

## Determinative diagrams for Al,Si order in plagioclases

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### Abstract

Crystal structure analyses of three dry-heated plagioclases, whose lattice parameters indicate that they are virtually as “high” as synthetic plagioclases, prove that there is a surprising degree of residual Al,Si order in high plagioclase of intermediate composition (Kroll, 1978). Specifically, An<sub>27.8</sub> (heated 22 days at 1160°C) has t<sub>1</sub>O ~ 0.4 Al in the T<sub>1</sub>O tetrahedral site and ~0.3 Al in each of the other three sites [*i.e.*,  $\langle t_{1,m} \rangle = 1/3(t_{1,m} + t_{2,m} + t_{3,m}) \sim 0.3$  Al]. An<sub>52</sub> (heated 29 days at 1255°C) has t<sub>1</sub>O ~0.48 Al,  $\langle t_{1,m} \rangle \sim 0.35$  Al, and An<sub>68.7</sub> (heated 42 days at 1365°C) has t<sub>1</sub>O ~0.52 Al,  $\langle t_{1,m} \rangle \sim 0.39$  Al.

These data require re-evaluation of the diagram for determining Al,Si distribution in plagioclases from the familiar  $\Delta 131 = 2\theta(131) - 2\theta(\bar{1}31)$  parameter as well as that from the direct lattice angle  $\gamma$ . Both  $\Delta 131$  and  $\gamma$  are plotted as a function of mole percent anorthite and have been contoured for t<sub>1</sub>O -  $\langle t_{1,m} \rangle$ . The  $\gamma$  plot gives more precise results and should be used if the orthoclase content of the plagioclase is not known, but lattice parameters must be carefully refined. The much more easily measured  $\Delta 131$  values can be used somewhat less precisely to determine structural states, but the orthoclase content must be known and its effect on  $\Delta 131$  must be corrected for if t<sub>1</sub>O -  $\langle t_{1,m} \rangle$  values are to be meaningfully compared from one sample to the next.

### Introduction

The use of X-ray powder diffraction techniques to distinguish between high-temperature (“disordered”) and low-temperature (“ordered”) series of plagioclases was first introduced by Tuttle and Bowen (1950). Since then there have been many attempts to discover which of the lattice parameters are most sensitive to “structural state,” *i.e.*, to the variety of possible Al,Si distributions among the four non-equivalent tetrahedral sites of the “average” albite subcell in the plagioclase structure. The literature on this subject is extensive, and the reader is referred to Ribbe (1972; 1975b, p. R-59f.) and Smith (1974, p. 307f.) for reviews.

It is our purpose to elaborate on two well-established X-ray methods, the  $\Delta 131$  and the  $\gamma$  method, both requiring knowledge of the anorthite (An) con-

tent of the plagioclase.<sup>1</sup> Bambauer *et al.* (1967a,b) characterized many carefully analyzed natural plagioclases by these methods, choosing a representative low series based on geologic observations. The  $\Delta 131$  values for a “high” series were measured from plagioclases synthesized by Eberhard (1967). Van Schmus and Ribbe (1968) characterized K-rich chondritic plagioclases using the direct lattice angle  $\gamma$ , because it serves as a measure of the difference in Al content between the T<sub>1</sub>O and T<sub>1,m</sub> sites (t<sub>1</sub>O - t<sub>1,m</sub>) in plagioclases and is unaffected by the presence or ab-

<sup>1</sup> An content can be determined to  $\pm 2$  mole percent by the Tsuboi (1934) and Tsuboi *et al.* (1977) method of measuring the lower value of the  $\alpha'$  refractive index directly on (001) or (010) cleavage fragments (see Morse, 1968; 1978), or by the K-exchange method of Viswanathan (1971), or ideally by electron microprobe, in which case mole percent orthoclase should also be determined.

sence of potassium. The structural reasons for these properties are discussed by Kroll (1973) and Kroll and Müller (1980).

Smith and Yoder (1956) introduced the  $\Delta 131$  method, which is based on a simple measurement of the spacing between the 131 and  $1\bar{3}1$  peaks (in degrees  $2\theta$ ) on a powder diffraction pattern taken with  $\text{CuK}\alpha$  radiation.  $\Delta 131$  is also a useful measure of  $t_{1O} - t_{1m}$ , but because it is closely related to the  $\gamma^*$  angle it is significantly influenced by potassium content, usually expressed as mole percent orthoclase (Or) (*cf.* Bruno and Facchinelli, 1974).

Ribbe (1972) first recognized that  $\Delta 131$  is a function of the difference between the mean T-O bond length for the  $T_{1O}$  tetrahedron and the average T-O bond length for the other three tetrahedra in the albite subcell of the average structure of plagioclase:<sup>2</sup>

$$\Delta\langle T-O \rangle \equiv \langle T_{1O}-O \rangle - 1/3[\langle T_{1m}-O \rangle + \langle T_{2O}-O \rangle + \langle T_{2m}-O \rangle]$$

Using bond length data from 12 crystal structure

<sup>2</sup> For a detailed discussion of the concept of average structures in plagioclases see Ribbe (1972, p. 5793 or 1975a, p. R-31f.).

analyses, he found empirical relations between  $\Delta 131$  and  $\Delta\langle T-O \rangle$  and established a determinative diagram for structural state (Ribbe, 1972, Fig. 1; revised 1975b, Fig. R-37). He showed that  $\Delta\langle T-O \rangle$ , together with total Al in the formula unit, could be used to calculate Al,Si distributions among the four tetrahedral sites.

