

## The crystal structures of two oligoclases: A comparison with low and high albite \*

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### Auszug

Die Kristallstrukturen von zwei Pegmatit-Oligoklasen  $An_{16}$  und  $An_{28}$  wurden verfeinert mit den Reflexintensitäten vom Typ  $a$ , wodurch sich die Atomparameter, die Bindungslängen und -Winkel der Überlagerungsstruktur ergaben, d.h. gemittelte Al/Si-Verteilungen. Diese sind:  $T_{10}$  0,74, 0,63 Al;  $T_{1m}$  0,11, 0,21 Al;  $T_{20}$  0,16, 0,22 Al und  $T_{2m}$  0,16, 0,22 Al. Die Strukturparameter und Besetzungswahrscheinlichkeiten werden verglichen mit Tief- und Hochalbit, wobei die Daten von RIBBE, MEGAW und TAYLOR sowie WAINWRIGHT und STARKEY benutzt wurden.

Die Na/Ca-Anisotropie und (Na/Ca)-O-Koordinationspolyeder der Oligoklasse sind denjenigen von Hochalbit bemerkenswert ähnlich. Die (Na/Ca)-O-Bindungslängen für jedes der ersten fünf Sauerstoffatome nehmen linear ab mit dem Mittelwert der beiden T-O-Bindungslängen jedes Sauerstoffatoms. Sauerstoffatome in Oligoklasen, die zu  $T_{10}$  gehören, zeigen bemerkenswerte Ähnlichkeiten mit den entsprechenden in Tiefalbit, dagegen sind  $O_A(2)$  (gebunden an  $T_{20}$  und  $T_{2m}$ ) den entsprechenden in Hochalbit ähnlich.

Die einzelnen T-O-Bindungslängen in Feldspäten werden natürlich hauptsächlich durch die Aluminium-Besetzung der Tetraeder bestimmt, obwohl die Bedeutung der Verknüpfungen (d.h. Si-O-Si oder Si-O-Al) sich klar aus den Darstellungen der mittleren T-O-Abstände über den individuellen T-O-Bindungslängen ergibt. Die kleinen Unterschiede in den T-O-T-Winkeln für ein gegebenes Sauerstoffatom stehen bei den vier Natrium-Plagioklasen im umgekehrten Verhältnis zum mittleren Al-Gehalt der beiden T-Plätze.

Obwohl Tiefalbit (Al:Si = 1:3) eine geordnete und Hochalbit eine ungeordnete Al/Si-Verteilung zeigt, und die beiden Tiefoligoklasse unterschiedliche Al/Si-Verhältnisse haben (1,16:2,84) mit einer teilweise ungeordneten Al/Si-Verteilung, scheinen die Gitterparameter  $b$ ,  $c$ ,  $\lambda$ ,  $\alpha^*$ ,  $\gamma$ ,  $\gamma^*$  und  $2\theta_{131} - 2\theta_{1\bar{3}1}$  linear mit der Differenz des Al-Gehaltes der  $T_{10}$ - und  $T_{1m}$ -Plätze zu variieren (wo  $Al_{T,m} = Al_{T_0} = Al_{T_2m}$ ).

\* Dedicated to Professor F. Laves on the occasion of his 65th birthday.

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### Abstract

The crystal structures of two pegmatitic oligoclases,  $An_{16}$  and  $An_{28}$ , have been refined using intensities from the type *a* reflections which give average atomic parameters, bond lengths and angles and thus average Al/Si distributions. These are:  $T_{10}$  0.74, 0.63 Al;  $T_{1m}$  0.11, 0.21 Al;  $T_{20}$  0.16, 0.22 Al and  $T_{2m}$  0.16, 0.22 Al, respectively. Structural and site-occupancy parameters are compared with low and high albite, using data from RIBBE, MEGAW and TAYLOR and WAINWRIGHT and STARKEY.

The Na/Ca anisotropy and (Na/Ca)–O coordination polyhedra of the oligoclases are remarkably similar to those of high albite. The (Na/Ca)–O bond lengths for each of the first five nearest oxygen atoms decrease linearly with the mean of the two T–O bond lengths to each oxygen atom. Those oxygen atoms in the oligoclases bonded to  $T_{10}$  show remarkable similarities to those in low albite, whereas  $O_A(2)$  (bonded to  $T_{20}$  and  $T_{2m}$ ) is like that in high albite.

Aluminum occupancy is, of course, the major factor governing individual T–O bond lengths in feldspars, although the importance of linkage (*i.e.*, Si–O–Si or Si–O–Al) is clearly evidenced in plots of mean T–O distances *vs.* individual T–O bond lengths. The small differences in T–O–T angles for a given oxygen atom amongst the four sodic plagioclases are inversely related to mean Al content of the two T sites.

Although low albite (Al:Si = 1:3) is ordered and high albite disordered with respect to Al/Si and the two low oligoclases have different Al:Si ratios (1.16:2.84 and 1.28:2.72) with partly disordered Al/Si distributions, it appears that the lattice parameters *b*, *c*,  $\alpha$ ,  $\alpha^*$ ,  $\gamma$ ,  $\gamma^*$  and  $2\theta_{131} - 2\theta_{\bar{1}31}$  vary linearly with the *difference* in the Al contents of the  $T_{10}$  and  $T_{1m}$  sites (where  $Al_{T,m} = Al_{T,0} = Al_{T,m}$ ).

### Introduction

The crystal structures of plagioclases of intermediate composition and low structural state are of interest for several reasons. The average distribution of Al and Si among the four non-equivalent tetrahedra of the  $c = 7 \text{ \AA}$  unit cell of albite is relevant to the problem of correlating structural state to certain physical parameters, particularly lattice constants, and to the problem of determining a workable model for the low intermediate structures. Because feldspars are petrologically so important, many efforts to correlate structural state to some easily determined physical parameters have been made. Recent progress toward this end has been made for the alkali feldspars (WRIGHT, 1968; WRIGHT and STEWART, 1968; STEWART and RIBBE, 1969); however, progress for the plagioclase feldspars has been slower, due in part to the lack of information about the average Al/Si distribution in plagioclases of intermediate composition.

RIBBE (1968) suggested that the trend of the  $\Delta 2\theta$  ( $\equiv 2\theta_{131} - 2\theta_{\bar{1}31}$ ) and  $\gamma^*$  curves can be explained in terms of the difference in average

aluminum occupancy between certain tetrahedral sites:

$$\Delta Al \equiv [Al_{T_{10}} + Al_{T_{1m}}] - [Al_{T_{20}} + Al_{T_{2m}}].$$

This has since been modified (with no change in values, since  $Al_{T_{1m}} \approx Al_{T_{20}} \approx Al_{T_{2m}}$  for all plagioclase structures determined to date) to read  $\Delta Al = Al_{T_{10}} - Al_{T_{1m}}$  (STEWART and RIBBE, 1969; RIBBE, STEWART and PHILLIPS, 1970). This implies that similar changes in  $\Delta 2\theta$  may be attained either by going toward the calcium end of the low structural state series or by going isocompositionally to a more disordered state: in both cases the value of  $\Delta Al$  is decreased (see Fig. 3, SMITH and RIBBE, 1969). The convergence of the  $\Delta 2\theta$  curves for low and high structural state plagioclases at anorthite is explained by the fact that the anorthite structure, if based on an average 7 Å cell, would always appear to be completely disordered with  $Al_{T_{10}} = Al_{T_{1m}} = Al_{T_{20}} = Al_{T_{2m}} = 0.5$ . Because both structural state and composition affect the  $\Delta Al$  value, it is appropriate to include high and low albite (RIBBE, MEGAW and TAYLOR, 1969; WAINWRIGHT and STARKEY, in preparation) in this discussion of the oligoclase structures.

