The Crystallographic investigation
of a
Strontium Labradorite

B.Sc. Thesis

by George CORDAHI

ABSTRACT

Precession photography was used to determine the lattice parameters, the crystal system, the space group and the structure of an artificial Sr-labradorite of composition: Ab27, SrAn73.
The lattice parameters determined are : a=8.361Å, b= 13.020Å, c= 7.107Å, $\alpha = \gamma = 90°$, $\beta = 115.834°$, The crystal system is monoclinic, space group = C2/m and structure is albite type, reflections being restricted to the 'a' type. The abundance, lithophile characteristics and appropriate ionic radii of elements in Groups IA and IIA are the factors governing their presence as cations of feldspars in nature.

The structure of feldspars are discussed as a function of the relative proportion of cations of a charge of +1 and +2.

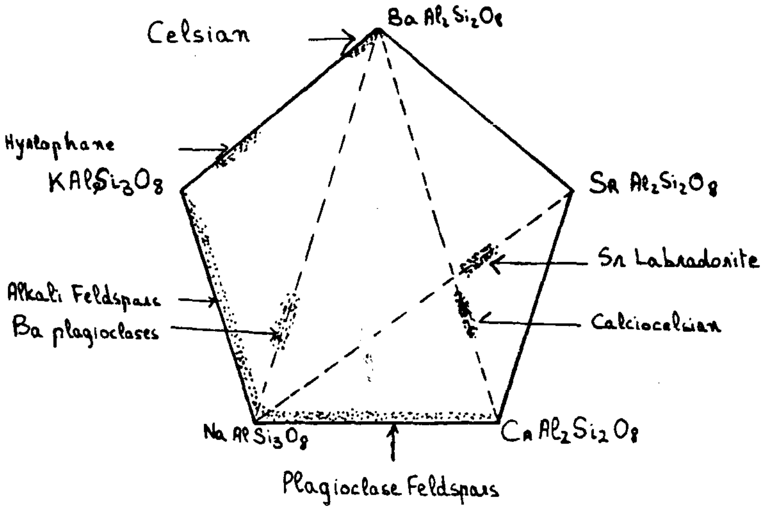
The crystal symmetry (i.e. monoclinicity or triclinicity) is discussed as a function of the ionic radius of the cation.

Introduction:

The purpose of the present work was to attempt to correlate the structure, crystal chemistry and lattice parameters of a Sr-Plagioclase of known composition with other members of the feldspar group of minerals.

Particular attention is given to:

1) Determination of the space group and lattice parameters of the Sr-feldspar crystal.
2) Prediction of the crystal structure of a hypothetical pure Sr-feldspar, and
3) to comment on the extent of ionic substitution of Ca, Na, K and Ba in Sr feldspars. (i.e. the amount of solid solution between these end members)



A subsequent refinement of the structure of the Sr-plagioclase by H.D. Grundy using the space group and preliminary lattice parameters determined in this work allowed an extension of the discussion.

Previous Work:

The structures of a number of feldspars (Table 1) have been refined. However most of those have compositions lying in the ternary system : Ca-Na-K Feldspar.

TABLE 1 Partial listing of feldspar structures determined

	Description & location (if known)	Composition	Reference
1.	Anorthite, Monte Somma, Vesuvius	An100	Kempster et al 1962
2.	Bytownite, St.Louis Co., Minn	Ab20 An80	Fleet et al 1966
3.	Oligoclase, Camedo, Switzerland	An16 Or2 Ab82	Phillips et al 1972
4.	Oligoclase, Mitchell Co., N.C.	An28 Or2 Ab70	Phillips et al 1972
5.	Low Albite Ramona;	Ab100;	Ribbe et al 1969
6.	High Albite,(heated low Ab) Va.	Ab100;	Ribbe et al 1969
7.	Maximum microcline (authigenic)	Or100;	Finney et al 1964
8.	Maximum microcline (igneous)	Or100;	Brown et al 1964
9.	Intermediate microcline (Spencer U)	Or100;	Bailey 1969
10.	Orthoclase,(Spencer C)	Or100;	Jones et al 1961 Colville et al 1968
11.	Sanidine, (heated Spencer C)	Or100;	Ribbe 1963
12.	Celsian	Cn100;	Newnham et al 1960

The structure of only one Ba Feldspar has been studied, although description and chemical analyses of other samples of the Ba variety have been published and are as follows:-

Celsian	Cn 90 Or 10	Gay 1956 Taylor et al 1934
Hyalophane	Cn10-30 Or70-90	Vermaas 1953
Calciocelsian	Cn44 An56	Segnit 1946

Feldspars in the system $(Ca,Ba,Sr)Al_2Si_2O_8(Na,K,Rb,Cs)AlSi_3O_8$ have been synthesized and the space groups of various end members and intermediates determined (Grove & Ito,1973). They concluded that the diffraction symmetry is a function of the cation radius and the Al/Si order.

For more comprehensive reviews of the feldspar structure readers are referred to Deer,Howie & Zusmann (1963) and Barth (1969).

EXPERIMENTAL WORK

Material:

Crystals of a Sr-Plagioclase feldspar with a ratio of Na:Sr of 3:7 were synthesized by Ito and Grove at Harvard University, and obtained at McMaster by H.D.Grundy.

Three crystals from fragments of the same sample were selected and inspected on a petrographic microscope to make sure that they were untwinned in order to facilitate the interpretation of the results. These crystals were numbered 1,2, and 3 and had the following dimensions:

Crystal #	Average Diameter (mm.)
1	0.1
2	0.7 (?)
3	0.2

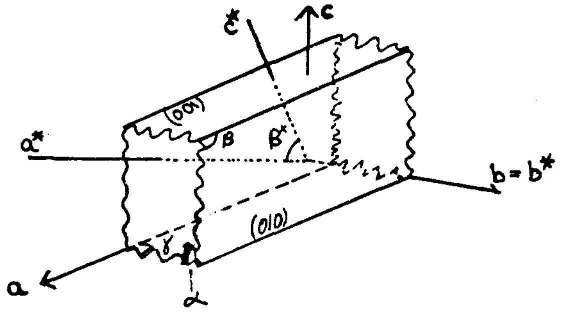
Experimental Method:

Characterisation of the space group and determination of the lattice parameters was made using X-Ray diffraction film techniques. A Buerger precession camera was used to obtain photographs of the reciprocal lattice.

The crystal was attached to the tip of a fine glass spindle held to a standard goniometer head by means of vaseline. The goniometer was then mounted on the drum of the precession camera, and the crystal placed into the path of the X-Ray beam by sighting through the telescopic viewer. Preliminary orientation of the crystal was made in one of three ways:-

1) The drum was rotated such that the smoothest planar surface (due to cleavage) of the crystal was made to face the X-Ray beam. In feldspars, good cleavage surfaces occur in the (001) and (010) planes. So if the crystal is mounted on the 'a' axis, then the a^*c^* plane would be expected to appear on the photograph if the X-Ray beam strikes the (010) cleavage sur-

surface ,& the b^* axis would be expected if the (001) surface is struck.