Because in all the 22 structure analyses of plagioclases chosen from the literature (Table 1),  $\langle T_{1m}-O \rangle \approx \langle T_{2O}-O \rangle \approx \langle T_{2m}-O \rangle$ , it has become convenient to average these bond lengths and to call the probability of finding an Al atom in any one of them  $\langle t_{1m} \rangle \equiv 1/3(t_{1m} + t_{2O} + t_{2m})$ . The difference function  $\Delta\langle T-O \rangle$  thus becomes useful as a measure of  $t_{1O} - \langle t_{1m} \rangle$ , where  $t_{1O}$  is the probability of finding an Al atom in the  $T_{1O}$  site.

The relation between  $\Delta\langle T-O \rangle$  and  $t_{1O} - \langle t_{1m} \rangle$  is best explained by an example (*cf.* Ribbe, 1975a, p. R-47). Mean T-O bond lengths for an oligoclase ( $\text{An}_{27.8}$ ) heated for 22 days at  $1160^\circ\text{C}$  are given in Table 1.  $\Delta\langle T-O \rangle = 1.662 - 1.649 = 0.013\text{\AA}$ . We know from structure analyses of low albite (neutron diffraction refinement by Harlow *et al.*, 1973) and primitive anorthite (X-ray refinement by Wainwright and Starkey, 1971) that  $\langle T-O \rangle$  for a tetrahedron con-

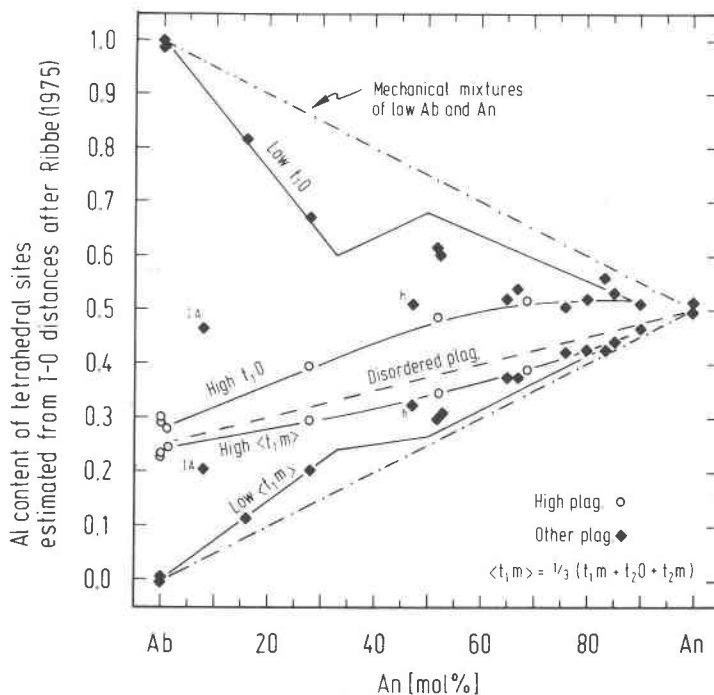


Fig. 1. Average aluminum contents of the  $T_{1O}$  sites ( $t_{1O}$ ) and the  $T_{1m}$ ,  $T_{2O}$ ,  $T_{2m}$  sites ( $\langle t_{1m} \rangle = 1/3[t_{1m} + t_{2O} + t_{2m}]$ ) determined by the method of Ribbe (1975a) and plotted against mole percent anorthite for 22 plagioclases whose structures are known (see Tables 1 and 2). IA = intermediate albite ( $\text{An}_8\text{Or}_{7.5}$ ); h = heated, but not fully disordered andesine ( $\text{An}_{48}$ ). The dash-dot lines represent curves of  $t_{1O}$  and  $\langle t_{1m} \rangle$  expected if low plagioclases  $\text{An}_0$ - $\text{An}_{100}$  were mixtures of ordered low Ab and  $\text{An}_{100}$  (whose  $c = 7\text{\AA}$  average structure is "disordered," *cf.* Smith and Ribbe, 1969, their Fig. 3). Sources of other lines are discussed in the text.

Table 1. Compositions, mean T-O distances for the T<sub>1</sub>O, T<sub>1m</sub>, T<sub>2</sub>O, T<sub>2m</sub> sites of the average structure of the plagioclase, site occupancy (Al/[Al + Si]), direct cell angle  $\gamma$ , and  $\Delta 131 = 2\theta(131) - 2\theta(1\bar{3}1)$  (for CuK $\alpha_1$  radiation) for 21 structurally analyzed plagioclases