Ordered Al/Si distributions are undefined where the Al/Si ratios differ appreciably from 1:3 or 2:2. Models have been suggested by MEGAW (1959, 1960), KOREKAWA and JAGODZINSKI (1967), SMITH and RIBBE (1969) and CINNAMON and BAILEY (in press) to explain the observed diffraction effects—non-Bragg type *e* and *f* maxima and diffuse reflections (see also GAY, 1956; BOWN and GAY, 1958). However, until recently precise data for even the “average” structures of intermediate plagioclases have not been available to test the validity of these models. This study presents the first two of several “average” structure determinations based on  $\alpha$ -type reflections for low plagioclases of intermediate composition<sup>3</sup>.

### Experimental procedure

The sodic oligoclase came from a pegmatite lens in a gneiss from Camedo, Switzerland (specimen no. 294, CORLETT and EBERHARD, 1967). Electron microprobe analysis on various grains from the bulk sample showed a compositional variation of 1–2 mole percent An, the average composition being  $An_{16}Or_2Ab_{82}$ . This analysis is slightly more

<sup>3</sup> Other structures studied include a heated volcanic andesine (KEMPSTER, 1957), which because of its intermediate structural state is not discussed in this paper, and a two-dimensional refinement of a low oligoclase,  $An_{22}$  (WARING, 1961).

calcic than that of CORLETT and EBERHARD (1967) who reported 14.7 mole percent An. Although the composition of this specimen lies near the peristerite solvus which marks the sodium end of the low intermediate structures, single-crystal photographs indicate that the cleavage fragment used was homogeneous.

The calcic oligoclase came from the Mitchell County, North Carolina, pegmatite. Its composition as determined by electron microprobe analysis is  $\text{An}_{28}\text{Or}_2\text{Ab}_{70}$ . The unit cell parameters and  $\Delta 2\theta$  ( $= 2\theta_{131} - 2\theta_{1\bar{3}1}$ ) indicate that both these pegmatitic oligoclases have a "low" structural state (*cf.* NISSEN, 1969; BAMBAUER *et al.*, 1967). The term "low" is used in preference to "ordered" because in the strictest sense of the word, perfect Al/Si order is not possible for plagioclases of intermediate composition.

Unit-cell parameters for both samples were determined by Dr. D. B. STEWART of the U.S.G.S. using powder techniques; however,  $\text{An}_{16}$  was refined with cell parameters determined by least-squares methods

Table 1. *Unit-cell parameters*

Estimated standard errors are in brackets and refer to the last decimal place

	$\text{An}_{16}$		$\text{An}_{28}$	
	(Weissenberg) <sup>1</sup>	(Powder) <sup>2</sup>	(Powder) <sup>2</sup>	(Powder) <sup>2</sup>
<i>a</i>	8.1553 (3) Å	8.154 (3) Å	8.169 (3) Å	8.169 (3) Å
<i>b</i>	12.8206 (5)	12.823 (2)	12.851 (4)	12.851 (4)
<i>c</i>	7.1397 (4)	7.139 (1)	7.124 (2)	7.124 (2)
$\alpha$	93° 57.9 (4)′	94° 3.5 (1.4)′	93° 37.8 (1.8)′	93° 37.8 (1.8)′
$\beta$	116° 28.5 (2)′	116° 29.7 (0.8)′	116° 24.0 (1.2)′	116° 24.0 (1.2)′
$\gamma$	88° 37.9 (3)′	88° 35.3 (1.2)′	89° 27.4 (1.2)′	89° 27.4 (1.2)′
<i>a</i> *	0.136990 (4) Å <sup>-1</sup>	0.13704 (5) Å <sup>-1</sup>	0.13669 (5) Å <sup>-1</sup>	0.13669 (5) Å <sup>-1</sup>
<i>b</i> *	0.078189 (3)	0.07818 (3)	0.07799 (2)	0.07799 (2)
<i>c</i> *	0.156807 (5)	0.15686 (3)	0.15705 (3)	0.15705 (3)
$\alpha^*$	86° 15.1 (3)′	86° 10.1 (1.8)′	86° 13.2 (1.8)′	86° 13.2 (1.8)′
$\beta^*$	63° 33.2 (2)′	63° 32.2 (1.8)′	63° 34.8 (1.2)′	63° 34.8 (1.2)′
$\gamma^*$	89° 33.3 (2)′	89° 33.3 (1.2)′	88° 48.0 (1.2)′	88° 48.0 (1.2)′
<i>V</i>	666.59 (5) Å <sup>3</sup>	666.4 (2) Å <sup>3</sup>	668.4 (2) Å <sup>3</sup>	668.4 (2) Å <sup>3</sup>
$\Delta 2\theta_{\text{calc}}^3$	1.42°		1.65°	1.65°
Space group	$C\bar{1}$		$C\bar{1}$	

<sup>1</sup> Determined by single-crystal precision back-reflection Weissenberg methods.

<sup>2</sup> Determined on bulk specimen by powder methods (courtesy D. B. STEWART, U.S.G.S.).

<sup>3</sup> For  $\text{CuK}\alpha$  radiation.

(BURNHAM, 1962) using 120 reflections from precision back-reflection Weissenberg photographs of the selected crystal. The  $2\theta$  values listed in Table 1 were calculated from the unit-cell parameters listed in the same table.

Intensity data for type *a* reflections only were collected with a scintillation counter on an equi-inclination Weissenberg diffractometer. Reflections were recorded on a strip chart using  $\text{MoK}\alpha$  radiation. The intensities were integrated, corrected for Lorentz, polarization and absorption effects and converted to  $|F_{\text{obs}}|$ . The absorption corrections were made using a cylindrical approximation for  $\text{An}_{16}$  ( $\mu R = 0.086$ ) and a spherical approximation for  $\text{An}_{28}$  ( $\mu R = 0.105$ ). Both refinements were obtained using the full-matrix least-squares program, ORFLS (BUSING, MARTIN and LEVY, 1962). The structural amplitudes were weighted according to the scheme proposed by HANSON (1965) and the variation of  $\langle w\Delta F^2 \rangle$  over the entire range of  $|F_{\text{obs}}|$  was minimized as suggested by CRUICKSHANK (1965).

Atomic scattering factors were taken from Vol. III of *International tables for x-ray crystallography* for  $\text{An}_{28}$  and from CROMER and WABER (1965) for  $\text{An}_{16}$ . In both cases the scattering curves for Na/Ca and Al/Si were weighted according to the chemical analysis.