Note:- a^*c^* is || to (010)

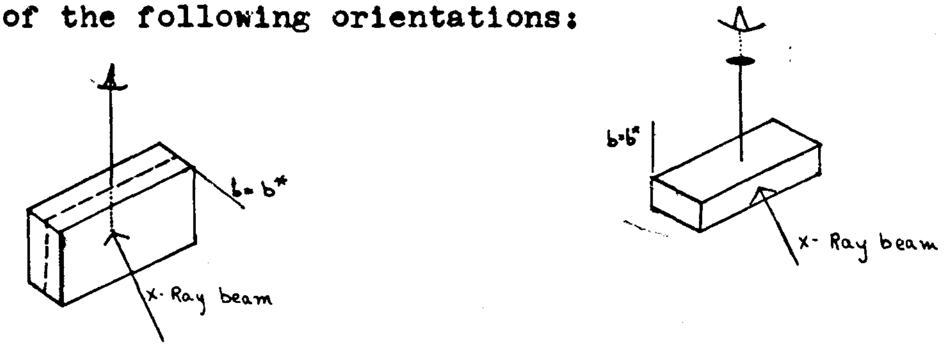
b^* is || to (001)

Fig. 2

2) If no good planar surface appeared on the crystal, or if the first method was unsuccessful, then the drum would be rotated at regular angular intervals (15 -30), and short time exposure photographs taken until one of the main axes was found.

3) A correct orientation was obtained for crystal # 3 by rotating the crystal to extinction under a petrographic microscope. In monoclinic crystals, extinction occurs when the crystal has one of the following orientations:

Fig. 3



a. <u>The mirror plane is vertical</u> b. <u>The diad is vertical</u>

The extinction orientation is measured on a vertical drum holding the goniometer head and sliding horizontally on the stage of the microscope. The bearing of the drum at extinction was transferred to the drum of the precession camera. In case a.(Fig 3) the X-Ray beam would strike the mirror plane and record the a^*c^* plane on the photograph while in case b. the b^* axis would appear.

When one of the three reciprocal lattice axes had been identified, further adjustment was performed by rotating the drum and/or the

the small perpendicular arcs on the goniometer, until the length of the axes on the photographs are at an equal distance from the center of the X-Ray beam. Details of procedures are best described by Buerger (1964).

Choice of Radiation:

The radiation used was MoKα with λ=0.7107A°.

The highest order of a reflection obtained depends on the angle of precessionθ, the wavelength of the radiation λ and the interplanar distance between parallel layers of the crystal lattice. Thus according to the Bragg equation :

$$n\lambda = 2\ d\ \text{Sin}\ \theta$$

i.e. $n \leq \frac{2d}{\lambda}\ \text{Sin}\ \theta$, where n is an integer

For feldspars, b = 13.0A°, i.e. d_{010} = 13.0A°

If the precession angle μ=20°, and $\theta = \mu$

then $n \leq \frac{2 \times 13.0}{\lambda\ (A°)} \cdot \text{Sin}\ 20°$

i.e. $n \leq 8.84/\lambda(A°)$

For λ = 0.7107A°, (MoKα)

$n \leq 12.4$ i.e. $n_{max} = 12$

If λ = 1.5418A° (CuKα)

$n \leq 5.7$ i.e. $n_{max} = 5$

It is apparent from the above calculation that shorter wave radiation allows a wider portion of the reciprocal lattice to be recorded, however at the same time, resolution of reflections decreases with the increase in scale.

Sr having a high atomic weight, has a large absorption coefficient but this is smaller for MoKα than for CuKα. Therefore, due to the high content of Sr in the sample, MoKα was used instead of CuKα in a special effort to record weak reflections.

Description of Photographs obtained:

Series #1 4photographs were taken of crystal #1. Those are of : 3 lattice planes perpendicular to the b* axis.

Film #	level (K=)
1	0
3	1
4	2

1 lattice plane (Film #2) perpendicular to the a*c* plane and enclosing b*.

The crystal gave fine, sharp and precise reflection points. Crystal #1 was subsequently used for Syntex 4-circle X-Ray diffraction analyses by H.D.Grundy.

Series #2 Those are long time exposures of crystal #2, of rectangular outline, and of a larger size than crystal #1. Long exposures were taken to make sure that no new reflections were found. Crystal #2 was lost. Those photographs are:

Film #	level (K=)
1,3	0
5	1 See Page 6a
6	2 " " 6b
2,4	perpendicular to the a*c* plane See Page 6c

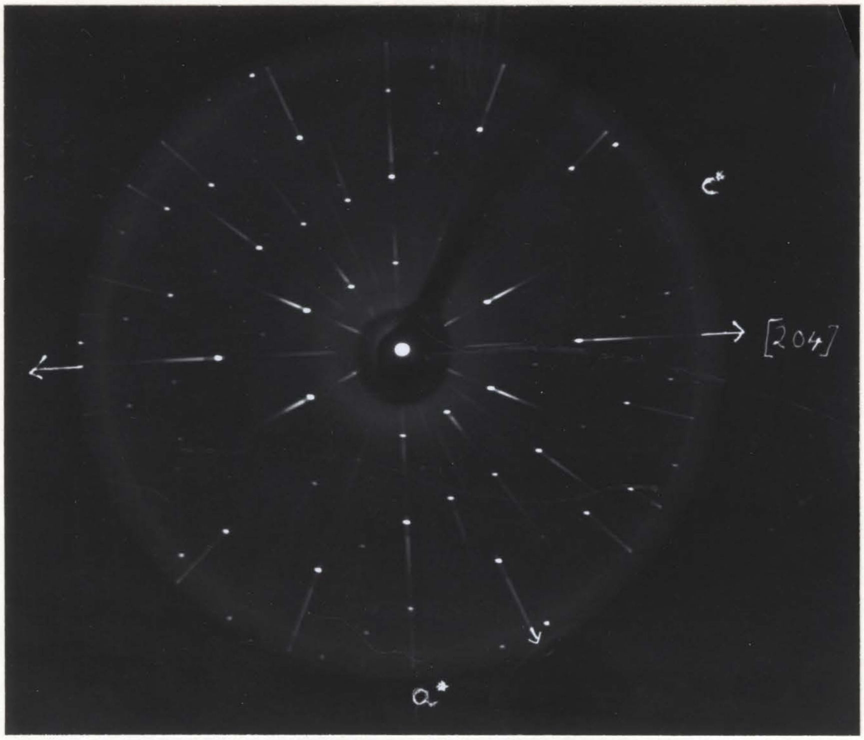
Reflections in series #2, were large oval smears. Although they were adequate to confirm the absence of weaker reflections, they could not be used for the measurement of lattice parameters.