Feldspar (Ref.)*[ ]**	Mol %			Mean T-O distances [Å]				Site occupancy		$\gamma$ [°]	$\Delta 131$ [°2 $\theta$ ] (CuK $\alpha_1$ )	Comments	
	An	Ab	Or	T <sub>1</sub> O	T <sub>1m</sub>	T <sub>2</sub> O	T <sub>2m</sub>	t <sub>1</sub> O	<t <sub>1m</sub> >				
Albite, low (1) [A]	0			1.743	1.608	1.614	1.615	1.005	0.000				
Albite, low (2) [B]	0	99.75	0.25	1.740	1.609	1.614	1.615	.985	.005	87.725	1.125		
Albite, high (3) [B]	0	99.75	0.25	1.650	1.640	1.641	1.643	.300	.235	90.115	1.986	htd.	
Albite, high (4) [B]	0	99.75	0.25	1.649	1.642	1.640	1.642	.290	.235	90.24(1)	1.998	htd. 60d, 1080°C	
Albite, high (5) [C]	1.2	98.3	0.5	1.646	1.641	1.641	1.642	.280	.245	90.257(3)	2.003	htd. 40d, 1060°C	
Albite, interm. (6) [D]	8.0	84.5	7.5	1.670	1.638	1.636	1.637	.465	.205	89.800(6)	1.677	unheated	
Oligoclase (7) [E]	16	82	2	1.718	1.622	1.629	1.630	.815	.115	88.632(5)	1.418		
Oligoclase (7) [F]	28	70	2	1.700	1.637	1.639	1.640	.670	.205	89.46(2)	1.654		
Oligoclase (8) [G]	27.8	68.1	4.1	1.662	1.649	1.649	1.649	.395	.295	90.275(4)	1.893	htd. 22d, 1160°C	
Andesine (9) [H]	47	49	4	1.676	1.653	1.656	1.656	.490	.330				
Labradorite (10) [I]	52	45.5	2.5	1.691	1.650	1.646	1.655	.615	.300	89.916(5)	1.827	exhibits schiller	
Labradorite (8) [I]	52	45.5	2.5	1.674	1.655	1.657	1.656	.485	.345	90.394(6)	1.998	htd. 29d, 1255°C, no schiller	
Labradorite (11) [I]	53	43	4	1.688	1.652	1.646	1.653	.600	.310	89.948(9)	1.826	exhibits schiller	
Labradorite (12) [J]	65.6	33.8	0.6	1.679	1.661	1.660	1.662	.520	.380	90.474(4)	2.068		
Labradorite (13) [K]	67			1.684	1.655	1.661	1.670	.540	.375	90.514(6)	2.085		
Labradorite (8) [L]	68.7	31.1	0.2	1.679	1.663	1.663	1.662	.520	.390	90.602(5)	2.108	htd. 42d, 1365°C	
Bytownite (14) [M]	76			1.678	1.666	1.663	1.672	.505	.420	90.670	2.131		
Bytownite (15) [N]	80			1.683	1.672	1.668	1.674	.525	.425	90.65(8)	2.167		
Bytownite (16) [O]	83.4	16.2	0.4	1.685	1.666	1.664	1.671	.560	.425	90.63(2)	2.136		
Bytownite (17) [P]	85			1.687	1.677	1.676	1.674	.530	.440	90.82(1)	2.186	htd. 48d, 1450°C	
Bytownite (18) [Q]	90			1.687	1.680	1.682	1.683	.510	.465	91.13(1)	2.255		
Anorthite (19) [R]	100	0	0	1.683	1.680	1.679	1.680	.515	.495	91.261(6)	2.272		

\*(1) Harlow *et al.* (1973)

(2) Wainwright &amp; Starkey (1968)

(3) Wainwright &amp; Starkey (In: Smith, 1974, v. 1, p. 71)

(4) Winter *et al.* (1979)(5) Prewitt *et al.* (1976)

(6) Kroll &amp; Tobi (to be published)

(7) Phillips *et al.* (1971)

(8) Kroll (1978)

(9) Hall *et al.* (In: Smith, 1974, v. 1, p. 76)

(10) Klein &amp; Korekawa (1976)

(11) Krahl (1976)

(12) Joswig *et al.* (1976)(13) Tagai *et al.* (1978)

(14) Wainwright (1969)

(15) Fleet *et al.* (1966)(16) Appleman *et al.* (1971; pers. comm., 1972)(17) Facchinelli *et al.* (1979)

(18) Berking (1976)

(19) Wainwright &amp; Starkey (1971)

The lattice parameters of samples (10) to (13) were redetermined by Kroll (unpublished).

## \*\*Locality:

[A] Amelia, Virginia, USA

[B] Tiburon, California, USA

[C] (synthetic)

[D] Dundee, Scotland

[E] Camedo, Switzerland

[F] Mitchell Co., N.C., USA

[G] Quebec, Canada

[H] Essex Co., New York, USA

[I] Labrador, Canada

[J] Surtsey, Iceland

[K] Lake Co., Oregon, USA

[L] Roneval, S. Harris, Scotland

[M] Crystal Bay, Minnesota, USA

[N] St. Louis Co., Minnesota, USA

[O] Moon, Apollo 12038 72

[P] Traversella, Switzerland

[Q] Moon, Apollo 14 310 106

[R] Val Pesmeda, Austria

taining only Al is about 1.743 to 1.747Å, on the average, and that  $\langle T-O \rangle$  for Si-containing tetrahedra is 1.612 to 1.614Å. So, roughly speaking, 0.13Å is the average difference between Al-O and Si-O bond lengths in plagioclase feldspars. The  $\Delta(T-O)$  value of 0.013Å for this crystal represents a difference  $t_{1O} - \langle t_{1m} \rangle \approx 0.10$  Al atoms. The formula for the heated oligoclase is  $Na_{0.681}Ca_{0.278}K_{0.041}Al_{1.278}Si_{2.722}O_8$ , and the total number of Al atoms is 1.278, or 1.000 + the An content. Thus because  $t_{1O} + t_{1m} + t_{2O} + t_{2m} = 1.278$ , and since  $t_{1m} \approx t_{2O} \approx t_{2m}$  and  $t_{1O} - \langle t_{1m} \rangle = 0.10$ , we may calculate the Al distribution among the four tetrahedral sites:  $t_{1O} = 0.395$  Al and  $t_{1m} = t_{2O} = t_{2m} = 0.295$  Al.