For  $\text{An}_{16}$  three refinements (isotropic, anisotropic, only Na/Ca anisotropic) were obtained using 934 non-zero structural amplitudes of the type  $0kl-8kl$ . The isotropic, Na/Ca anisotropic, and full aniso-

Table 2. *Final positional parameters*

Estimated standard errors are in brackets and refer to the last decimal place

Atom	$\text{An}_{16}$			$\text{An}_{28}$		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Na/Ca	.2685 (3)	.9949 (2)	.1423 (4)	.2689 (4)	.0040 (4)	.1331 (6)
T <sub>1</sub> 0	.0079 (2)	.1673 (1)	.2104 (2)	.0078 (2)	.1658 (1)	.2124 (3)
T <sub>1</sub> <i>m</i>	.0035 (2)	.8189 (1)	.2347 (2)	.0035 (2)	.8178 (1)	.2328 (3)
T <sub>2</sub> 0	.6902 (2)	.1099 (1)	.3160 (2)	.6882 (2)	.1095 (1)	.3169 (3)
T <sub>2</sub> <i>m</i>	.6823 (2)	.8806 (1)	.3589 (2)	.6824 (2)	.8796 (1)	.3574 (3)
O <sub>A</sub> (1)	.0052 (5)	.1312 (2)	.9716 (5)	.0049 (7)	.1304 (4)	.9766 (7)
O <sub>A</sub> (2)	.5891 (4)	.9954 (2)	.2797 (5)	.5871 (5)	.9938 (3)	.2789 (7)
O <sub>B</sub> (0)	.8125 (5)	.1090 (2)	.1900 (5)	.8135 (6)	.1072 (3)	.1903 (7)
O <sub>B</sub> ( <i>m</i> )	.8190 (5)	.8513 (3)	.2532 (5)	.8189 (7)	.8511 (4)	.2507 (9)
O <sub>C</sub> (0)	.0143 (4)	.2983 (2)	.2740 (5)	.0148 (6)	.2949 (3)	.2771 (7)
O <sub>C</sub> ( <i>m</i> )	.0209 (5)	.6916 (2)	.2246 (5)	.0188 (6)	.6902 (3)	.2187 (7)
O <sub>D</sub> (0)	.2032 (5)	.1092 (2)	.3871 (5)	.2007 (6)	.1091 (3)	.3866 (7)
O <sub>D</sub> ( <i>m</i> )	.1854 (5)	.8673 (2)	.4334 (5)	.1878 (6)	.8670 (4)	.4320 (7)

Table 3. *Temperature factors\**  
 Estimated standard errors are in brackets and refer to the last decimal place

Am16

Atom	isotropic $B$	anisotropic					
		$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Na/Ca	4.8 (1) Å <sup>2</sup>	0.0082 (3)	0.0138 (3)	0.0296 (8)	0.0004 (3)	0.0033 (5)	- 0.0147 (4)
T <sub>10</sub>	1.13 (5)	.0060 (3)	.0018(1)	.0067 (3)	- .0006 (1)	.0028 (2)	.0003 (1)
T <sub>1m</sub>	0.85 (5)	.0045 (3)	.0013 (1)	.0050 (3)	.0003 (1)	.0020 (2)	.0003 (1)
T <sub>20</sub>	0.92 (5)	.0044 (2)	.0012 (1)	.0059 (3)	- .0002 (1)	.0020 (2)	.0001 (1)
T <sub>2m</sub>	0.87 (5)	.0038 (2)	.0012 (1)	.0060 (3)	.0001 (1)	.0019 (2)	.0002 (1)
O <sub>A</sub> (2)	1.4 (1)	.0054 (6)	.0016 (2)	.0087 (7)	- .0003 (2)	.0023 (5)	.0007 (3)
O <sub>B</sub> (0)	1.6 (1)	.0073 (7)	.0025 (2)	.0105 (9)	- .0006 (3)	.0041 (6)	- .0002 (3)
O <sub>B</sub> (m)	2.1 (1)	.0105 (8)	.0029 (2)	.0161 (9)	.0007 (3)	.0084 (7)	.0002 (3)
O <sub>C</sub> (0)	1.6 (1)	.0065 (6)	.0025 (2)	.0101 (7)	- .0009 (3)	.0032 (6)	- .0008 (3)
O <sub>C</sub> (m)	1.6 (1)	.0083 (7)	.0024 (2)	.0102 (8)	.0005 (3)	.0037 (6)	.0001 (3)
O <sub>D</sub> (0)	1.5 (1)	.0079 (7)	.0023 (2)	.0083 (7)	.0002 (3)	.0028 (6)	.0006 (3)
O <sub>D</sub> (m)	1.6 (1)	.0082 (7)	.0022 (2)	.0100 (8)	.0000 (3)	.0024 (6)	- .0002 (3)

\* These temperature factors were obtained using an average scattering factor for all four tetrahedral sites.

Table 3. (Continued)  
An<sub>28</sub>

Atom	isotropic <i>B</i>	anisotropic					
		$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Na/Ca	5.4 (2) Å <sup>2</sup>	0.0060 (4)	0.0189 (5)	0.0374 (13)	0.0011 (4)	0.0010 (6)	-0.0219 (7)
T <sub>10</sub>	0.92 (4)	.0053 (2)	.0017 (1)	.0051 (3)	-.0005 (1)	.0023 (3)	.0003 (1)
T <sub>1m</sub>	0.85 (4)	.0044 (2)	.0016 (1)	.0042 (3)	.0005 (1)	.0015 (2)	.0004 (1)
T <sub>20</sub>	0.81 (4)	.0039 (2)	.0012 (1)	.0051 (3)	.0000 (1)	.0016 (2)	.0004 (1)
T <sub>2m</sub>	0.82 (4)	.0038 (2)	.0013 (1)	.0053 (3)	.0001 (1)	.0019 (2)	.0003 (1)
O <sub>A</sub> (1)	2.0 (1)	.0110 (8)	.0030 (3)	.0079 (10)	.0006 (4)	.0044 (8)	.0011 (4)
O <sub>A</sub> (2)	1.0 (1)	.0050 (6)	.0015 (2)	.0078 (9)	-.0004 (3)	.0025 (6)	.0010 (3)
O <sub>B</sub> (0)	1.6 (1)	.0080 (7)	.0024 (2)	.0104 (11)	-.0009 (3)	.0045 (8)	.0002 (4)
O <sub>B</sub> (m)	2.3 (1)	.0094 (9)	.0031 (3)	.0169 (14)	.0006 (4)	.0073 (9)	.0007 (5)
O <sub>C</sub> (0)	1.7 (1)	.0074 (7)	.0023 (2)	.0102 (10)	-.0007 (3)	.0025 (8)	.0004 (4)
O <sub>C</sub> (m)	1.5 (1)	.0075 (7)	.0025 (2)	.0080 (9)	.0015 (13)	.0017 (7)	-.0001 (4)
O <sub>D</sub> (0)	1.3 (1)	.0058 (6)	.0024 (2)	.0073 (9)	.0005 (3)	.0019 (7)	.0004 (4)
O <sub>D</sub> (m)	1.7 (1)	.0071 (3)	.0030 (3)	.0073 (10)	-.0006 (3)	.0088 (8)	-.0008 (4)

Table 4. (Na/Ca)—O *interatomic distances*

Estimated standard errors are in brackets and refer to the last decimal place. All interatomic distances and angles were calculated using ORFFE (BUSING, MARTIN and LEVY, 1964)

