, or for comparison between AnQ and AnWS. In this paper they will be used for these purposes only. The bond-strength sums that are calculated on the T sites on the other hand, are nearly equal to the T formal charge. Therefore, as an obvious consequence of the low value of Ca—O bond strength, the average sum of bond strengths on O atoms is lower than two.

Al–Si distribution

The greatest difference between AnWS and AnQ (Bruno *et al.*, 1976) consists of the Al–Si distribution, which is almost perfectly ordered in AnWS and partially disordered in AnQ. In primitive anorthite, the only possible ordering scheme is the one compatible with the Al-avoidance rule (Loewenstein, 1954) and which shows a perfect Al–Si alternation. As a consequence, every bridging O is bonded to one Al and one Si. Of the 16 T sites, 8 are occupied by Al and the other 8, related to the first by the pseudo-symmetry vectors (**a** + **b**)/2 or **c**/2, are occupied by Si. The pseudo-symmetry vector (**a** + **b** + **c**)/2, on the other hand, relates sites with equal chemistry.

By calculating the averages of the Al occupancy over the sites related by the pseudo-symmetry vectors (**a** + **b** + **c**)/2 and **c**/2, four values are obtained that correspond to the four independent sites [$T_1(0)$, $T_1(m)$, $T_2(0)$, $T_2(m)$] in a 7 Å average structure $C\bar{1}$. These four average values are useful for analysing the disorder observed in AnQ, and for comparing 7 and 14 Å feldspars (Smith & Ribbe, 1969). In AnQ the Al occupancies calculated with the equation proposed by Ribbe & Gibbs (1969), are: $t_1(0) = 0{\cdot}56$; $t_1(m) = 0{\cdot}46$; $t_2(0) = 0{\cdot}51$; $t_2(m) = 0{\cdot}47$. In AnWS all four values are equal to 0·5. The disorder in the Al–Si alternation in AnQ is not random but leads to a preferential concentration of Al in $T_1(0)$ sites. On the other hand, in triclinic alkali feldspars the concentration of Al in $T_1(0)$ is a parameter inversely correlated with the thermal state, which measures the degree of order (*i.e.* thermal treatment at high temperature tends to decrease, or eventually eliminate, such concentration). It seems odd that an increase of temperature induces a modification of Al–Si distribution in AnQ that, analysed in terms of average structure, is opposite to the one induced in alkali feldspars.

The important question to ask is why the variation in the Al–Si distribution caused by the thermal treatment in anorthite is not random, but tends to segregate Al in

$T_1(0)$ sites. As there is this analogy of Al–Si distribution between AnQ and the partially ordered alkali feldspars, it is useful here to review the main hypotheses proposed to explain the Al concentration in $T_1(0)$ for the alkali feldspars. Two basic explanations have been suggested, one involving charge balance, and the other involving π bonding. In the first (Ferguson, Traill & Taylor, 1958; Gait, Ferguson & Coish, 1970; Ribbe, 1975) it was observed that in alkali feldspars, O atoms of tetrahedron $T_1(0)$ receive more bond strength from the non-tetrahedral cation than do the O atoms of the other tetrahedra. Consequently a favourable charge balance is obtained by placing Al in $T_1(0)$. The second explanation (Brown & Gibbs, 1970) proposes that π bonding is a significant factor and states that: 'in framework silicates Si should prefer those tetrahedral sites involved in the widest average T–O–T angles and Al, B, Be and Mg those involved in the narrowest T–O–T angles'. These two hypotheses can be alternative (Baur, 1971) or complementary. Smith (1974) suspects that 'there is merit in both kinds of ideas' and both are more or less empirically confirmed by the data available from the structure refinements of alkali feldspars. It can be supposed that the factor controlling the ordering processes in alkali feldspars is the same one that controls the diffusion of Al and Si in AnQ. To test the first hypothesis one can try to verify in which way (and to what extent) the Ca–O bond-strength sums on the O atoms of the various tetrahedra are balanced by the T–O bond strength, both in AnQ and in AnWS. For that purpose the bond strength–bond length curves, following Brown & Kang Kun Wu (1976), have been used as in the previous paragraph. The four O atoms of each tetrahedron are considered to be a group (with formal charge equal to eight) receiving bond strength both from the 'inside' (T atom) and from the 'outside' (T and Ca atoms). This is because the Al occupancy affects contemporaneously the four O atoms of each tetrahedron. A statistical analysis has been carried out with the following set of variables (each summation is extended to the four O atoms of each tetrahedron):