## Al,Si distribution in plagioclases with known structures

The preceding calculation has been done for all plagioclase structures listed in Table 1, and  $t_{1O}$  and  $\langle t_{1m} \rangle$  values are plotted in Figure 1 as a function of mole percent anorthite. The locus of fully disordered structures is the dashed line between  $t_{1O} = t_{1m} = t_{2O} = t_{2m} = 0.25$  for Ab and  $t_{1O} = t_{1m} = t_{2O} = t_{2m} = 0.50$  for An (as averaged onto the  $c = 7\text{Å}$  albite sub-cell); the dash-dot lines represent  $t_{1O}$  and  $\langle t_{1m} \rangle$  values that would be expected if the low plagioclases were ideal mixtures of completely ordered low albite and primitive anorthite (*cf.* Smith and Ribbe, 1969,

Fig. 3). Of special significance are the new structure refinements from Kroll (1978) of plagioclases which were heated dry at  $\sim 30^\circ\text{C}$  below the solidus in runs lasting from 22 to 42 days. The data points are plotted as solid open circles in Figure 1. They deviate significantly from the line representing complete disorder. Therefore, these structures were not disordered completely by the heat-treatment, nor were any of the three heated Na-feldspars (high albites) which are plotted here.

This observation leads one to question whether these heated samples are indeed high plagioclases. The accepted high series of plagioclases has been represented by synthetic specimens, which were prepared by dry devitrification of glasses a few degrees (mostly  $\sim 30^\circ\text{C}$ ) below the solidus temperature (Kroll, 1971; Kroll and Müller, 1980). Because of the crystallization conditions, it is safe to assume that these samples represent structural states of the highest possible degree of disorder attainable by normal synthesis or heat-treatment. The lattice parameters of the synthetic specimens differ distinctly from low plagioclases, at least for the range  $\text{An}_0\text{--An}_{85}$  (see data compiled by Smith, 1974, Fig. 7-41, p. 307). On the other hand, the lattice parameters of the heated specimens in question closely agree with the synthetic high series. Therefore, we accept them to represent high plagioclases.

With regard to nomenclature we will follow the suggestions of Laves (1952, 1960). He stated that "high albite" is topochemically triclinic, that is, it has a highly disordered but unequal distribution of Al

and Si among the tetrahedral sites and thus cannot become monoclinic upon heating without further diffusion of Al,Si. Like the term "high albite," our use of the term "high plagioclase" means that the average structure of the plagioclase has a highly disordered but topochemically triclinic Al,Si distribution. Except in the case of the Na-feldspars, however, there has never been any explicit statement about the actual Al,Si distribution among the four nonequivalent tetrahedral sites in high plagioclases. This can now be given from a compilation of the data from the heat-treated and synthetic specimens listed in Table 2.

#### Al,Si distribution from the lattice angle $\gamma$

In Figure 2 we have plotted the direct lattice angle  $\gamma$  as a function of mole percent anorthite. Data were taken from Bambauer *et al.* (1967b) and several refined crystal structures to establish the curve for the low series. The limiting "high" series is represented by the synthetic specimens of Kroll, 1971 (Table 2). The  $\gamma$  angles of three heat-treated natural plagioclases ( $\text{An}_{27.8}$ ,  $\text{An}_{52}$ ,  $\text{An}_{68.7}$ ) plot on or very close to the "high" plagioclase curve, demonstrating that their structural states are nearly the same as those of the synthetic samples.

However, differences between  $\langle T_1\text{O--O} \rangle$  and the other mean T-O distances (Table 1) tell us that they are not completely disordered. It might be argued that these differences are caused solely by secondary bonding effects, inasmuch as  $T_1\text{O}$  and  $T_m$  tetrahedra are different with respect to T-O-T angles and

Table 2. Compositions,  $\gamma$  angles, and  $\Delta 131 = 2\theta(131) - 2\theta(\bar{1}\bar{3}1)$  ( $\text{CuK}\alpha_1$  radiation) for (a) synthetic, (b) K-Na exchanged, and (c) heated plagioclases

(a) Synthetic plagioclases prepared by dry devitrification of glasses within $120^\circ\text{C}$ (mostly $30^\circ\text{C}$ ) below solidus temperature (Kroll, 1971)					(b) Plagioclases prepared from natural low plagioclases by (1) K-exchange ( $850^\circ\text{C}$ , 6h), (2) dry heat-treatment ( $1100^\circ\text{C}$ , 10 days), and (3) Na-exchange ( $810^\circ\text{C}$ , 4h)					
Sample No.	An [mol %]	Ab [mol %]	$\gamma$ [ $^\circ$ ]	$\Delta 131$ [ $^\circ 2\theta$ ] ( $\text{CuK}\alpha_1$ )	Sample No.	An [mol %]	Ab [mol %]	Or [mol %]	$\gamma$ [ $^\circ$ ]	$\Delta 131$ [ $^\circ 2\theta$ ] ( $\text{CuK}\alpha_1$ )
144	0	100	90.24(1) <sup>1</sup>	2.000	170 <sup>2</sup>	25.3	74.7		90.343(4)	2.020
107b	10	90	90.27(1)	1.985	31 <sup>2</sup>	27.8	72.2		90.423(8)	2.025
107a	20	80	90.27(1)	1.975						
34b	30	70	90.28(1)	1.975						
33b	40	60	90.32(1)	1.995						
33a	50	50	90.41(1)	2.045						
20	60	40	90.50(1)	2.080						
23	67.5	32.5	90.60(1)	2.120						
3428a	70	30	90.61(1)	2.120						
26	71	29	90.68(1)	2.140						
32a	77	23	90.76(1)	2.170						
33c	80	20	90.82(1)	2.185						
25	90	10	91.02(1)	2.250						
1139b	100	0	91.23(1)	2.300						

<sup>1</sup>Estimated standard error given in parentheses refers to the last decimal place.