Series #3 It consists of:-

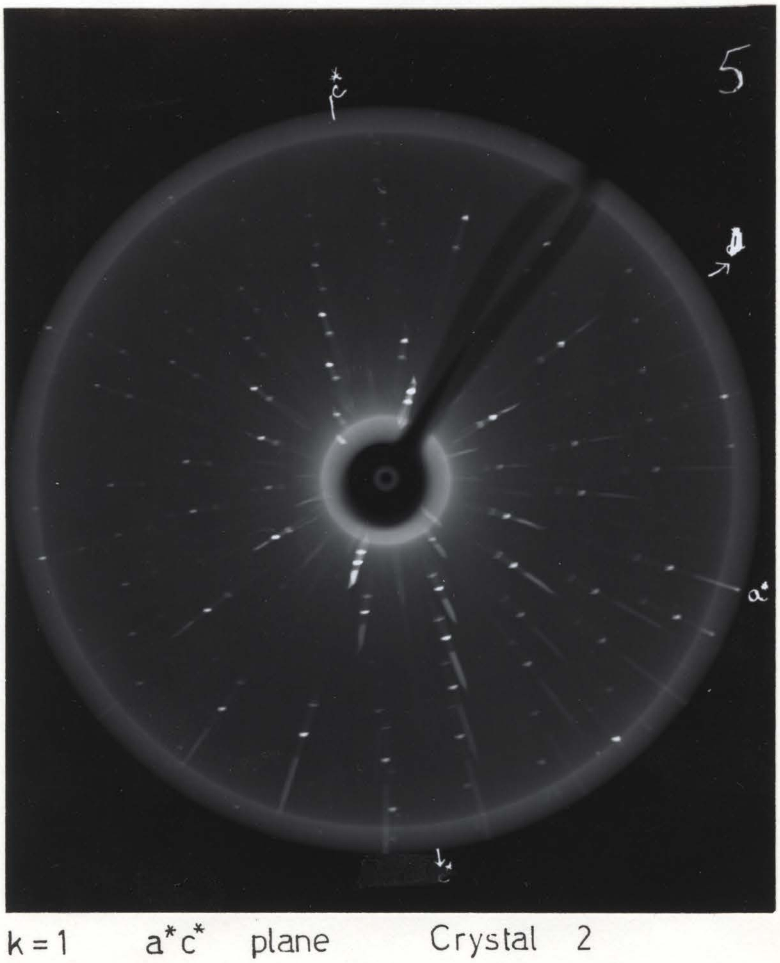
Film #	description
1,4	perpendicular to the a*c* plane
2,3	k=0 See Page 6a

Crystal #3 was chosen for its small size in order to measure the lattice parameters. However, while the parameters obtained confirmed those measured before, the reflections were not as sharp as those of series #1.

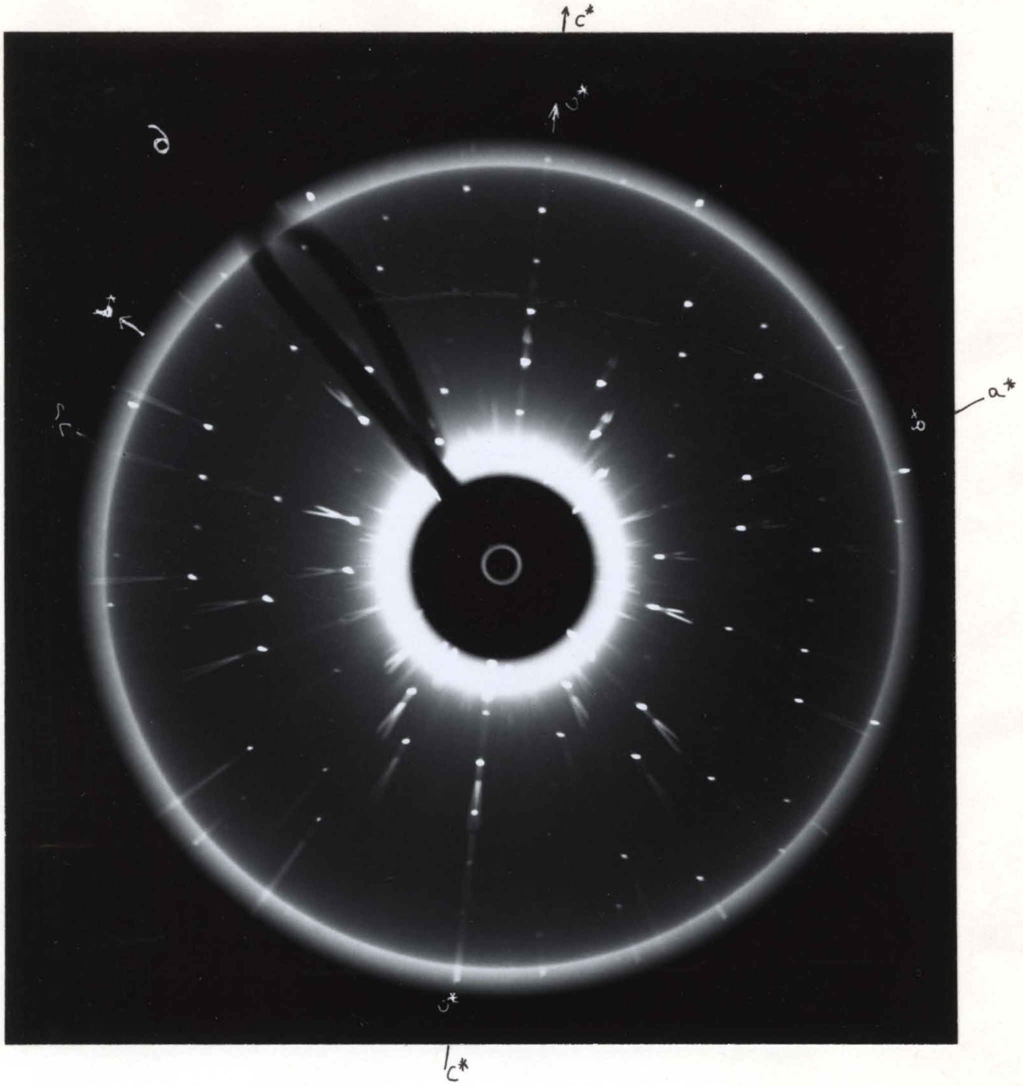
When precession photographs of a large crystal (e.g.#2) are taken, the reflections are large, and assumed to be diffuse individual points. It was important to make sure of the nature of the diffusity.



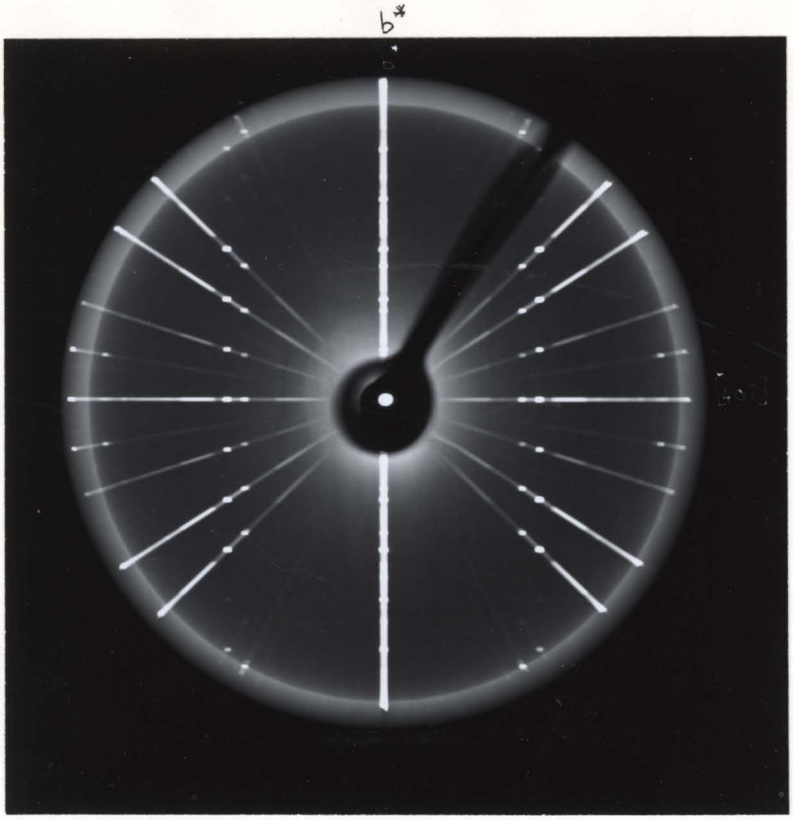
Zero level $a^* c^*$ plane Crystal 3



$k = 1$ $a^* c^*$ plane Crystal 2



k = 2   a*c* plane   Crystal 2



Zero level b^* Crystal 2

as it may be confused with 'e' type reflections that occur as satelites to 'a' reflections,the only kind found in any of the photographs.(Bown and Gay 1958). See Fig 4 for the pattern of reflections in the Plagioclase series. Long time exposure photographs of the smaller crystals (#1,3) were taken to confirm the absence of any extra reflections around the 'a' positions. A Weissenberg rotation photograph was taken of specimen #3, that revealed no new reflections beside the previously found 'a' type.