(*a*) $\sum s(\text{Ca–O})$: bond-strength sums from Ca atoms;

(*b*) $\sum s(\text{T–O})_{\text{in}}$: bond-strength sums from the T atom 'inside' the tetrahedron;

(*c*) $\sum s(\text{T–O})_{\text{out}}$: bond-strength sums from the T atoms 'outside' each tetrahedron.

(*d*) $\sum s(\text{T–O})_{\text{tot}}$: bond-strength sums from both internal and external T atoms [of course, $\sum s(\text{T–O})_{\text{tot}} = \sum s(\text{T–O})_{\text{in}} + \sum s(\text{T–O})_{\text{out}}$].

The correlation of the variable $\sum s(\text{Ca–O})$ with the other three has been tested for AnWS by regression analysis carried out with the *SPSS* program (Nie, Hull, Jenkins, Streinbrenner & Bent, 1975). Obviously for $\sum s(\text{T–O})_{\text{in}}$ and $\sum s(\text{T–O})_{\text{out}}$ the Al-rich and Si-rich tetrahedra have been treated separately.

For AnQ, given that the standard errors on interatomic distances are large, the significance of the parameter variations has been checked as follows: the standard deviation (square root of the variance) of the population of 16 tetrahedra has been compared with the average error on the single values. If the standard deviation is not greater than the standard error, the variation of the parameter is not significant. Consequently, any correlation of that parameter with another variable would be meaningless. Tested in this way the variations on the $\sum s(\text{Ca–O})$ are highly significant, but the other three are not. The same regression analysis carried out for AnWS gives, for AnQ, the predictable result of non-correlation. It should be noted that the high standard errors in AnQ are due to uncertainties in the positions of the split atoms. These uncertainties are derived from the very high correlations in the least-squares refinement matrix between parameters of couples of atoms related by the pseudo-symmetry vector $(\mathbf{a} + \mathbf{b} + \mathbf{c})/2$ (Bruno *et al.*, 1976). Therefore, it should be expected that when the variables referring to the two tetrahedra related by the same pseudo-symmetry vector $(\mathbf{a} + \mathbf{b} + \mathbf{c})/2$ are averaged, the error should decrease by more than $1/\sqrt{2}$ as required by statistics. Some of the regressions carried out on the average of two tetrahedra, are in effect significant when tested at the 95% or even 99% confidence level.

If one looks at the results of the regression analysis shown in Table 4, the following observations can be made. (i) The high inverse correlation between $\sum s(\text{Ca–O})$ and $\sum s(\text{T–O})_{\text{tot}}$ for AnWS simply means that there is good compensation between the contribution of the Ca and T atoms to the bond-strength sums on the four O atoms of each tetrahedron. The slope and intercept of the regression equation approxi-

Table 4. *Linear regression analyses: dependent variable* $\sum s(\text{Ca–O})$

a = slope and b = intercept in the regression equation; N = sample size; r^2 = square correlation coefficient; t = Student's statistic.