<sup>2</sup>Numbers refer to the Corlett & Eberhard (1967) collection.

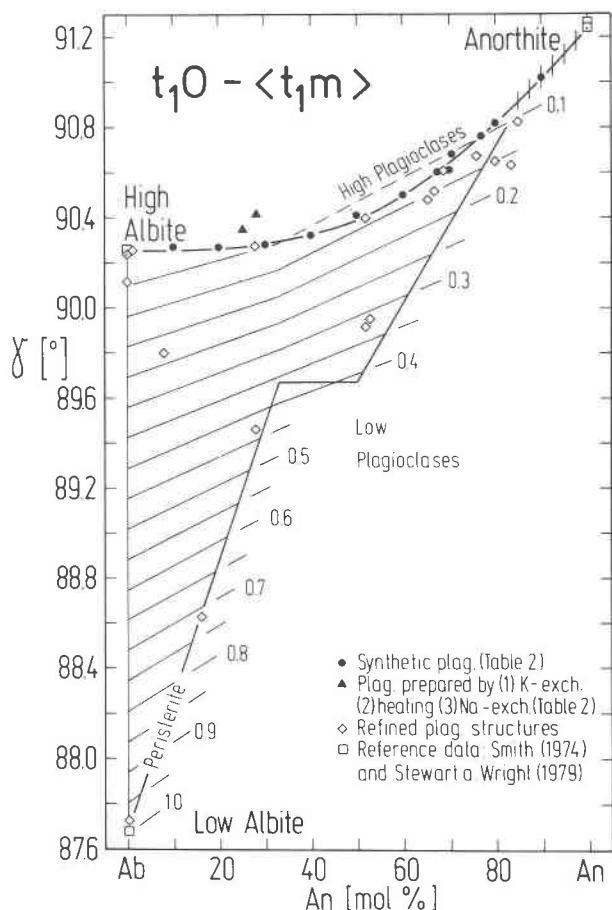


Fig. 2. The direct lattice angle  $\gamma$  (in degrees) as a function of mole percent anorthite for plagioclases of low, high, and intermediate structural states. The plot is contoured for values of  $t_1O - \langle t_1m \rangle$ . Data are in Tables 1 and 2 and the equations for the contours in Table 3.

Na,Ca coordination. If for this reason high plagioclases would only appear not to be completely disordered, but in fact were truly disordered, one would expect (1) that it would not be possible to prepare plagioclases with a degree of disorder higher than that of the synthetic samples and (2) that K-exchange experiments would result in metrically monoclinic K,Ca-feldspars, at least for K-rich compositions. However, both expectations prove wrong, as can be shown from experiments done by Kroll (1971 and unpublished results). (1) Two low plagioclases,  $An_{25.3}$  and  $An_{27.8}$ , taken from the Corlett and Eberhard (1967) collection, were heated (6 hours,  $850^\circ\text{C}$ ) in molten KCl to exchange Na for K. The K-exchanged samples were then dry-heated (10 days,  $1100^\circ\text{C}$ ) and found to be monoclinic, which demonstrates that their Al,Si distributions had changed to monoclinic topochemistry. The samples were then re-converted

to plagioclases by cation exchange in molten NaCl (4 hours,  $810^\circ\text{C}$ ) and their lattice parameters were re-determined. The  $\gamma$  angles plot well above the high plagioclase curve (Fig. 2), indicating that they have a higher degree of disorder than their synthetic equivalents, *i.e.* the first expectation proves wrong. (2) On the other hand, when the original low  $An_{27.8}$  sample is first heat-treated (22 d,  $1160^\circ\text{C}$ ) and then K-exchanged, the resulting K,Ca-plagioclase is found to be triclinic, which says that its Al,Si distribution is topochemically triclinic, *i.e.* the second expectation also proves wrong. This finding agrees with the structure refinement of the dry-heated  $An_{27.8}$  where  $\langle T_1O-O \rangle = 1.662\text{\AA}$  and  $\langle T_{1m}-O \rangle = \langle T_2O-O \rangle = \langle T_{2m}-O \rangle = 1.649\text{\AA}$ . Thus we reject the possibility that bond-length differences between  $\langle T_1O-O \rangle$  and  $\langle T_{1m}-O \rangle$  are due to secondary bonding effects and reaffirm the fact that the difference in Al content between the  $T_1O$  and  $T_{1m}$  tetrahedra is the primary cause.