Distance	An <sub>16</sub>	An <sub>28</sub>
(Na/Ca)—O <sub>A</sub> (1)	2.574(4) Å	2.561(7) Å
—O <sub>A</sub> (1)	2.633(4)	2.635(7)
—O <sub>A</sub> (2)	2.348(4)	2.338(5)
—O <sub>B</sub> (0)	2.459(4)	2.455(6)
—O <sub>B</sub> ( <i>m</i> )	3.358(5)	3.215(8)
—O <sub>C</sub> (0)	3.108(4)	3.275(7)
—O <sub>C</sub> ( <i>m</i> )	3.148(5)	3.012(7)
—O <sub>D</sub> (0)	2.434(4)	2.443(6)
—O <sub>D</sub> ( <i>m</i> )	3.039(5)	3.133(8)

Table 5. T—O *bond lengths*

Estimated standard errors are in brackets and refer to the last decimal place

	An <sub>16</sub>	An <sub>28</sub>		An <sub>16</sub>	An <sub>28</sub>
T <sub>1</sub> 0—O <sub>A</sub> (1)	1.726(3) Å	1.702(5) Å	T <sub>2</sub> 0—O <sub>A</sub> (2)	1.648(3) Å	1.655(4) Å
—O <sub>B</sub> (0)	1.718(3)	1.702(5)	—O <sub>B</sub> (0)	1.614(4)	1.636(5)
—O <sub>C</sub> (0)	1.706(3)	1.689(5)	—O <sub>C</sub> ( <i>m</i> )	1.628(4)	1.639(5)
—O <sub>D</sub> (0)	1.722(3)	1.705(5)	—O <sub>D</sub> ( <i>m</i> )	1.625(3)	1.626(5)
Mean	1.718	1.700	Mean	1.629	1.638
T <sub>1</sub> <i>m</i> —O <sub>A</sub> (1)	1.618(3) Å	1.645(5) Å	T <sub>2</sub> <i>m</i> —O <sub>A</sub> (2)	1.656(3) Å	1.663(4) Å
—O <sub>B</sub> ( <i>m</i> )	1.610(4)	1.620(5)	—O <sub>B</sub> ( <i>m</i> )	1.627(4)	1.634(6)
—O <sub>C</sub> ( <i>m</i> )	1.635(3)	1.643(5)	—O <sub>C</sub> (0)	1.612(3)	1.624(5)
—O <sub>D</sub> ( <i>m</i> )	1.626(3)	1.639(5)	—O <sub>D</sub> (0)	1.625(3)	1.637(5)
Mean	1.622	1.637	Mean	1.630	1.639

tropic refinements yielded unweighted residuals of 0.078, 0.040 and 0.035, respectively. The positional parameters from all three refinements are within two standard deviations of one another; however, the standard errors of the two anisotropic refinements are only about half as large as those of the isotropic. HAMILTON's (1965) *R*-factor ratio test indicates the complete anisotropic refinement is not significantly better than the refinement obtained by considering *only* the Na/Ca cation as anisotropic, and indeed both anisotropic refinements yield T—O distances that differ by 0.002 Å or less. However, all An<sub>16</sub> parameters quoted in this paper are from the full anisotropic refinement.



Table 6. O—O interatomic distances  
 Estimated standard errors are in brackets and refer to the last decimal place

Tetrahedron	<i>A</i> <sub>116</sub>						Tetrahedral mean
	O <sub>A</sub> —O <sub>B</sub>	O <sub>A</sub> —O <sub>C</sub>	O <sub>A</sub> —O <sub>D</sub>	O <sub>B</sub> —O <sub>C</sub>	O <sub>B</sub> —O <sub>D</sub>	O <sub>C</sub> —O <sub>D</sub>	
T <sub>10</sub>	2.692(5) Å	2.913(4) Å	2.704(4) Å	2.841(4) Å	2.852(5) Å	2.808(5) Å	2.802 Å
T <sub>1<i>m</i></sub>	2.697(5)	2.706(4)	2.693(4)	2.650(4)	2.682(5)	2.645(5)	2.649
T <sub>20</sub>	2.673(4)	2.582(5)	2.641(4)	2.685(5)	2.678(4)	2.687(4)	2.658
T <sub>2<i>m</i></sub>	2.659(4)	2.697(4)	2.659(4)	2.661(5)	2.667(4)	2.707(4)	2.660
Mean	2.658	2.702	2.652	2.709	2.720	2.712	

Tetrahedron	<i>A</i> <sub>138</sub>						Tetrahedral mean
	O <sub>A</sub> —O <sub>B</sub>	O <sub>A</sub> —O <sub>C</sub>	O <sub>A</sub> —O <sub>D</sub>	O <sub>B</sub> —O <sub>C</sub>	O <sub>B</sub> —O <sub>D</sub>	O <sub>C</sub> —O <sub>D</sub>	
T <sub>10</sub>	2.653(8) Å	2.887(7) Å	2.665(6) Å	2.809(6) Å	2.832(6) Å	2.781(6) Å	2.771 Å
T <sub>1<i>m</i></sub>	2.622(8)	2.728(7)	2.625(7)	2.683(7)	2.703(7)	2.671(6)	2.672
T <sub>20</sub>	2.673(6)	2.601(6)	2.655(6)	2.707(7)	2.694(7)	2.715(7)	2.674
T <sub>2<i>m</i></sub>	2.686(7)	2.626(6)	2.667(6)	2.682(7)	2.677(8)	2.719(6)	2.676
Mean	2.659	2.710	2.653	2.720	2.727	2.722	

Table 7. *Interatomic angles*

Estimated standard errors are in brackets and refer to the last decimal place

T-O-T angles		
Angle	An <sub>16</sub>	An <sub>28</sub>
T <sub>1</sub> 0 - O <sub>A</sub> (1) - T <sub>1</sub> m	141.2(2)°	140.7(3)°
T <sub>2</sub> 0 - O <sub>A</sub> (2) - T <sub>2</sub> m	129.0(2)	128.5(3)
T <sub>1</sub> 0 - O <sub>B</sub> (0) - T <sub>2</sub> 0	138.9(2)	138.2(3)
T <sub>1</sub> m - O <sub>B</sub> (m) - T <sub>2</sub> m	159.7(2)	159.3(3)
T <sub>1</sub> 0 - O <sub>C</sub> (0) - T <sub>2</sub> m	130.4(2)	130.6(3)
T <sub>1</sub> m - O <sub>C</sub> (m) - T <sub>2</sub> 0	134.7(2)	134.0(3)
T <sub>1</sub> 0 - O <sub>D</sub> (0) - T <sub>2</sub> m	133.8(2)	133.6(3)
T <sub>1</sub> m - O <sub>D</sub> (m) - T <sub>2</sub> 0	151.4(3)	151.0(3)
Mean	139.9	139.5
O-T-O angles		
Angle	An <sub>16</sub>	An <sub>28</sub>
O <sub>A</sub> (1) - T <sub>1</sub> 0 - O <sub>B</sub> (0)	102.8(2)°	102.4(3)°
- O <sub>C</sub> (0)	116.1(2)	116.7(3)
- O <sub>D</sub> (0)	103.3(2)	102.9(3)
O <sub>B</sub> (0) - - O <sub>C</sub> (0)	112.1(2)	111.9(2)
- O <sub>D</sub> (0)	112.0(2)	112.5(2)
O <sub>C</sub> (0) - - O <sub>D</sub> (0)	110.0(2)	110.0(2)
Mean	109.4	109.4
O <sub>A</sub> (1) - T <sub>1</sub> m - O <sub>B</sub> (m)	107.8(2)°	106.8(3)°
- O <sub>C</sub> (m)	112.6(2)	112.1(3)
- O <sub>D</sub> (m)	106.7(2)	106.1(3)
O <sub>B</sub> (m) - - O <sub>C</sub> (m)	109.5(2)	110.6(3)
- O <sub>D</sub> (m)	111.9(2)	112.1(3)
O <sub>C</sub> (m) - - O <sub>D</sub> (m)	108.4(2)	108.9(2)
Mean	109.5	109.5
O <sub>A</sub> (2) - T <sub>2</sub> 0 - O <sub>B</sub> (0)	110.0(2)°	108.6(2)°
- O <sub>C</sub> (m)	104.0(2)	104.3(2)
- O <sub>D</sub> (m)	107.6(2)	108.0(3)
O <sub>B</sub> (0) - - O <sub>C</sub> (m)	111.8(2)	111.5(3)
- O <sub>D</sub> (m)	111.6(2)	111.4(3)
O <sub>C</sub> (m) - - O <sub>D</sub> (m)	111.4(2)	112.6(3)
Mean	109.4	109.3
O <sub>A</sub> (2) - T <sub>2</sub> m - O <sub>B</sub> (m)	108.2(2)°	109.1(3)°
- O <sub>C</sub> (0)	105.8(2)	106.0(2)
- O <sub>D</sub> (0)	108.3(2)	107.8(2)
O <sub>B</sub> (m) - - O <sub>C</sub> (0)	110.5(2)	110.9(3)
- O <sub>D</sub> (0)	110.2(2)	109.9(3)
O <sub>C</sub> (0) - - O <sub>D</sub> (0)	113.5(2)	113.0(3)
Mean	109.4	109.5