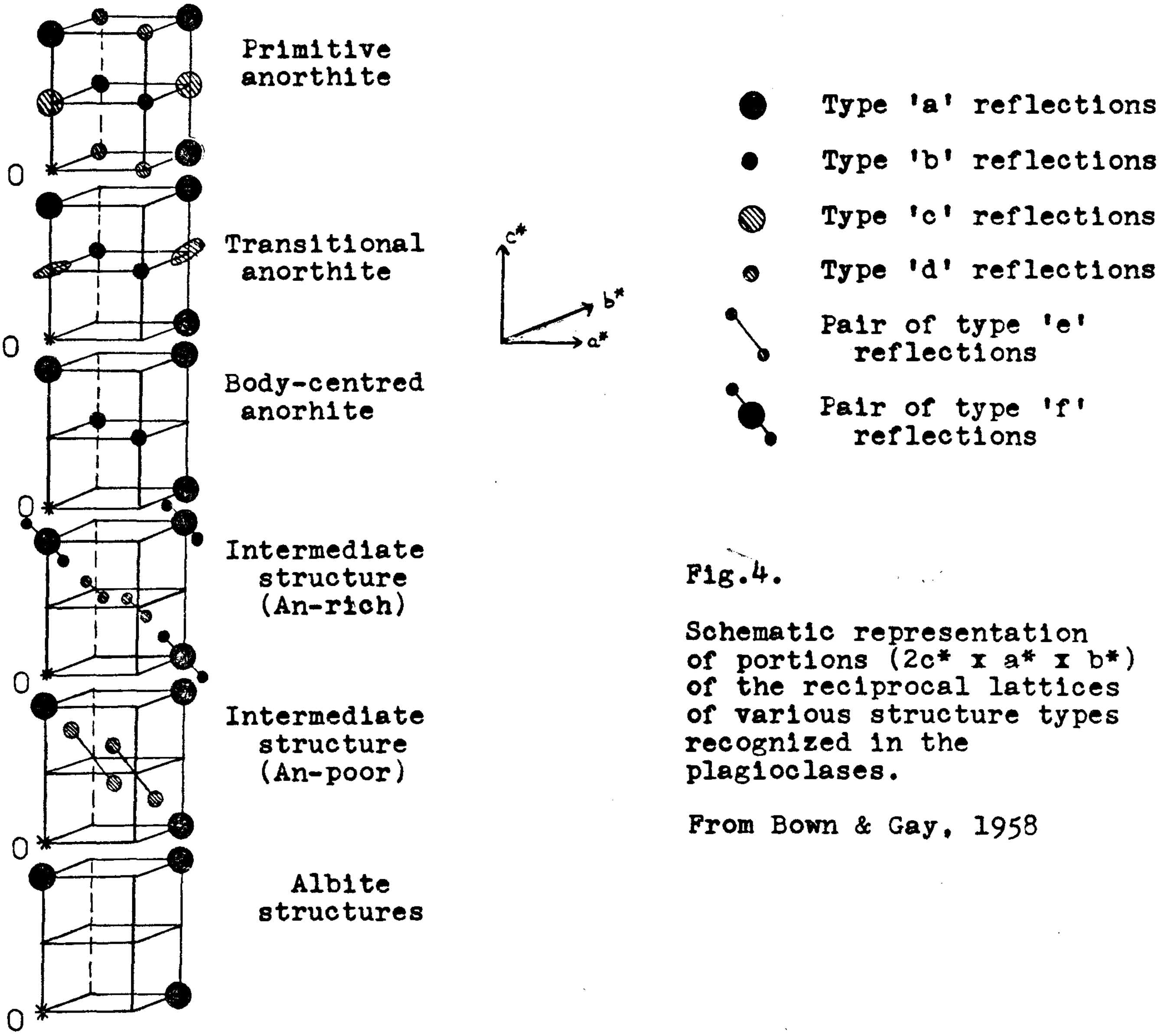


Fig.4.

Schematic representation of portions (2c* x a* x b*) of the reciprocal lattices of various structure types recognized in the plagioclases.

From Bown & Gay, 1958

Measurement of Lattice Parameters

The a*,b* and c* axes were recognized by the intensity of their reflections, but especially by the correspondance of the lattice geometry with that expected for feldspars. $<\beta^*$ is especially useful as its measurement is easy and can thus be directly compared with known values. Measurement of a* & c* were made on the zero level photographs of the a*c* plane, while b* was measured on the zero level photograph perpendicular to the a*c* plane. All measurements are made in 'mm.'. β^* is measured directly on the a*c* plane, while α^* and γ^* are assumed to be 90°, as the b* axis is always obtained by rotating the a*c* plane by 90°, whatever the mounting axis is, as it has to belong to the a*c* plane.

The normal lattice parameters are determined by performing the following operations on the measured parameters in 'mm.'.

$a^*(\text{Å}^{-1}) = a^*(\text{mm.}) / M.\lambda$

where $\lambda = 0.7107\text{Å}$
M = magnification constant
= 60 mm.

similarly for $b^*(\text{A}^{-1})$, $c^*(\text{A}^{-1})$

$\beta = 180 - \beta^*$ $\alpha = \alpha^* = 90$, $\gamma = \gamma^* = 90$

$b(\text{Å}) = 1/\ b^*(\text{A}^{-1})$

$a(\text{Å}) = 1/a^*(\text{Å}^{-1}) \operatorname{Sin}\beta$

$c(\text{Å}) = 1/c^*(\text{Å}^{-1}) \operatorname{Sin}\beta$

Systematic determination of the Space group:

1. Friedel Symmetry(diffraction symmetry) =

Symmetry of crystal + center of symmetry

a. The a*c* plane is a mirror plane. This is determined by inspection of all photos of planes enclosing b*, which is perpendicular to a*c*.

b. The b* axis is a two-fold axis. This is determined by inspection of the symmetry in the upper levels(k=1,2,) of the a*c* plane. The presence of two-fold symmetry on the zero level photograph is a reflection of the center of symmetry that is superimposed on the symmetry of the crystal by diffraction.

c. The absence of systematic absences of points parallel to c* indicates that no glide plane is determined, although not ruled out. No screw axes were found.

therefore Laue group symmetry = 2/m

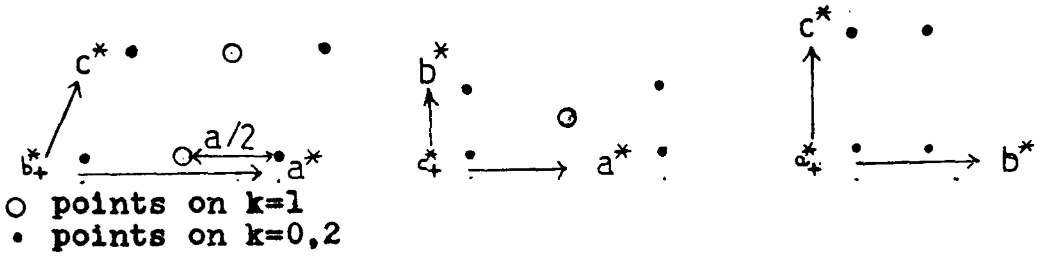
2. Space lattice type:-

Points on adjacent layers of the a*c* plane coincide when one level is displaced by a*/2, Therefore:

Reciprocal Space Lattice type = C*

The reasoning behind the above determination is explained by inspecting the following sketches: (Fig 5)

Fig. 5



The C* reciprocal lattice is equivalent to the C direct space lattice.