The  $\gamma$  diagram has been contoured for  $t_1O - \langle t_1m \rangle$  from a regression analysis of the data listed in Table 1. We started the analysis from the assumption that  $\gamma$  is a linear function of  $t_1O - \langle t_1m \rangle$  and mole fraction An:  $\gamma = a_1 + a_2 \cdot n_{An} + a_3 \cdot (t_1O - \langle t_1m \rangle)$ . However, inspection of the residuals indicated that subdividing the  $\gamma$  diagram into two regions of different An content, using non-parallel contours in each, would be more appropriate. Therefore, one more term was added to the original model:  $a_4 |c_1 - n_{An}| \cdot [c_2 - (t_1O - \langle t_1m \rangle)]$ . This term vanishes when  $n_{An} = c_1$  or  $t_1O - \langle t_1m \rangle = c_2 \cdot c_1$  is the boundary value between the two An regions in the diagram.  $c_2$  causes one line in the contours, for which  $t_1O - \langle t_1m \rangle = c_2$ , to behave like a mirror line, reflecting one part of the contours into the other. Simultaneous refinement of the parameters  $a_1$  to  $a_4$  and  $c_1$  and  $c_2$  showed that  $c_2$  was significantly different from zero and thus had to be kept in the equation. Furthermore,  $c_1$  turned out to be close to 0.33, where a kink occurs in the  $\gamma$  diagram. Thus our final equation was chosen to be:  $\gamma = a_1 + a_2 \cdot n_{An} + a_3(t_1O - \langle t_1m \rangle) + a_4 \cdot |0.33 - n_{An}| \cdot [0.35 - (t_1O - \langle t_1m \rangle)]$ . The result of the refinement is given in Table 3 as equation (1). It might be interesting to ask for the error (*e.s.d.*) associated with the estimation of  $t_1O - \langle t_1m \rangle$  from equation (1), as predicted from the error propagation law. This may in our case be formulated as

$$\text{var}(t_1O - \langle t_1m \rangle) = \sum_{i=1}^4 [\delta(t_1O - \langle t_1m \rangle) / \delta a_i]^2 \cdot \text{var}(a_i)$$

neglecting any covariance terms. If equation (1) is evaluated according to this formula it is seen that

$\text{var}(t_1O - \langle t_1m \rangle)$  varies with  $\gamma$  and to a lesser degree with  $n_{An}$ . As a consequence, the error on  $t_1O - \langle t_1m \rangle$  amounts to a maximum of 0.05 Al for large differences between  $\gamma$  and the coefficient  $a_1$  (e.g. in case of low albite), and reduces to 0.01–0.02 Al when  $\gamma$  is within  $1^\circ$  of  $a_1$ . In addition to these errors, which arise from the uncertainty in estimating the coefficients  $a_1$  to  $a_4$ , we have to allow for errors which result from a wrong measurement of  $\gamma$  and  $n_{An}$ . If we assume that  $n_{An}$  is wrong by 0.01 mol% and  $\gamma$  by  $0.01^\circ$ , then the accumulated error in  $t_1O - \langle t_1m \rangle$  would be 0.01 Al. In summary, we estimate the total error associated with  $t_1O - \langle t_1m \rangle$  to lie within the range 0.02 to 0.06 Al.

The regression analysis was not done in the usual way, where it is assumed that only the dependent variable ( $\gamma$  in our case) is subject to error. It is obvious that  $n_{An}$  as well as  $t_1O - \langle t_1m \rangle$  cannot be found without error. Therefore, in a regression situation of this type it is actually inappropriate just to minimize the weighted sum of squares due to deviation  $\sum \omega_i (y_i - \hat{y}_i)^2$ , where  $y = f(x_1, x_2 \dots x_n)$ , and to forget about the errors associated with the  $x_i$ 's. To account for these, Kroll and Stöckelmann (1979) suggested minimizing the sum of the harmonic means of the squared deviations from expectation of the  $y$  and  $x_i$  values:

$$\left[ \frac{\sigma_{y_i}^2}{(y_i - \hat{y}_i)^2} + \frac{\sigma_{x_{1i}}^2}{(x_{1i} - \hat{x}_{1i})^2} + \frac{\sigma_{x_{2i}}^2}{(x_{2i} - \hat{x}_{2i})^2} + \dots \right]^{-1} \rightarrow \text{Minimum!}$$

This type of regression analysis has been given the name "harmonic least-squares analysis" (HLS).

In the case of a straight-line relationship  $y = f(x)$ , where  $\sigma^2(x_i)$  is taken to be zero, it is seen that the HLS function is identical with the usual sum of squares due to deviation. When both  $y$  and  $x$  are assumed to be subject to error, the HLS function reduces to the function used in geochronology to fit isochrons for age determination (Brooks *et al.*, 1972).

The errors associated with  $n_{An}$  and  $\gamma$  entering the HLS formula were taken from the literature, those associated with  $t_1O - \langle t_1m \rangle$  were calculated from errors in T–O distances applying the error propagation law. When no errors were quoted we choose  $\sigma(n_{An}) = 0.01$  mol%,  $\sigma(\gamma) = 0.02^\circ$  and  $\sigma(T-O) = 0.003\text{\AA}$ . Furthermore, the  $An_{90}$  sample (#18 in Table 1) was given zero weight because of its extreme deviation from the linear relation between grand mean T–O distances and Al content  $Al/(Al+Si)$  in feldspars.  $An_{80}$  (#15) was given zero weight because of its

poorly known An content.  $An_8$  (#6) was given a small weight because of its high Or content. Low albite  $An_0$  (#1, #2) was substituted by the reference data of Smith (1974, p. 219) and Stewart and Wright (1974, p. 362).

#### Al,Si distribution from $\Delta 131 \equiv 2\theta(131) - 2\theta(\bar{1}\bar{3}\bar{1})$

The plot of  $\Delta 131$  vs. mole percent An (Fig. 3) has been contoured for  $t_1O - \langle t_1m \rangle$  from a regression analysis like that applied to the  $\gamma$  diagram [equation (2) in Table 3].  $\Delta 131$  can be measured very easily (in less than 5 minutes), but it has an unfortunately strong dependence on the potassium content of the plagioclase. Thus, before the  $\Delta 131$  values of Table 1 could enter the regression analysis, they had to be corrected for Or content. For this purpose we have prepared Figure 4, using data from Orville (1967) and Kroll (1971 and unpublished results). The correction is only approximate, and the reader should be careful not to overestimate the precision of  $t_1O - \langle t_1m \rangle$  determined from  $\Delta 131$  using either Figure 3 or equation (2).