		AnQ – average of two tetrahedra					AnWS – single tetrahedra				
Sites	Independent variable	N	a	b	r^2	t	N	a	b	r^2	t
Si-rich	$\sum s(\text{Si–O})_{\text{in}}$	4	−2·16	9·35	0·97	8·4	8	−2·15	9·67	0·23	1·4
	$\sum s(\text{Al–O})_{\text{out}}$	4	−3·43	11·17	0·49	1·4	8	−2·14	7·10	0·84	5·6
Al-rich	$\sum s(\text{Al–O})_{\text{in}}$	4	−1·66	5·82	0·81	2·9	8	−3·46	10·94	0·55	2·7
	$\sum s(\text{Si–O})_{\text{out}}$	4	−2·27	9·79	0·68	2·1	8	−1·58	7·34	0·88	6·6
All	$\sum s(\text{T–O})_{\text{tot}}$	8	−1·40	10·57	0·95	10·7	16	−1·28	9·85	0·79	7·2

Table 5. *Linear regression analyses: dependent variable* $\sum s$(Ca—O)

Average of four tetrahedra related by the pseudo-symmetry vectors (**a** + **b** + **c**)/2 and **c**/2. The variables are defined in the legend to Table 4.

Independent variable	N	AnQ a	AnQ b	AnQ r^2	AnQ t	AnWS a	AnWS b	AnWS r^2	AnWS t
$\sum s(\text{T—O})_{\text{in}}$	4	−1·92	7·51	0·92	4·7	−6·28	22·88	0·55	1·6
$\sum s(\text{T—O})_{\text{out}}$	4	−3·99	14·73	0·85	3·3	−1·80	7·15	0·99	22·6
$\sum s(\text{T—O})_{\text{tot}}$	4	−1·43	10·81	0·99	12·9	−1·55	11·71	0·99	17·2

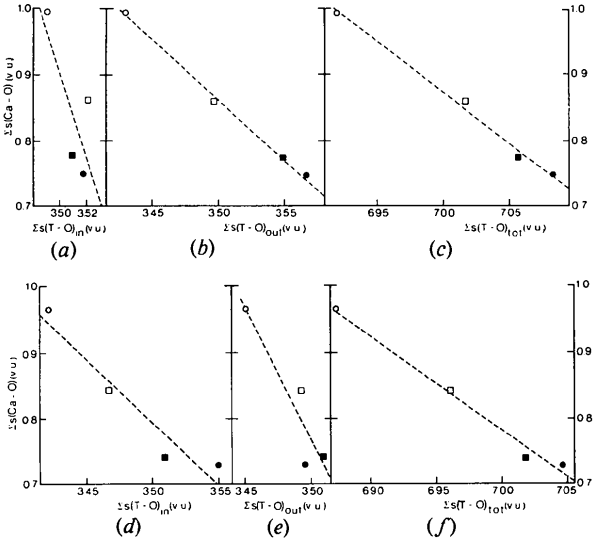

Fig. 1. Ca—O bond-strength sums to the four O atoms of each tetrahedron plotted *vs* T—O bond strength sums; the *T* atoms internal to the tetrahedron are considered in (*a*) and (*d*); the T atoms of neighbouring tetrahedra in (*b*) and (*e*); all T atoms in (*c*) and (*f*). Each point represents the average of the four tetrahedra of the 'average site': $T_1(0)$ open circle, $T_1(m)$ full circle, $T_2(0)$ open square, $T_2(m)$ full square. (*a*), (*b*), (*c*) plots refer to AnWS and (*d*), (*e*), (*f*) to AnQ.

mately verify the charge balance on the four O atoms considered as a group. For AnQ, since the average of two tetrahedra are considered and since it is a disordered structure, this correlation should not be strictly interpreted in terms of local charge balance because it only refers to average situations [see Mackenzie & Smith (1959) for an extensive discussion on this subject]. (ii) In AnWS the low correlation between $\sum s$(Ca—O) and $\sum s(\text{T—O})_{\text{in}}$ is a consequence of the almost perfect Al–Si distribution; a high $\sum s$(Ca—O) − $\sum s(\text{T—O})_{\text{out}}$ correlation is observed, as expected. (iii) In AnQ the interesting result is that the correlation between $\sum s$(Ca—O) and $\sum s(\text{T—O})_{\text{in}}$ is much higher than that between $\sum s$(Ca—O) and $\sum s(\text{T—O})_{\text{out}}$.