From the above determinations,:

the Diffraction Symbol = 2/m C -/-

For Monoclinic Symmetry, possible space groups are listed :

Diffraction Symmetry	2/m		
Crystal class Diffraction symbol	m	2	2/m
2/m P -/-	Pm	P2	P2/m
2/m P -/c	Pc		P2/c
2/m $P2_1$/-		$P2_1$	$P2_1/m$
2/m $P2_1$/c			$P2_1/c$
2/m C -/c	Cc		C 2/c
2/m C -/-	Cm	C2	C 2/m

(Buerger(1942), p.511)

∴ the space groups possible are: Cm , C2 , and C2/m .

Since all previous determinations of monoclinic feldspars resulted in a C2/m space group, then C2/m is the most probable of the three space groups consistent with the symmetry of the lattice planes.

RESULTS:

A. Lattice Parameters:

I. Determined in this work:

$a = 8.361$ Å $\quad \alpha = 90$
$b = 13.020$ Å $\quad \beta = 115.834$
$c = 7.107$ Å $\quad \gamma = 90$

II. More accurate lattice parameters were determined during the structural refinement of crystal #1, by the 4-circle diffraction method, and are as follows:

$a = 8.3282(8)$ Å $\quad \alpha = 90$
$b = 12.9801(12)$ Å $\quad \beta = 115.599$
$c = 7.1358(6)$ Å $\quad \gamma = 90$

B. Space Group = C2/m

C. Structure:-

By indexing the reflections on the precession photographs, it is concluded that all reflections fit the

$h + k$ even, $\quad l$ even, rule

that describes 'a' type reflections. (See Fig.4). The absence of any other reflections characterizes the structure as <u>ALBITE type</u>.

Note:- All 'l' levels are considered even, as the indexing is based on the anorthite cell that has a doubled 'c' length, and ½c* compared with albite.

Certain results of the structure refinement conducted by H.D. Grundy on crystal #1 which are pertinent to the following discussion:

D. Composition as determined by 4-circle X-Ray diffraction:

$$Na_{0.27}Sr_{0.73}Al_{1.73}Si_{2.27}O_8$$

E. Distribution of Al in T1 and T2 sites :

	T1	T2
%Al	49	37

DISCUSSION:

Geochemistry of the Feldspar system:

1 Cations of naturally occuring feldspars all belong to groups IA and IIA of the Periodic Table: See Table. 3.

Table 3: Ionic radii in Angstroms,(Coordination Number = 6)

Group IA elements	Radius of cation		Group IIA elements	Radius of cation	
	P-A*	S-P*		P-A*	S-P*
Li^+	0.68	0.74	Be^{++}	0.35	-
Na^+	0.97	1.02	Mg^{++}	0.66	0.72
K^+	1.33	1.38	Ca^{++}	0.99	1.00
Rb^+	1.47	1.49	Sr^{++}	1.12	1.16
Cs^+	1.67	1.70	Ba^{++}	1.34	1.36

P-A* : Paulings values supplemented by Ahrens - Ahrens(1952)
S-P* : Shannon & Prewitt(1969)

The more recent S-P* values will be used in the discussion.

From Table 3, it is noted that naturally occuring feldspars, i.e. celsians, plagioclase and alkali feldspars contain mono or divalent cations (Na^+,K^+,Ca^{++} & Ba^{++}) that have radii in the range 1.00-1.38A.

2. Other cations that fit the 2 above requirements are listed in Table 4

Table 4: Ionic radii in Angstroms (Coord. # = 6)

Ion	Radius of cation		Group in Periodic Table
	P-A*	S-P*	
Cd^{++}	0.97	0.95	IIB
Cu^{++}	0.96	----	IB
Au^+	1.37	----	IB
Pb^{++}	1.20	1.18	IVB
Hg^{++}	1.10	1.02	IIB
Ag^+	1.26	1.15	IB

The reason why the feldspars with these cations (together with Sr^{++}) do not occur in nature is probably related to their abundance in environments where felspars crystallize. To be specific, elements in Groups IA & 2A are lithophile(associated with silicates) while the other elements listed are chalcophile (concentrated with sulfides) or nobel. As feldspars are aluminosilicates, the cations within their frameworks would be of lithophile elements. The absence of naturally occuring Sr feldspars on the other hand can be related to the low abundance of strontium in nature.

3. Complete solid solution exists at high temperature in the alkali feldspar series (K-Na) between sanidine and high albite, as evidenced by perthites and antiperthites which consist of the unmixed phases stable at low temperature, as demonstrated by experimental work. (Kozu and Endo 1921, McKenzie and Smith 1955). The plagioclase series represents nearly complete solid solution at high temperature (Bowen 1913). The exception is the structural transition between high albite and transitional anorthite phases. (Fleet et al 1966, Ribbe @ Megaw 1962). Peristerites (Laves 1954) and plagioclases displaying a Schiller effect (Laves et al 1965) consist of the unmixing of high temperature plagioclases of albitic and intermediate composition.

No structural series is known to occur in nature between celsian and any of the three other pure end member varieties of feldspar. This could be due to the rarity of the Barium feldspars and the resulting lack of specimens of intermediate compositions. However some minerals of intermediate compositions do occur. Those are: <u>i</u>. Hyalophane consisting of $KAlSi_3O_8$ with less than 30% celsian was considered to be an intermediate member of an isomorphous series between Or and Cn (Taylor, Derbyshire and Strunz, 1934) but more recent X-ray powder work suggested that a break in structure occurs at Cn_{40-45} (Vermaas, 1953). <u>ii</u>. 'Ba plagioclases' (Nockolds and Zies, 1933) and <u>iii</u>. Calciocelsians (Segnit, 1946) represent minerals of intermediate compositions between celsian and albite or anorthite respectively.