The effect of Or content on  $\Delta 131$  is seen from the equation given by McKie and McConnell (1963):

$$\Delta 131 = 4\sin^{-1}[\Phi(c^*\cos\alpha^* + a\cos\gamma^*)], \text{ where}$$

$$\Phi = 3\lambda b^*/(d_{131}^* + d_{\bar{1}\bar{3}\bar{1}}^*)\cos \frac{1}{2}(\theta_{131} + \theta_{\bar{1}\bar{3}\bar{1}})$$

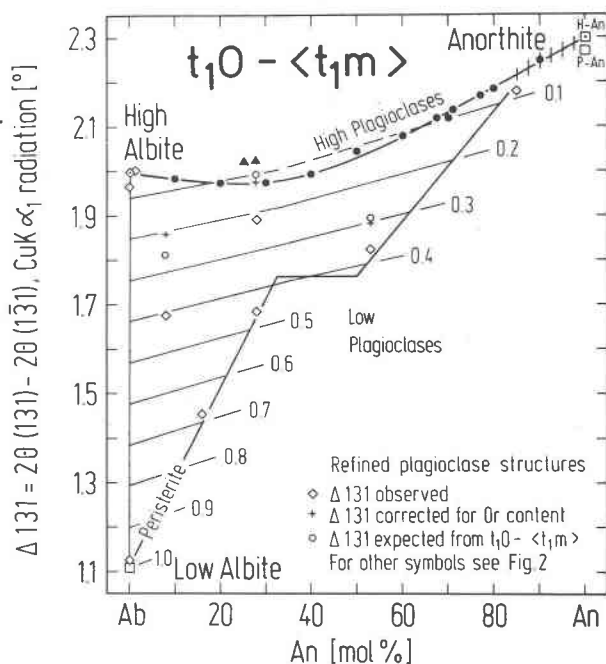


Fig. 3. The parameter  $\Delta 131 \equiv 2\theta(131) - 2\theta(\bar{1}\bar{3}\bar{1})$ , measured in  $^\circ 2\theta$  using  $CuK\alpha_1$  radiation, as a function of mole percent anorthite. See other comments as in Fig. 2.

Table 3. Equations and coefficients to calculate  $t_{1O} - \langle t_{1m} \rangle$  from mole fraction An and  $\gamma$  (equation 1) or  $\Delta 131$  (equation 2)

$$(1) \quad t_{1O} - \langle t_{1m} \rangle = \frac{\gamma - a_1 - a_2 \cdot n_{An} - 0.35 \cdot a_4 |0.33 - n_{An}|}{|a_3 - a_4 |0.33 - n_{An}|}$$

$$(2) \quad t_{1O} - \langle t_{1m} \rangle = \frac{\Delta 131 - b_1 - b_2 \cdot n_{An} - 0.35 \cdot b_4 |0.33 - n_{An}|}{b_3 - b_4 |0.33 - n_{An}|}$$

$$t_{1O} = 0.25(1 + n_{An}) + 0.75(t_{1O} - \langle t_{1m} \rangle)$$

$$t_{1m} = 0.25(1 + n_{An}) - 0.25(t_{1O} - \langle t_{1m} \rangle)$$

$n_{An}$  = mole fraction An ( $0 < n_{An} < 1$ )  
 $\Delta 131 \equiv 2\theta(131) - 2\theta(1\bar{3}1)$  [ $^\circ 2\theta$ ],  $CuK\alpha_1$  radiation

Coefficients*			
$a_1$	$a_2$	$a_3$	$a_4$
90.252(24)	0.816(41)	-2.362(64)	1.030(212)
$b_1$	$b_2$	$b_3$	$b_4$
2.011(11)	0.247(19)	-0.860(28)	0.201(98)

\* Errors are given in parentheses and refer to the last decimal place.

The Or content affects  $a^*$  slightly, but  $\gamma^*$  is proportionately much more sensitive. Thus for high albite  $\gamma^* = 87.95^\circ$ ,  $\cos\gamma^* = 0.0358$ , and  $\Delta 131 = 2.0^\circ$ ; for high  $Ab_{90}Or_{10}$   $\gamma^* = 88.23$ ,  $\cos\gamma^* = 0.0309$ , and  $\Delta 131 = 1.7^\circ$ . If one were ignorant of the Or content in the latter, the  $\Delta 131$  plot would give  $t_{1O} - \langle t_{1m} \rangle = 0.35$  Al instead of the correct value of 0.04 Al. If a comparison is made between Figure 3 and the  $\Delta 131$  diagram of Ribbe (1975b, Fig. R-37) it is seen that the largest differences in  $t_{1O} - \langle t_{1m} \rangle$  occur with the high

plagioclase series, where they range from 0.04 to 0.14 Al. This mainly results from the assumption that high plagioclases were completely disordered ( $t_{1O} - \langle t_{1m} \rangle = 0$ ), which we now know needs to be corrected. The differences decrease towards the low series, where they range from 0 to  $\sim 0.07$  Al. In the low series, they arise from the specific choice of  $\Delta 131$  values which we now know needs to be corrected. The differences decrease towards the low series, where they range from 0 to  $\sim 0.07$  Al. In the low series, they arise from the specific choice of  $\Delta 131$  values made by Ribbe. In contrast, Figures 2 and 3 are now contoured from a regression analysis in which no reference to the position of the limiting "high" and "low" series was necessary.