To discuss the Al occupancies in the four 'average' sites $T_1(0)$, $T_1(m)$, $T_2(0)$, $T_2(m)$ in AnQ, the average value (over the four tetrahedra of each average site respectively) of the variables (*a*), (*b*), (*c*) and (*d*) should be considered. The results of the regression analysis carried out with the four values so obtained for each variable, both for AnQ and AnWS, are listed in Table 5. Fig. 1 shows the corresponding plots. These results confirm those already obtained for single tetrahedra for AnWS, and for the average of two tetrahedra for AnQ. (For the latter the same comment made on the significance of the correlations for the average of two tetrahedra can be extended to the average of four tetrahedra.)

Looking at the whole series of the regression-analysis results, one can draw the following conclusions: for the average of four tetrahedral sites as well, the different Ca—O bond-strength sums are balanced by different T—O bond strengths. In the two structures this balance takes place in two different ways. In AnWS the bond-strength sum from the T atom 'internal' to the tetrahedron is almost constant and the balance is obtained by different contributions of bond strength from the T atoms of the neighbouring tetrahedra. This can take place because of the distortion of tetrahedra (stress) already pointed out by other authors (*e.g.* Megaw, Kempster & Radoslovich, 1962). In this way no departure from the perfect Al–Si alternation imposed by the Al-avoidance rule is needed. In AnQ the balance of the $\sum s$(Ca—O) variations is preferentially obtained by different contributions of the $\sum s(\text{T—O})_{\text{in}}$, *i.e.* by variation of the average T—O distances of each tetrahedron, and therefore of the Al occupancy. The high correlation between $\sum s$(Ca—O) and Al occupancy evinced in the plot of Fig. 2(*a*) is therefore explainable in terms of charge balance.

A model that could rationalize these results is that at very high temperatures a certain degree of dynamic disorder occurs, which consists of a diffusion and interchange between Al and Si cations, violating the Loewenstein rule. Under these conditions, the 'length of stay' of Al and Si in the various T sites is controlled by the different bond-strength contributions from Ca to the O atoms of each tetrahedron. These contributions are practically the same at high and low temperature [see the structures refined at 800°C by Foit & Peacor (1973) and at 1430°C by Czank (1973)], but only at temperatures near to the melting point can the Al–Si exchanges take place. Al prefers those tetrahedral sites that receive higher bond-strength sums from Ca, and Si

prefers those sites that receive lower bond-strength sums. This equilibrium can be described as a compromise between the tendencies towards three different configurations: (*a*) the perfect Al–Si alternation required by the Al-avoidance rule; (*b*) the Al–Si disorder required by reasons of entropy; (*c*) an Al–Si configuration that would balance the different bond-strength contributions to each tetrahedron from the non-tetrahedral cation, *i.e.* $t_1(0) > t_2(0) > t_2(m) > t_1(m)$. The quenching from 1530°C freezes the dynamic equilibrium described above. The Al occupancies observed in AnQ at room temperature are, consequently, space averages corresponding to the different 'lengths of stay' of Al and Si in the T sites (*i.e.* to the time average) in the dynamic disorder at high temperature. It should be emphasized that the dynamic disorder at high temperature is an equilibrium state, while the static disorder after quenching is obviously a metastable one.