4. The distribution and occurence of some solid solutions but not

others can be explained by the common rules of substitution and isomorphism :-

i. The <u>alkali feldspar</u> series:-

The radius differance between K^+ and Na^+ = 1.38-1.02/1.02 = 0.36/1.02 = 36 % . This is tolerable in the disordered high temperature series but is sufficient to disrupt the more ordered low temperature series.

ii. The radius difference between the cations at both ends of the <u>plagioclase</u> series is negligable. The structural discontinuity in the high temperature series is due to the internal reorganisation resulting from the substitution of Al^{3+} for Si^{4+} in the framework to make up for the + charge excess of the cation due to replacement of Na^+ with Ca^{2+}.

iii. No solid solution series exists between K and Ca feldspars as this would require simultaneous internal reallignment due to the charge difference, and loss of order due to increased cation size (i.e. a situation of two extremes with no intermediate).

iv. The size difference between Ba^{++} and K^+ is negligible and an Or - Cn series would be the large radius equivalent of the plagioclase series with hyalophane as an intermediate member.

v. A series between Cn and An can be expected from consideration of the radius difference between Ca^{++} and Ba^{++}: 1.36-1.00/1.00= 36%. This is comparable to the radius difference in the alkali feldspar series. However Bruno & Gazzoni (1970) demonstrated that Ca can substitute for Ba to the extent of 25% only at 1500C, but may increase to 31% at higher temperature. However they do not exclude the possibility of the occurence of complete miscibility at still higher temperature (i.e. that could be revealed if the material were maintained at the high temperature during the structural work).

vi. Sr^{++} has an intermediate radius between that of Ca^{2+} and Ba^{2+} and could be an intermediate in a series between the latter two.

Thus (rBa-rSr)/rSr = (1.36-1.16)/1.16

= 0.20/1.16 = 17%

and (rSr-rCa)/rCa = (1.16-1.00)/1.00

= 0.16/1.00 = 16%

Although no natural feldspars of such composition have been discovered, Nager, Hoffman and Nissen (1969) demonstrated the complete miscibility in the series of Ca-Sr feldspars in synthetic specimens produced at 1500 C.

vii. The structural series of Sr plagioclases (Na-Sr) would result from the simultaneous variation of both factors:- charge difference and radius difference. The material examined in this work occurs intermediatly within such a series. The combination of the two factors governing solid solutions in the feldspar system within the Na-Sr series is thus unique.

The relationship between the synthetic Sr-Labradorite investigated and other feldspars:

The synthetic crystals used lies within the solid solution $(Na_xSr_{1-x})(Al_{2-x}Sr_{2+x})O_8$,(x = 0--1). No minerals of such composition are known to occur naturally.

The following observations can be drawn from a comparison of the synthetic Sr-feldspar with naturally occuring feldspars. See Table 5.

1. The Sr feldspar referred to as Sr-Labradorite is similar to high temperature plagioclase feldspar of intermediate composition, in having an albite type cell, as determined by obtaining only 'a' type reflections in reciprocal lattice photographs. Thus the substitution of Sr in the plagioclase series has the effect of rearranging the tetrahedral framework resulting in C2/m symmetry which is analagous to that of high albite at above 1000 C close to its melting point (Grundy, et al 1967).
2. Sr. Labradorite lattice parameters are distincty larger than those of comparable plagioclase feldspars. This is to be expected due to the larger radius of Sr^{2+} over that of Na^+ or Ca^{++}. By contrast only the *a* and *c* parameters are larger than those of the alkali or barium feldspars, but the *b* parameter is intermediate between that of hyalophane and sanidine. The β angle is lower than the values for the plagioclases and intermediate between that for celsian and sanidine. A decrease in β represents a tendancy to orthorhombic symmetry, and as such it is an indicator of increasing disorder and symmetry. But the main indicator of increasing order is the change over from triclinicity in the plagioclases to monoclinicity in the feldspars with larger cations. In order for the symmetry to be

Table 5. Lattice parameters of some feldspars

	Sr-Labradorite (synthetic)		Some natural plagioclases			K-feldspar	Celsian	Hyalophane
Composition	Ab-27		An-51	An-50 (synthetic)	An-80	Or-100 !	Cn-100 !	Cn-66 Or-33 !
rystal system & Space Group	Monoclinic C2/m		C1	Triclinic C1	I1	Monoclinic C2/m	Monoclinic $I2_1/c$	Monoclinic
Lattice Parameters	Precession	Syntex						
		(7)	(2)	(2)		(3)	(4,5)	(6)
(A°) a	8.361	8.3282	8.180	8.178	8.178	8.5642	8.627	8.52
b	13.020	12.9801	12.859	12.870	12.870	13.030	13.045	12.95
c	7.107	7.1358	7.112	7.107	2 7.093	7.1749	2x7.204	7.14
(°) α	90	90	93.52	93.56	93.50	90	90	90
β	115.83	115.599	116.27	116.18	115.90	115.96	115.25	116
γ	90	90	89.89	90.40	90.65	90	90	90
Structure	albite type simple i.e. only main 'a' type (h+k=2n, l=2n) reflections. (1)		Albite at high T. Intermediate at low temperatue, See Fig 4.		body centred anorthite	sanidine	Anorthite, like, weak 'b' type,	"Low K feldspar" i.e. Orthoclase or Microcline

<u>References</u>:-
1) Bown & Gay, 1958
2) Smith, J.V. 1956
3) Cole et al 1949
4) Newnham & Megaw 1960
5) Gay, P 1956
6) Vermaas, 1953
7) Grundy, personal communication

Note:- SYNTEX Method:-
= 4 circle X-ray crystal diffraction method

monoclinic, the distribution of Al and Si in the framework has to satisfy the presence of a mirror plane and the two fold axis. This aspect will be discussed in a later section.

Factors involved in changing structure and symmetry:

A. Effect of substitution of divalent for monovalent cations on cell structure:

As stated previously, Al substitution for Si accompanies the substitution of divalent for monovalent cations within the plagioclase series in order to maintain electrostatic neurality. The ordering of the tetrahedral framework that takes place as the proportion of Al increases towards anorthite can be explained by considering a model that assumes that plagioclases of intermediate composition to be physical mixtures (Smith & Ribbe 1969) of the two end members of the series: completely ordered Anorthite and variably ordered Albite in the ratio of the divalent to the monovalent cation. The reason why Anorthite is completely ordered and its c axis doubled lies in Loewenstein's rule of Al avoidance, whereby Al and Si alternate in adjacent tetrahedral sites (Loewenstein,1954). This rule is only effective when Al:Si = 1:1 .

A chain showing two rings from the framework of an anorthite is sketched in Fig.6. To satisfy Loewenstein's rule, consecutive rings need to have Al and Si alligned in an opposite configuration. Due to this arrangement, a unit cell of Anorthite would have to enclose two consecutive rings, hence the c axis has to be doubled. If a 7Å cell is considered, Al and Si would be completely disordered

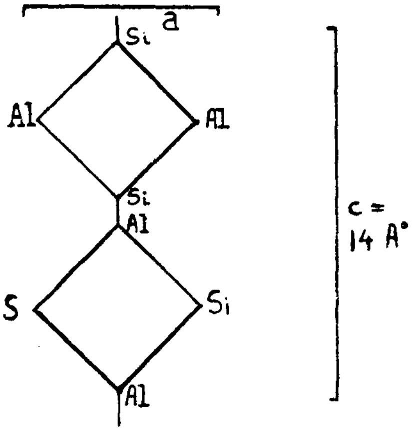
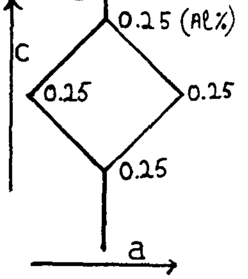


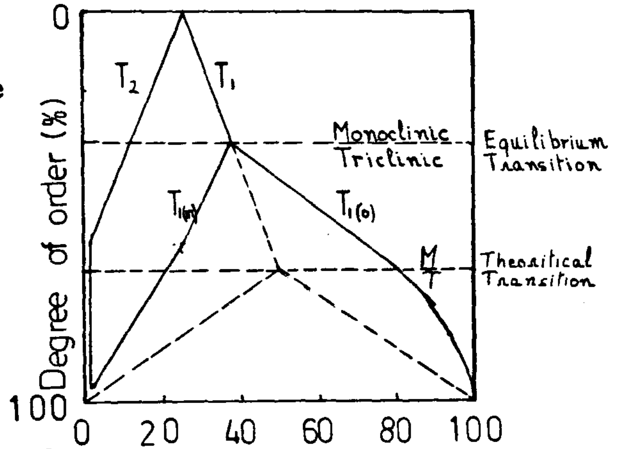
Fig. 6

within it , as the probability of finding Al or Si within each of the original tetrahedral sites would be equally 0.5.