The errors associated with the estimation of  $t_{1O} - \langle t_{1m} \rangle$  from  $\Delta 131$  [equation (2)] are virtually the same as those arising with equation (1), not considering the uncertainties due to Or content.

### Examples and conclusions

Diagrams similar to that for  $\Delta 131$  vs. mole percent An could be constructed for  $\gamma^*$ ,  $\Delta 241 \equiv 2\theta(241) - 2\theta(\bar{2}41)$ ,  $\Gamma \equiv 2\theta(131) + 2\theta(220) - 4\theta(1\bar{3}1)$  or  $\sigma$  (for the rhombic section). All are strongly related to  $\gamma^*$  and thus to Or content and have weaknesses similar to  $\Delta 131$  diagrams of Ribbe (1972, Fig. 1; 1975b, Fig. R-37), which should be abandoned in favor of Figure 3. But in spite of difficulties, the  $\Delta 131$  method should not be abandoned. Many researchers have access to an electron microprobe to determine Or and An contents of their plagioclases who do not have the patience (or perhaps the computing facilities) to undertake the lattice parameter determinations required

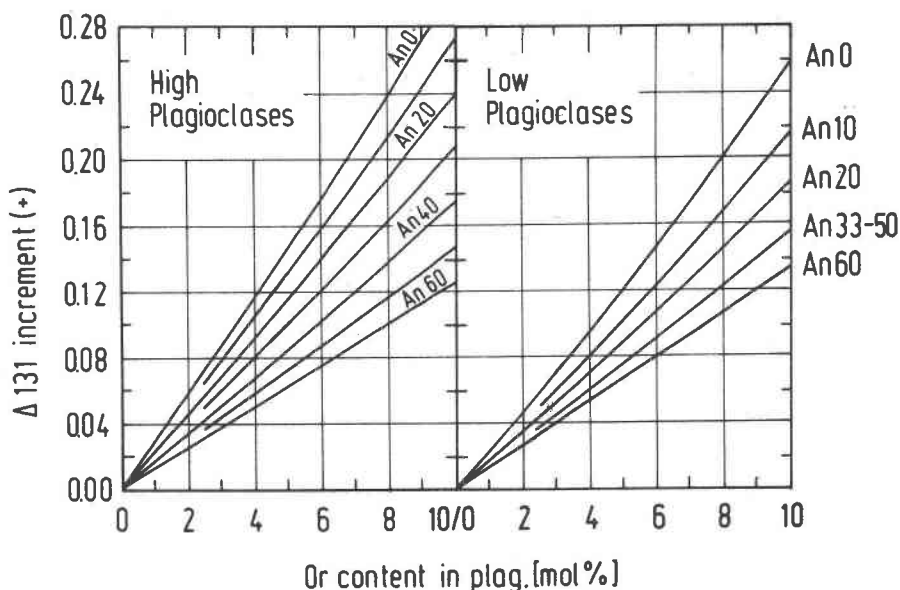


Fig. 4. Graphs to aid in correction of  $\Delta 131$  values for mole percent  $KAlSi_3O_8$  (Or) in high and low plagioclases. Data are from Orville (1967) and Kroll (1971 and unpublished results).

for the  $\gamma$  method. Since Or in solid solution with low plagioclases averages 2 mole percent or less (Corlett and Ribbe, 1967), corrections to  $\Delta 131$  are usually small, but not insignificant. High plagioclases often contain more Or than low, and of course ternary feldspars contain substantial amounts. An extreme case, the  $An_8Or_{7.5}$  sample (Table 1) whose structure is known, can be used to illustrate the correction process and its limitations.

The observed  $\Delta 131$  value for  $An_8Or_{7.5}$  is  $1.68^\circ$  (plotted as  $\diamond$  in Fig. 3). Using Figure 4 to "correct" this value for the effect of Or content gives an increment of  $+0.18^\circ$  and thus an estimated  $t_1O - \langle t_1m \rangle$  value of 0.20<sub>5</sub>. This is not very close to the value determined from bond lengths:  $t_1O - \langle t_1m \rangle = 0.465 - 0.205 = 0.26$  Al. Notice, however, that the lattice angle  $\gamma$  is  $89.80^\circ$ , predicting  $t_1O - \langle t_1m \rangle = 0.23$  Al (Fig. 2). For the heated  $An_{27.8}Or_{4.1}$  sample (Table 1), the  $\Delta 131$  value corrected for Or content estimates  $t_1O - \langle t_1m \rangle = 0.12_5$  Al, well within expected errors of the 0.10 Al predicted from mean T-O bond lengths (cf. Fig. 1). But  $\gamma$  is  $90.27_5^\circ$  and gives a better estimate: 0.09 Al. A third crystal with a large Or content is  $An_{53}$  where  $\gamma$  and  $\Delta 131$  estimate  $t_1O - \langle t_1m \rangle = 0.31_5$  Al and 0.30 Al, respectively, whereas from bond lengths we would expect 0.29 Al.

Although considerable effort may be involved in collecting and refining X-ray data to obtain precise lattice parameters, the  $\gamma$  plot is clearly the more reliable method for determining the structural state of plagioclase relative to what we now consider to be well-characterized "high" and "low" series. Or content may be ignored because it does not significantly affect  $\gamma$  (for reasons discussed by Kroll and Müller, 1980), but special care must be exercised to obtain properly indexed and calibrated diffraction data.

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