The *d–p* π-bonding hypothesis (Cruickshank, 1961) from which Brown & Gibbs (1970) affirm that the Al occupancies are related to the average T–O–T angles of the various T sites ($\langle$T–O–T$\rangle_{site}$) remains to be discussed. Referring to the dynamic equilibrium described above, one could affirm that the different 'lengths of stay' of the tetrahedral cations in the various T sites at high temperatures (and therefore the Al occupancies at room temperature after quenching) are controlled by the tendency of Si to prefer those tetrahedral sites with wider $\langle$T–O–T$\rangle_{site}$, and of Al to prefer those sites with narrower $\langle$T–O–T$\rangle_{site}$. The experimental data for AnQ are not in contrast to this theory, even though the correlation between $\langle$T–O–T$\rangle_{site}$ and Al occupancy is much lower ($r^2 = 0{\cdot}51$) than that found between $\sum s$(Ca–O) and Al occupancy. In fact, the plot of Fig. 2(*b*) shows that, at least as a general trend, low values of $\langle$T–O–T$\rangle_{site}$ correspond to high values of Al occupancy and *vice versa*. The very high correlation between $\sum s$(Ca–O) and Al occupancy shown in Fig. 2(*a*) ($r^2 = 0{\cdot}997$, significant when tested at the 99·9% level) implies that a low correlation between $\sum s$(Ca–O) and $\langle$T–O–T$\rangle_{site}$ exists, which is very similar to that between $\langle$T–O–T$\rangle_{site}$ and Al occupancy. The corresponding plot is shown in Fig. 2(*c*). This correlation between $\sum s$(Ca–O) and $\langle$T–O–T$\rangle_{site}$, which relates the two variables used to verify the influence of the two

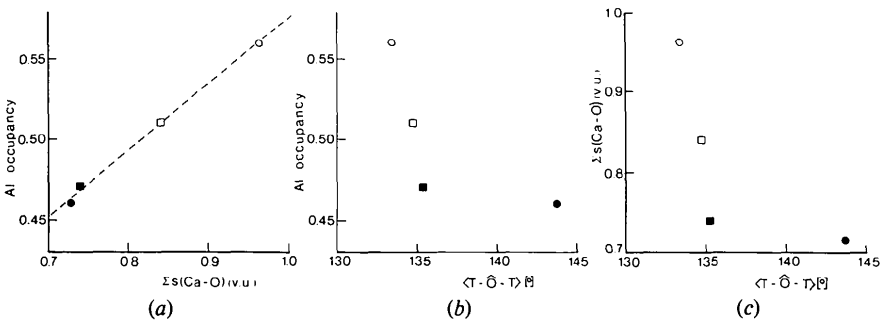

Fig. 2. (*a*) Al occupancies plotted *vs* Ca–O bond strength sums; (*b*) Al occupancies plotted *vs* average T–O–T angles; (*c*) Ca–O bond strength sums plotted *vs* average T–O–T angles. Plots refer to the four 'average sites' of AnQ. Symbols as in Fig. 1.

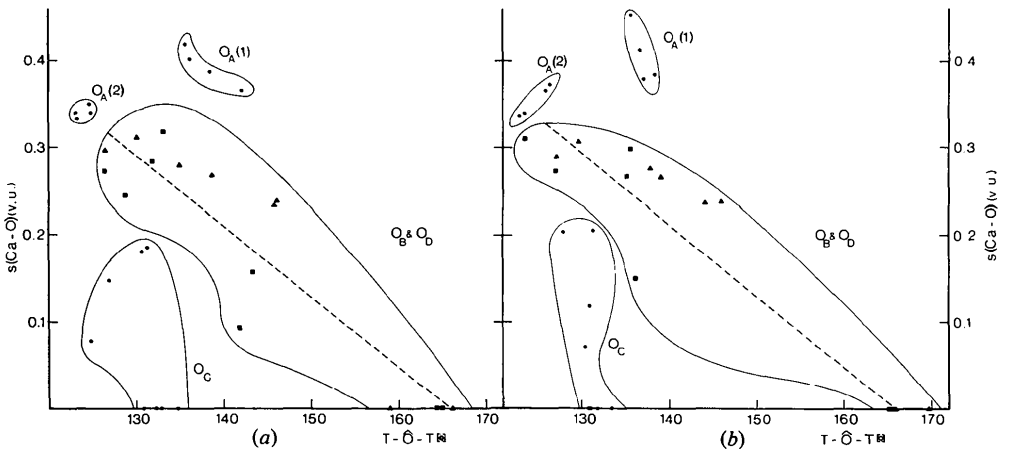

Fig. 3. Total bond strength from Ca to single O atoms plotted *vs* T–O–T angle for (*a*) AnQ and (*b*) AnWS. Different groups of O atoms are surrounded by a full line. The dotted line represents the regression line of the O_B and O_D group. Symbols: O_B triangles, O_D squares, all the remaining O atoms dots.