The Albite phase on the other hand contains Si and Al in a ratio Si:Al = 3:1. At high temperature, Albite occurs in a completely disordered form, whereby Al would be equally distributed in the 4 sites of a ring: $T_{1(0)} = T_{1(m)} = T_{2(0)} = T_{2(m)}$ .. See Fig 7.

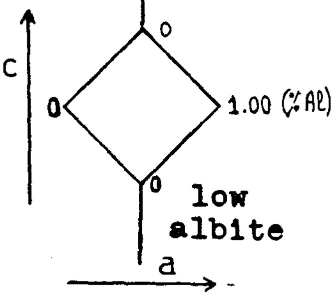
Fig. 7a
high albite





7.b Al occupancy in each tetrahedron

Fig. 7c



low albite

At low temperature, the Albite is ordered, as the Al is segregated into only 1 site in each ring, namely $T_{1(0)}$.

The increase in order in Albite does not occur congruently, but by the enrichment or depletion of each site at a different 'pace'.

A scheme depicting the order-disorder relationship with segregation of Al into distinct sites has been devised emperically for K feldspars but is applicable to Albite, since the composition of the framework is identical. See Fig. 7b.

The degree of ordering of a tetrahedral framework that satisfies Al:Si = 1:3 can be evaluated by the S function devised by Smith and McKenzie(1961).

Thus

$$S = \frac{\sum_{i=4}^{i=1} |0.25 - T_i|}{1.5} \times 100$$

where T = % Al in sites $T_{1(0)}$, $T_{1(m)}$, $T_{2(0)}$, $T_{2(m)}$.

& S = degree of ordering

The S function having the configuration of the high Ab in Fig 7a would be : $S = \frac{4(0.25-0.25)}{1.5} \times 100 = 0.0$

The S of the low albite in Fig7c would be

$$S = \frac{|0.25-1.00| + 3\,|0.25-0.00|}{1.5} \times 100 = \frac{1.5}{1.5} \times 100 = 100\%$$

According to the mixing model described above, the Sr-labradorite can be considered to be a physical mixture of $SrAl_2Si_2O_8$ and $NaAlSi_3O_8$ in the ratio 0.73/0.27.

Thus the Sr Anorthite component would be:

Sr(0.73) Al(1.46) Si(1.46) O(8 X 0.73)

Since in a 7Å'unit cell' of Anorthite : T_1 = 50% Al
T_2 = 50% Al

then $Al(T_1) = 0.73$ $Al(T_2) = 0.73$
$Si(T_1) = 0.73$ $Si(T_2) = 0.73$

The population of the 4 sites in the albite phase can be derived by subtracting the Sr-Anorthite constituents from a formula unit of Sr-Labradorite:- Sr(0.73)Na(0.27) Al(1.73) Si(2.27) O(8) in which by structural analyses: T(1)= 49%Al
T(2)= 37%Al

Thus since there are 2 T_1 sites and 2 T_2 sites in a formula unit.

$Al(T_1) = 0.98 + Al(T_2) = 0.74+(.01) = Al= 1.73$

$Si(T_1) = 1.02 + Si(T_2) = 1.26-(.01) = Si= 2.27$

By subtraction of Sr-Anorthite from Sr-Labradorite:

Na(0.27) Al(0.27) Si(0.81) O(8 X 0.27)

$Al(T_1) = 0.25$ $Al(T_2) = 0.02$
$Si(T_1) = 0.29$ $Si(T_2) = 0.52$

Thus in a formula unit of albite $NaAlSi_3O_8$

$\%Al \text{ in } T_1 = 0.25/(0.25 + 0.29) = 0.25/0.54 = 0.46$

$\%Al \text{ in } T_2 = 0.02/(0.02 + 0.52) = 0.02/0.54 = 0.04$

The degree of ordering in such an Albite is:

$$S = \frac{(2\,|0.25-0.46| + 2\,|0.25-0.04|)}{1.5} \times 100 = 56\%.$$

The Albite phase of the crystal being investigated can be considered an intermediate between high and low Albite.

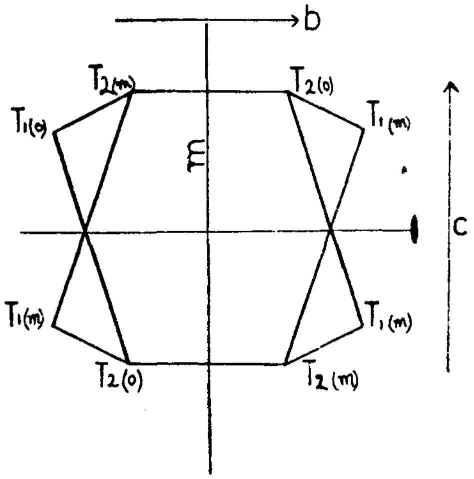
B. Effect of substitution of a larger ion in the cation site of plagioclases on symmetry:

The series $(Na,K)AlSi_3O_8$ occurs in a stable form at high temperature (above 700 C°) but the high temperature mixture unmixes at low temperature. The latter is to be expected in view of the large difference in size of K^+ and Na^+, which are 1.38A° and 1.02A° respectively, and the difference = (1.38-1.02)/1.02 = 36% of the radius of Na. Usually the limits for ionic substitution has been taken at 15%. It has been suggested that on heating a crystal to about 700 C° the vibration of the small Na atom is greater than that of the K atom, such that the effective radius of Na approaches that of K with increasing temperature, and the difference between the two decreases to less than 15%.

In the alkali feldspar series, the high temperature form is entirely monoclinic except for very pure albite that would have to be heated to near its melting point for the triclinicity to be lost (Grundy et al 1967). In this series the change in symmetry is entirely due to the differing size of the cations, as no rearrangement of the tetrahedral framework occurs. Barth (1969) explains the effect of ion size on symmetry as follows:

> If K^+ is replaced by the smaller Na^+, strain develops that is strong enough to transform the monoclinic lattice into triclinic symmetry if Na enters beyond a certain limit. The large K ions block up the cavities of the lattice much better than do the smaller Na ions. If too much Na is introduced, the structure will collapse and become triclinic to suit the modest space requirements of Na.

The rule that $T_{1(0)} = T_{1(m)}$ and $T_{2(0)} = T_{2(m)}$ holds only in the presence of a mirror plane parallel to the ac plane, and a diad parallel to b. See Fig 8. When



all the tetrahedral positions within a unit cell are dissimilar, the mirror plane and the diad are lost as a result of the distortion, and the structure inverts to triclinicity.