Table 8. *Aluminum occupancy of the tetrahedral sites\**

Structure	Al/(Al + Si) occupancy			
	T <sub>10</sub>	T <sub>1m</sub>	T <sub>20</sub>	T <sub>2m</sub>
Low albite (RIBBE <i>et al.</i> , 1969)	.92 <sub>8</sub>	.03 <sub>3</sub>	.06 <sub>6</sub>	.04 <sub>6</sub>
An <sub>16</sub>	.74 <sub>4</sub>	.11 <sub>2</sub>	.15 <sub>8</sub>	.16 <sub>5</sub>
An <sub>28</sub>	.62 <sub>5</sub>	.21 <sub>1</sub>	.21 <sub>7</sub>	.22 <sub>4</sub>
High albite (RIBBE <i>et al.</i> , 1969)	.28 <sub>3</sub>	.25 <sub>7</sub>	.22 <sub>4</sub>	.25 <sub>0</sub>

\* All values were calculated using the equation

$$\text{Al}/(\text{Al} + \text{Si}) = 6.58 [\langle \text{T}-\text{O} \rangle - 1.605] \text{ (RIBBE and GIBBS, 1969).}$$

Intensity data for An<sub>28</sub> were collected from two crystals. More than six hundred reflections  $0kl-4kl$  were measured on the first crystal and more than nine hundred reflections  $hk0-hk5$  on the second. The two sets of data were initially scaled together using fifty medium-intensity structural amplitudes. Separate refinements of the structure produced similar atomic parameters for each set of data, although standard errors were large. In the final analysis the data sets were combined, but two scale factors were maintained throughout. The final residuals for the isotropic and anisotropic refinements were 0.124 and 0.061 respectively, using approximately 1400 non-zero structural amplitudes. Data obtained from the refinements are presented as follows:

Atomic coordinates (Table 2), temperature factors (Table 3), (Na/Ca—O distances (Table 4), T—O distances (Table 5), O—O distances (Table 6), interatomic angles (Table 7) and aluminum occupancy of the tetrahedral sites (Table 8).

### Discussion

There are two unique Al/Si ordering schemes in plagioclase, low albite (Al:Si = 1:3) and anorthite (Al:Si = 2:2). In low albite Al is concentrated in the T<sub>10</sub> site with Si in T<sub>1m</sub>, T<sub>20</sub> and T<sub>2m</sub> (RIBBE, MEGAW and TAYLOR, 1969) whereas in anorthite Al and Si alternate in the tetrahedral framework, thereby doubling the 7 Å *c* axis of albite (KEMPSTER, MEGAW and RADOSLOVICH, 1962; MEGAW, KEMPSTER and RADOSLOVICH, 1962; WAINWRIGHT and STARKEY, 1970). Both ordered structures illustrate the Al-avoidance principle (LOEWEN-

STEIN, 1954) which states that Al—O—Al linkages are energetically unfavorable in aluminosilicate-framework structures. As evidenced by exsolution in the peristerite range,  $An_{02}$ — $An_{15}$ , low albite does not accept Al in excess of 1.00, because the additional Al would have to share an oxygen atom which is bonded to Al in  $T_{10}$ . Likewise the anorthite ordering scheme is maintained at temperatures up to the melting point (LAVES and GOLDSMITH, 1955), because any disordering of Al/Si would of necessity produce Al—O—Al linkages.

Plagioclases with intermediate compositions cannot be ordered in the sense of low albite or anorthite because there are non-integral numbers of Al and Si to be distributed over four tetrahedral sites. Of course, ordering schemes can be imagined which would involve large supercells (DEVORE, 1956) but there is no diffraction evidence for these. In fact Al/Si ordering in annealed "low-temperature" intermediate plagioclases probably takes place within albite- and anorthite-like domains which account for the non-Bragg diffraction maxima (type *e* and *f* reflections) observed in the composition range  $An_{15}$ — $An_{75}$  (see SMITH and RIBBE, 1969). CINNAMON and BAILEY (in press) have measured the separation and diffuseness of the *e* reflections along the *x*, *y* and *z* crystallographic directions and have deduced the average sizes of the antiphase domains which vary with composition (see their Fig. 4).

Since the *e* reflections in our oligoclases were extremely diffuse, no attempt was made to interpret the nature of their domain structures. However, based on CINNAMON and BAILEY's results we have approximated the average domain sizes for  $An_{16}$  and  $An_{28}$  to be  $4 \times 75 \times 2$  and  $5 \times 40 \times 3$  unit cells, respectively, along the *x*, *y* and *z* crystallographic directions.

There are as yet no data on the nature of the short-range (local) order within these antiphase domains (this is one of the most challenging problems in feldspar crystal chemistry), and until recently there was no data on the long range (distant) order of any low plagioclases of intermediate composition.

An unpublished two-dimensional refinement of  $An_{22}$  was completed by WARING in 1961, but experience has shown that two-dimensional refinements of feldspars produce somewhat misleading results (*e.g.* low albite: compare the two-dimensional refinement by FERGUSON, TRAILL and TAYLOR, 1958 with the three-dimensional by RIBBE, MEGAW and TAYLOR, 1969). Thus a preliminary three-dimensional refinement of  $An_{28}$  was reported by COLVILLE and RIBBE (1966) and one of  $An_{16}$  by PHILLIPS and RIBBE (1969). These structure analyses are based on

intensities from the  $a$  reflections so that the resulting atomic parameters and bond lengths represent "average" structures which give information on long-range order only. As stated in the introduction, this sort of information is valuable in the interpretation of lattice parameters which are also primarily related to long-range order (for a conflicting view see SMITH, 1970.)