theories on the Al occupancy, is therefore a critical point which deserves a more detailed analysis. The plot s(Ca—O) *versus* T—O—T angle for single O atoms, shown in Fig. 3(*a*) for AnQ and in Fig. 3(*b*) for AnWS, evinces the low correlation between the two variables already pointed out for the latter compound by several authors. Bearing in mind the structural subdivision of O atoms into types O_A, O_B, O_C and O_D (Megaw *et al.*, 1962) one can observe that in the plot the various types of O atoms are not randomly distributed. For the O_B and O_D there is a good linear correlation ($r^2 = 0{\cdot}84$, $t = 8{\cdot}5$ for AnQ, and $r^2 = 0{\cdot}88$, $t = 10{\cdot}0$ for AnWS) between the two variables. The $O_A(2)$ lie on the best-fit line of the O_B and O_D, while the $O_A(1)$ are grouped in a distinct region of the plot. The latter is also true for the O_C atoms. Keeping in mind this distribution of the various types of O atoms in the plot, one can try to interpret the low correlation of the two variables $\sum s$(Ca—O) and $\langle$T—O—T$\rangle_{\rm site}$. In feldspar structures the formation of coordination polyhedra around the non-tetrahedral cations is conditioned by the peculiarity of the framework. Cations with a large ionic radius (*e.g.* Sr and Ba) can have a coordination polyhedron satisfying the electroneutrality principle without severe modifications of the framework (*i.e.* both *M*—O distances and T—O—T angles show a small range of variation). In anorthite, on the other hand, because the dimension of Ca is too small for the uncollapsed cavity, a coordination polyhedron satisfying the electroneutrality principle can be obtained only through departure of the O atoms from their positions in the feldspar aristotype. Since every O atom is the binding element between two tetrahedra, any movement of the O atoms causes a tilt of the tetrahedra and consequently a variation of the T—O—T angle. It is easy to see that a shift of an O atom towards the Ca narrows the T—O—T angle and *vice versa*. As is well known, not all the T—O—T angles are equally free to vary. In particular, the T—O_C—T angles are quite rigid in all feldspar structures, probably because of the particular position of the O_C atoms in the framework.

In conclusion, in anorthite the variations of Ca—O distances and T—O—T angles must be considered as two aspects of the unitary phenomenon of adaptation of the framework around the non-tetrahedral cation. The very low correlation between s(Ca—O) and T—O—T angles is due to the separation of the T—O—T angles into some groups that are free to vary and into other groups that are not. When the $\sum s$(Ca—O) and $\langle$T—O—T$\rangle_{\rm site}$ are considered, a slight correlation is present because one atom of each of the four types (O_A, O_B, O_C and O_D) belongs to every tetrahedron. Of the four O atoms of each tetrahedron, $O_A(2)$, O_B and O_D have highly correlated values of s(Ca—O) and T—O—T; the presence in the tetrahedra of the $O_A(1)$ and O_C atoms decreases, but does not completely destroy, this good correlation. The $\sum s$(Ca—O) and $\langle$T—O—T$\rangle_{\rm site}$ show, consequently, a similar trend, if not a strong linear dependency.

Given all these considerations it is more evident how the low $\langle$T—O—T$\rangle_{\rm site}$–Al occupancy correlation is merely a corollary of the other two: $\sum s$(Ca—O)–Al occupancy and $\sum s$(Ca—O)–$\langle$T—O—T$\rangle_{\rm site}$. This result does not lead one to reject the validity of the *d–p* π-bonding theory. It simply means that it is not possible to confirm the hypothesis of the influence of the average T—O—T angles on the Al occupancy independent of the Ca—O bond strength, when the average of four tetrahedra are considered. On the other hand, if the implications of the two theories on the single T—O distance are considered [*i.e.* the dependence of T—O from s(Ca—O) for the first theory and from T—O—T angles for the second theory] it is possible to isolate in the anorthite structure typical situations in which the two mechanisms in discussion work separately. Not having to deal with Al occupancy the following analyses have been carried out on AnWS, rather than on AnQ, since AnWS presents lower standard errors on the T—O distances. For example, for the O_C atoms that show almost constant T—O—T angles, 75% of the variation of the average Si—O and Al—O distances can be explained in terms of the s(Ca—O) variation. This confirms the correctness of the bond-strength hypothesis. On the other hand, for those O_B, O_C and O_D atoms that are not coordinated by the Ca in anorthite [and for which, therefore, s(Ca—O) is constantly equal to zero] 60% of the variation of the average T—O distance is explained in terms of the variation of the T—O—T angles. In this case, as well as for some silica polymorphs (Gibbs, Hamil, Louisnathan, Bartell & Yow, 1972; Gibbs, Prewitt & Baldwin, 1978) the influence of the *d–p* π-bonding theory is verified, since the effect of the bond strength from the non-tetrahedral cation is absent.

We are grateful to I. D. Brown for constructive criticism in reading the manuscript; to R. Rinaldi and M. G. Vezzalini for the electron microprobe analysis; to L. Pagani for typing and to L. Turco for drawings. Finally, the Consiglio Nazionale delle Richerche of Italy is acknowledged for financing the electron microprobe laboratory at the Istituto di Mineralogia e Petrografia at the Università di Modena, whose facilities were used in the present work.

References

ALBEE, A. L. & RAY, L. (1970). *Anal. Chem.* **42**, 1408–1414.

BAUR, W. H. (1971). *Am. Mineral.* **56**, 1573–1599.

BROWN, G. E. & GIBBS, G. V. (1970). *Am. Mineral.* **55**, 1587–1607.

BROWN, I. D. (1977). Personal communication.

BROWN, I. D. & KANG KUN WU (1976). *Acta Cryst.* B**32**, 1957–1959.

BRUNO, E., CHIARI, G. & FACCHINELLI, A. (1976). *Acta Cryst.* B**32**, 3270–3280.
BRUNO, E. & FACCHINELLI, A. (1974). *Bull. Soc. Fr. Minéral. Cristallogr.* **97**, 378–385.
CANNILLO, E., CODA, A. & FAGNANI, G. (1966). *Acta Cryst.* **20**, 301–309.
CRUICKSHANK, D. W. J. (1961). *J. Chem. Soc.* pp. 5486–5504.
CZANK, M. (1973). *Strukturen des Anorthits bei höheren Temperaturen.* Thesis, ETH, Zürich.
FERGUSON, R. B., TRAILL, R. J. & TAYLOR, W. H. (1958). *Acta Cryst.* **11**, 331–348.
FOIT, F. F. & PEACOR, D. R. (1973). *Am. Mineral.* **58**, 665–675.
GAIT, R. I., FERGUSON, R. B. & COISH, H. R. (1970). *Acta Cryst.* B**26**, 68–77.
GIBBS, G. V., HAMIL, M. M., LOUISNATHAN, S. J., BARTELL, L. S. & YOW, H. (1972). *Am. Mineral.* **57**, 1578–1613.
GIBBS, G. V., PREWITT, C. T. & BALDWIN, K. J. (1978). *Z. Kristallogr.* In the press.
LINDBLOOM, J. T., GIBBS, G. V. & RIBBE, P. H. (1974). *Am. Mineral.* **59**, 1267–1271.
LOEWENSTEIN, W. (1954). *Am. Mineral.* **39**, 92–96.
MACKENZIE, W. S. & SMITH, J. V. (1959). *Acta Cryst.* **12**, 73–74.
MEGAW, H. D., KEMPSTER, C. J. E. & RADOSLOVICH, E. W. (1962). *Acta Cryst.* **15**, 1017–1035.
MORTIER, W. J., PLUTH, J. J. & SMITH, J. V. (1976). *Z. Kristallogr.* **143**, 319–332.
NIE, N. H., HULL, C. H., JENKINS, J. G., STEINBRENNER, K. & BENT, D. H. (1975). *Statistical Package for the Social Sciences*, 2nd ed. New York: McGraw-Hill.
PHILLIPS, M. W., GIBBS, G. V. & RIBBE, P. H. (1974). *Am. Mineral.* **59**, 79–85.
RIBBE, P. H. (1975). Editor, *Feldspars Mineralogy*, Vol. 2, pp. R1–R51. Blacksburg (VA): Southern Printing Co.
RIBBE, P. H. & GIBBS, G. V. (1969). *Am. Mineral.* **54**, 85–94.
SMITH, J. V. (1974). *Feldspar Minerals.* Vol. 1. *Crystal Structure and Physical Properties.* Berlin: Springer.
SMITH, J. V. & RIBBE, P. H. (1969). *Contrib. Mineral. Petrol.* **21**, 157–202.
TAKÉUCHI, Y. & DONNAY, G. (1959). *Acta Cryst.* **12**, 465–470.
TAKÉUCHI, Y., HAGA, N. & ITO, J. (1973). *Z. Kristallogr.* **137**, 380–398.
WAINWRIGHT, J. E. & STARKEY, J. (1971). *Z. Kristallogr.* **133**, 75–84.
ZIEBOLD, T. O. & OGILVIE, R. E. (1964). *Anal. Chem.* **36**, 322–327.