### The Na/Ca anisotropy

The Na/Ca atoms in  $An_{16}$  and  $An_{28}$  are very similar to Na in high albite (RIBBE *et al.*, 1969). The isotropic temperature factors are  $\sim 5 \text{ \AA}^2$  in all three cases (Table 3), reflecting the extreme anisotropy which amounts to root-mean-square displacement  $> 0.4 \text{ \AA}$  along the principal vibration axis. Difference maps through the large cation sites (Fig. 1 a, b) show that the anisotropic electron distributions in  $An_{28}$  and high albite

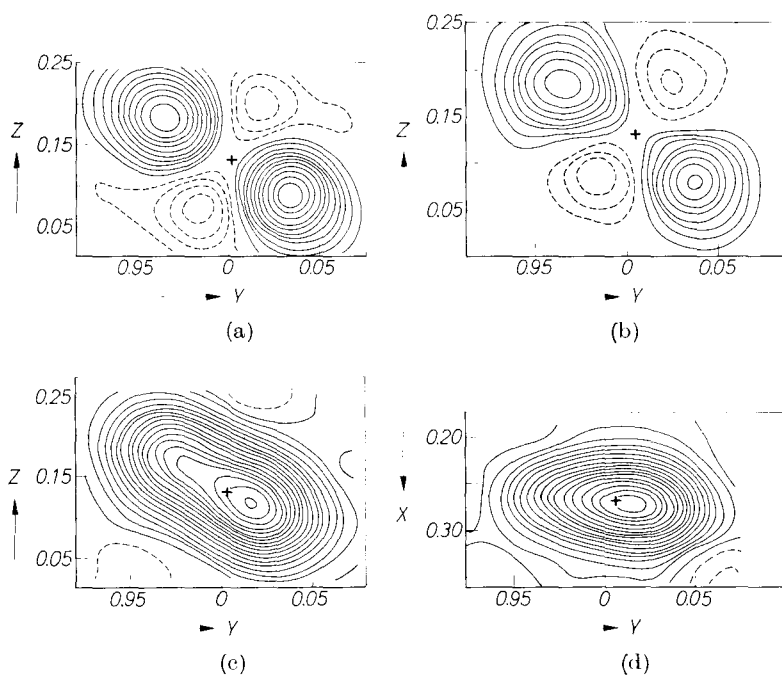


Fig. 1. (a) Difference map ( $\rho_0 - \rho_c$ ) through the large cation site of  $An_{28}$  parallel to (100). (b) Difference map through the large cation site of high albite parallel to (100). After RIBBE, MEGAW and TAYLOR (1969). (c) Fourier map parallel to (100) through the large cation site of  $An_{28}$ . (d) Fourier map parallel to (001) through the large cation site of  $An_{28}$ . Zero contours are omitted; contour interval is arbitrary

are nearly indistinguishable. Fourier maps parallel to (100) and (001) (Fig. 1c, d) indicate the asymmetrical nature of the site in  $An_{28}$  suggesting that Na and Ca may in fact be ordered in oligoclase, and thus the extreme anisotropy may be the result of the superposition of two or more different subcells or domains, each of which has slightly different atomic positions. Na/Ca ordering was first suggested by FLEET, CHANDRASEKHAR and MEGAW (1966, p. 798) for bytownite,  $An_{80}$ , which also has a domain or "average" structure. The idea of positional disorder in high albite was expounded by RIBBE *et al.* (1969) and the large isotropic thermal parameters of the T (for tetrahedral Al or Si) atoms

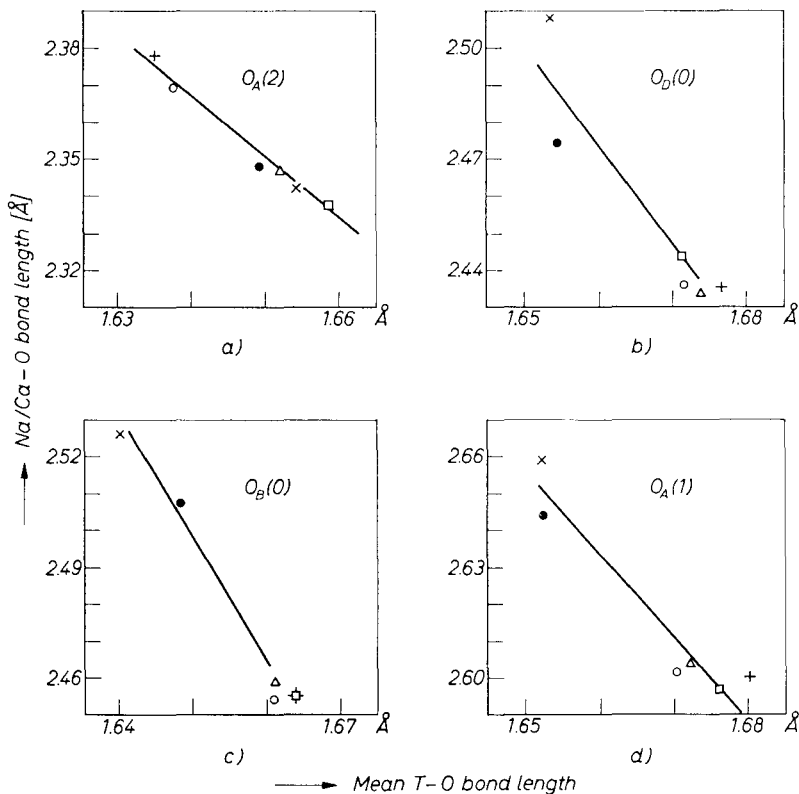


Fig. 2. A plot of the (Na/Ca)-O distance against the mean of the two T-O bond lengths to the same oxygen atom for the five nearest neighbors to Na/Ca. The (Na/Ca)- $O_A(1)$  distances represent the average of two values because  $O_A(1)$  is coordinated to two Na/Ca. The open and solid circles represent data for low and high albite refined by WAINWRIGHT and STARKEY (personal communication). The crosses + and × represent low and high albite (RIBBE *et al.*, 1969), the triangle  $An_{16}$  and the square  $An_{28}$

and the oxygen atoms were cited as evidence. Similarly large  $B$  values are found for  $An_{16}$  and  $An_{28}$  (Table 3), which indicate that similar domain textures can be argued for oligoclase. Of course the diffuse  $e$  reflections are positive evidence of these domains, even though nothing specific about the structure within the domains can be stated at present.

#### Na/Ca coordination

Four of the five oxygen atoms nearest to Na/Ca in low and high albite,  $An_{16}$  and  $An_{28}$  are bonded to  $T_{10}$  which never has less Al than any of the other three T sites. It is apparent from Fig. 2 that the mean of the two T—O bond lengths to a particular oxygen atom is related to the (Na/Ca)—O distance in a predictable manner: the longer the mean T—O distance, the shorter the (Na/Ca)—O distance. Of course the individual T—O distances are primarily related to the Al content of the tetrahedral sites. Thus for the  $O_A(2)$  atom which is bonded to the  $T_{20}$  and  $T_{2m}$  tetrahedra, the (Na/Ca)—O distances for the low oligoclases are similar in length to the Na—O distances for high albite (Fig. 2a.) Likewise for the  $O_D(0)$ ,  $O_B(0)$  and  $O_A(1)$  atoms: the (Na/Ca)—O distances for the low oligoclases are nearly equal in length to the Na—O distances for the *low* albite because each of these oxygen atoms are bonded to one Al-rich and one Si-rich site. This remarkable grouping of data points (Figs. 2b, c, d) can be attributed to the fact that the mean Al content of the two T sites is nearly constant (0.42—0.46 Al) regardless of bulk composition (Table 8).