Acta Cryst. (1978). B**34**, 1764–1770

Neubestimmung der Kristallstruktur von Tetrabutylammoniumhexawolframat

VON JOACHIM FUCHS, WILFRIED FREIWALD UND HANS HARTL

Institut für Anorganische Chemie der Freien Universität Berlin, Fabeckstrasse 34/36, 1000 *Berlin* 33, *Bundesrepublik Deutschland*

(*Eingegangen am* 27. *September* 1977; *angenommen am* 28. *Dezember* 1977)

Tetrabutylammonium hexatungstate, $[(C_4H_9)_4N]_2W_6O_{19}$, crystallizes in the space group $P\bar{1}$ with a = 11·803 (3), b = 12·636 (4), c = 19·592 (15) Å, α = 78·27 (4), β = 73·61 (4), γ = 62·46 (5)°, Z = 2. The structure was determined by difference Fourier methods starting with the W positions given by Henning & Hüllen [*Z. Kristallogr.* (1969), **130**, 162–172]. Least-squares refinement of all atoms except H led to R = 4·2% for 6081 reflexions including 1442 unobserved. In the W_6O_{19} unit six distorted WO_6 octahedra are bonded *via* common edges with one O atom common to each of them. The symmetry of the anion $W_6O_{19}^{2-}$ is nearly $m3m$. Diffuse scattering on films taken with long exposures shows that there exists no intermolecular coupling between the W_6O_{19} units, isolated by the matrix consisting of tetrabutylammonium cations. There is a relation between the W—O distances in polytungstates and the bond orders calculated under the precondition that the W atoms are located in the centres of charge of the WO_6 octahedra.

Einleitung

Der Polyanionentyp $M_6O_{19}^{z-}$ wurde erstmals bei der Strukturuntersuchung des $HNa_7Nb_6O_{19}.15H_2O$ (Lindqvist, 1953) und des $K_8Ta_6O_{19}.16H_2O$ (Lindqvist & Aronsson, 1955) erkannt. Inzwischen hat sich gezeigt, dass dieser Strukturtyp sehr häufig vertreten ist. So wurden bei Versuchen zur Darstellung polysaurer Salze mit organischen Kationen die Tetrabutylammoniumsalze $[N(C_4H_9)_4]_2W_6O_{19}$ (Jahr, Fuchs & Oberhauser, 1968) und $[N(C_4H_9)_4]_2Mo_6O_{19}$ (Fuchs & Jahr, 1968) entdeckt. Die Untersuchung der Anionenstruktur des Wolframats (Henning & Hüllen, 1969) bewies dessen Isotypie mit dem Polyniobation. Die Strukturanalogie