Although the first five nearest oxygen atoms behave in this manner, the sixth and seventh do not. The coordination number of Na in albite has been discussed by FERGUSON, TRAILL and TAYLOR (1958) and GAIT, FERGUSON and COISH (1970). Based on the hypothesis that the most stable form of low albite is one in which local electrostatic charge balance is maintained<sup>4</sup> FERGUSON and his co-workers arrive at a coor-

<sup>4</sup> FERGUSON's treatment of low albite as purely ionic can be questioned on the basis of ionization potentials. Although it requires only 5.1 eV to ionize Na to the neon configuration, 53 eV are required for  $Al^{3+}$  and 103 eV for  $Si^{4+}$  (COTTON and WILKINSON, 1966, pp. 414, 434, 456). In fact the total ionization and electron-affinity energies required to form the ions in low albite is one order of magnitude greater than the heat of formation from the elements. Recently BROWN, GIBBS and RIBBE (1969) presented structural evidences for  $d-p$   $\pi$ -bonding in feldspars. In this model highly charged ions are not considered, hence the question of ionization energy does not arise. Various other objections to FERGUSON's model have been raised by MACKENZIE and SMITH (1959), LAVES and GOLDSMITH (1961), BROWN and BAILEY (1964) and APPLEMAN and CLARK (1965).

dination number of *six* for low albite, even though there are five short ( $< 2.7$  Å) Na—O distances and two others nearly equidistant at 2.978 and 3.003 Å (WAINWRIGHT and STARKEY, 1968).

In the oligoclases the order of the first five nearest oxygen atoms is the same as in low and high albite; however, the sixth nearest is  $O_C(0)$  in low albite, but  $O_C(m)$  in the oligoclases and high albite. The seventh nearest oxygen is  $O_D(m)$  for all four structures; the eighth and ninth are  $O_C(m)$  and  $O_B(m)$  for low albite and  $O_B(m)$  and  $O_C(0)$  for the other structures<sup>5</sup>.

### Tetrahedral bond lengths and angles

A number of factors have been recognized as influencing individual and therefore mean T—O bond lengths in feldspars. Most significant is the average Al/Si occupancy of the site, first noted by COLE, SÖRUM and KENNARD (1949) and later characterized by SMITH (1954) and SMITH and BAILEY (1963). JONES (1968) and RIBBE and GIBBS (1969) presented linear regression curves relating the grand mean T—O bond lengths of 13 structurally determined feldspars to their Al/(Al + Si) ratios. These curves, as well as those of SMITH and BAILEY, have been used to predict the average Al content of *individual* tetrahedral sites with only moderate success because there are other factors which appreciably affect individual T—O bond lengths. Of considerable importance is linkage. CLARK and PAPIKE (1967) observed that the mean Si—O bond lengths in Si—O—Si linkages are  $\sim 0.03$  Å longer than the mean Si—O bond lengths in Si—O—Al linkages. Likewise, in ordered feldspars estimates of pure Al—O bond lengths are always affected by Si in Al—O—Si linkages (see BROWN, GIBBS and RIBBE, 1969).

Using data from the six structure analyses considered in this paper, a preliminary multiple linear regression analysis of the factors influencing the individual T—O bond lengths indicates that although Al content is by far the major factor and linkage is of lesser importance, T—O—T angle and (Na/Ca)—O distance have measurable effects. JONES and TAYLOR (1968) recognized that the interbond (T—O—T) angle at an oxygen atom modifies the tetrahedral bonds, but in the context of their ionic model they did not attempt to explain this. BROWN *et al.* (1969) showed that in 16 framework silicates “. . . approximately

<sup>5</sup> In reedmergerite (APPLEMAN and CLARK, 1965) the sequence of increasing Na—O distances is the same as in high albite and the oligoclases except for a reversal of the order of the first two,  $O_D(0)$  and  $O_A(2)$ .



50 percent of the variation in T—O can be explained in terms of a linear dependence on T—O—T . . .” when composition and linkage are factored out. This relationship was offered as evidence for  $d-p$   $\pi$  bonding. They also found that the (Na/Ca)—O distances are related in part to T—O—T angle and T—O bond length, and our study confirms this for the oligoclases (see *Na/Ca coordination* above). There is also an effect of oxygen coordination number on T—O, but this is apparently more important in anorthite (MEGAW, KEMPSTER and RADOSLOVICH, 1962) than in alkali feldspars (see BROWN *et al.*, 1969).

The structural parameters of these albites and oligoclases show systematic trends which permit further evaluation of the T—O bond lengths and the interbond angles. For example, it was found that for a given oxygen atom [ $O_A(1)$ ,  $O_A(2)$ ,  $O_B(0)$ , etc.] the T—O—T angles of these plagioclases are within several degrees of one another (see Table 7 and *cf.* MEGAW *et al.*, 1962). Any observed small variations can be related inversely to the mean of the two T—O bond distances involved in the angle. Thus variations in individual angles at bridging oxygen atoms are primarily related to the T site occupancies. This is not true of variations in O—T—O angles, although the range of values for a given angle are similarly limited to  $1-3^\circ$  (Table 7).

To avoid some of the difficulties inherent in the linear model relating mean T—O distance to the Al content of a tetrahedron, we have plotted individual T—O distances for low and high albite,  $An_{16}$  and  $An_{28}$  against their respective tetrahedral means. Figure 3a contains the plots for the four  $T_{10}$ —O bond lengths. The slopes are all very close to  $45^\circ$ , implying that all the individual bonds from  $T_{10}$  are of a similar nature. This arises from the fact that the Al contents of the three tetrahedra linked to  $T_{10}$  increase linearly and equally as the Al in  $T_{10}$  decreases for all four structures (see Table 8). The T—O bonds of these other tetrahedra differ from  $T_{10}$  in this respect. For example, in  $T_{1m}$  (Fig. 3b)  $O_A(1)$  is linked to the Al-rich  $T_{10}$  site, whereas  $O_B(m)$ ,  $O_C(m)$  and  $O_D(m)$  are linked to tetrahedra which have essentially the same Al occupancy as  $T_{1m}$ . This linkage explains why the slope of the line relating  $T_{1m}$ — $O_A(1)$  to  $\langle T_{1m}$ —O  $\rangle$  is less than  $45^\circ$ . The individual bond length increases faster than the mean because  $T_{10}$  becomes progressively more Si-rich from low to high albite and from low albite to  $An_{28}$ . Likewise linkage explains the steeper slopes for the other three oxygen atoms because, unlike  $O_A(1)$ , they are bonded to sites which become progressively more Al-rich with disorder. The same argument applies to the  $T_{20}$  and  $T_{2m}$  tetrahedra; however,  $T_{2m}$  is somewhat different in

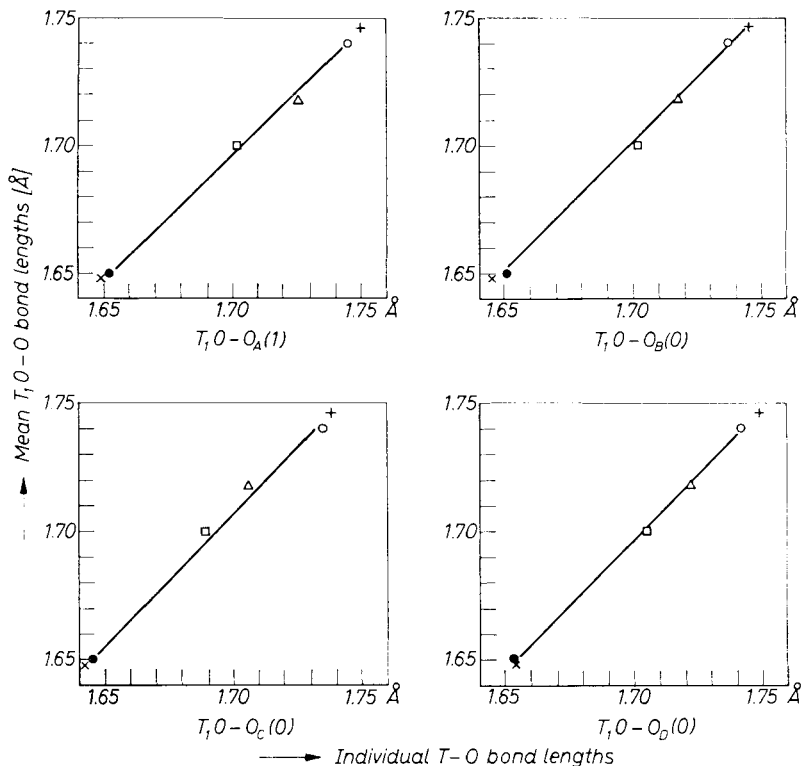


Fig. 3a

Fig. 3. Plots of individual T—O bond lengths as a function of mean tetrahedral distance  $\langle T-O \rangle$  for low and high albite,  $An_{16}$  and  $An_{28}$ . Symbols described in caption for Fig. 2. (a)  $\langle T_1O-O \rangle$  vs.  $T_1O-O_A(1)$ ,  $-O_B(0)$ ,  $-O_C(0)$ ,  $-O_D(0)$ . (b) Mean vs. individual bond lengths for the Si-rich tetrahedra,  $T_{1m}$ ,  $T_{20}$ ,  $T_{2m}$

that it is linked to *two*  $T_{10}$  tetrahedra. Although the  $\langle T_{2m}-O \rangle$  distances are nearly the same for  $An_{28}$  and high albite, there is a substantial difference in the Al content of the  $T_{10}$  tetrahedra linked through the  $O_C(0)$  and  $O_D(0)$  atoms. Therefore, for high albite the  $T_{2m}-O_C(0)$  and  $T_{2m}-O_D(0)$  distances are noticeable longer than those for  $An_{28}$ . The bond lengths to  $O_A(2)$  and  $O_B(m)$  must compensate by being shorter in order to maintain an essentially constant tetrahedral bond strength (CRUICKSHANK, 1961). Inexplicably, this same phenomenon, though expected, is not observed for  $T_{1m}-O_A(1)$  and  $T_{20}-O_B(0)$ .

In the T—O and Na—O plots previously discussed, linear trends are observed even though the structures considered are those of *ordered*

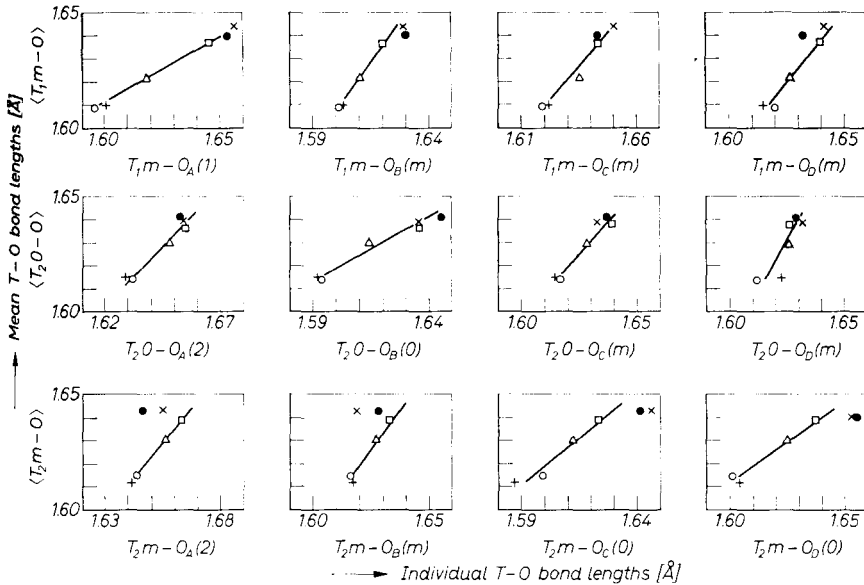


Fig. 3b

low albite, *disordered* high albite and *low* oligoclases of different compositions. From these linear relationships it appears that the effect of changing composition in low sodic plagioclases is the same as varying the structural state in albite. This is also reflected in the lattice parameters. The  $b$  and  $c$  cell edges,  $\alpha$ ,  $\Delta^*$ ,  $\gamma$ ,  $\gamma^*$  and  $\Delta 2\theta$  parameters all vary

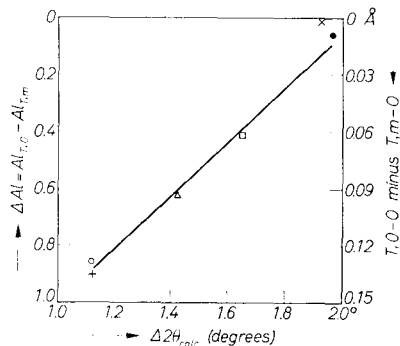


Fig. 4. The variation of  $\Delta 12\theta$  ( $\equiv 2\theta_{131} - 2\theta_{151}$ ) calculated from the cell parameters with  $\Delta Al$  ( $\equiv Al_{T_2O} - Al_{T_{1m}}$ ) on the left ordinate scale and the difference in mean T-O distances  $\langle T_{1,0}-O \rangle$  minus  $\langle T_{1m}-O \rangle$  on the right ordinate scale

linearly with the difference in Al content ( $\Delta\text{Al}$ ) between the  $\text{T}_{10}$  and  $\text{T}_{1m}$  sites (see Fig. 4). Because  $\text{Al}_{\text{T}_{1m}} \approx \text{Al}_{\text{T}_{20}} \approx \text{Al}_{\text{T}_{2m}}$  for all 7 Å plagioclase structures determined to date, the justification for choosing  $\text{T}_{1m}$  is based on the studies of alkali feldspars by STEWART and RIBBE (1969).

A detailed discussion of the relation of Al/Si distribution to these lattice parameters awaits completion of the refinement of the average structure of a low andesine ( $\text{An}_{50}\text{Or}_{0.4}$ ) which shows no evidence of exsolution lamellae [see RIBBE, STEWART and PHILLIPS (1970) for a preliminary report].

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We particularly wish to pay tribute to Professor Dr. FRITZ LAVES on the occasion of his sixty-fifth birthday for the outstanding contributions he has made to our understanding of feldspar crystal chemistry.

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