Although the explanations given above for the effect of cation size on symmetry discusses the alkali feldspars, the same reasoning for the symmetry transition at the divalent end of the feldspar field is valid.

Bruno and Gazzoni (1970) studied the Ca-Ba feldspar series(which is the divalent equivalent of the alkali feldspar series having a comparable radius span ΔR(Ca-Ba) =(1.36-1.00)/1.00 = 36%.) by synthesizing crystals of intermediate composition at 1450 C°. They concluded that while they could only recover at room temperature homogenized monoclinic celsian with less than 25-31% An, that the complete solid solution at high temperature could not be ruled out. It should be remembered that the melting points of Ba and Ca are higher than those of Na and K, and hence a larger domain of mixing is possible: Table 5 lists the melting points of pure end member feldspars:

Table 5

End Member Feldspar	M.P.(C°)	Reference
$KAlSi_3O_8$	1150	Barth 1969
$NaAlSi_3O_8$	1118	Barth 1969
$CaAl_2Si_2O_8$	1553	Barth 1969
$BaAl_2Si_2O_8$	1640	Ginzberg 1915
	1717?	Dittler & Lasch, 1930

The radius span between Ca^{2+} and Sr^{2+} is smaller, and the intermediate members of a Ca-Sr feldspar series would be expected to be stable at ordinary temerature: Δr =(1.16-1.00)/ 1.00 = 16%. Indeed Nager and Hoffman (1969) produced a series of intermediate members at 1500 C°, that can exist at room temperature. Within that series, the transition from triclinic to monoclinic symmetry occurs at 91% $SrAl_2Si_2O_8$.

In the alkali feldspar system, the transition between monoclinic and triclinic symmetry occurs at Or_{37}, with the monoclinic field increasing with increasing temperature. (See Fig.9)

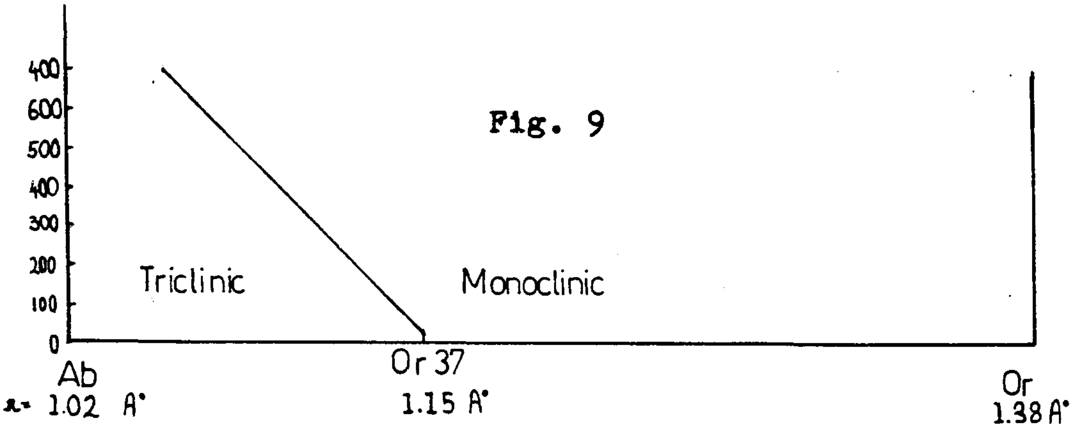


Fig. 9

If the radius effect increases linearly with the increase in K, then the average cation in an intermediate alkali feldspar would be equivalent to an ion radius:

$$r_{Na^+} + \%K^+ (r_{K^+} - r_{Na^+}) \ r \ Or_x$$

for the transition composition, Or_{63}:-

$$1.02 + 0.37(1.38-1.02) = 1.02 + 0.13 = 1.15 \text{ A}$$

A similar calculation to obtain the transition radius between Ca^{2+} and Sr^{2+} feldspar yields:-

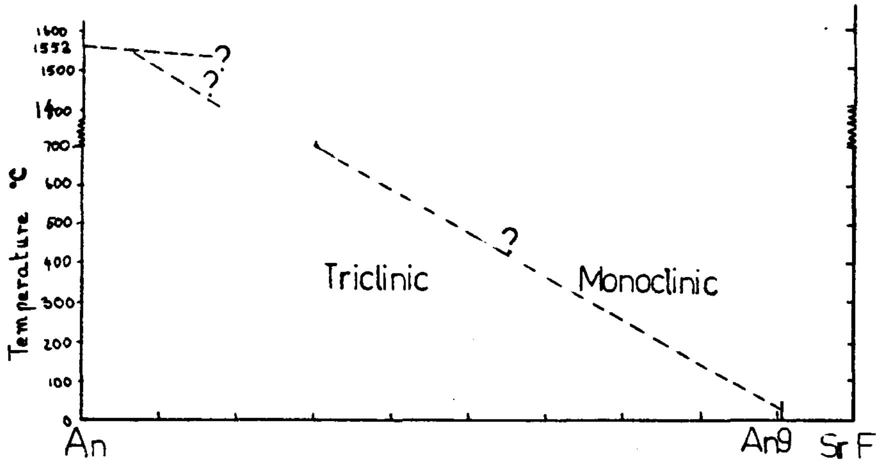
$$1.00 + 0.91(1.16-1.00) = 1.00 + 0.15 = 1.15 \text{ A}$$

The similarity in transition radius in the two instances is evidence that the transition in symmetry between triclinicty and monoclinicity is dependent on cation radius and temperature only, factors that act to the same degree if the tetrahedral framework is of the albite or the anorthite type.

Restating the structure of the available Sr-Labradorite as a proportional physical mixture of 56% ordered triclinic albite and ordered Sr-Anorthite, it appears that the Sr-Anorthite has to be monoclinic (as confirmed by Nagel et al 1969) in order that the resulting mixed crystal be monoclinic.

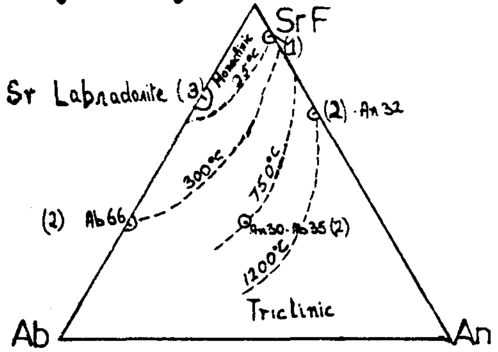
Symmetry of pure Sr-Feldspar:

From the previous discussion, it appears that pure Sr-Feldspar would be monoclinic under most circumstances with the possibility that it reverts to triclinic at temperatures below room temperature, since the monoclinic field shrinks with decreasing temperature. See Fig.10.



The Ternary Sr-Feldspar, anorthite and albite system :

The symmetry fields in this system are shown in Fig. 11 below.



Reference for data used in Fig.11

1. Nager et al., 1969
2. Grove and Ito, 1973
3. This work

It should be noted that the triclinic field extends to a greater extent in the Sr-Feldspar --Anorthite series than on the Albite side, indicating that minerals of mixed An and Ab structures are more susceptible to monoclinicity than those with a framework that is distinctly albitic or anorthitic.

ACKNOWLEDGEMENTS

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APPENDIX

Raw Data from precession work

Specimen No. 1 **Date**: 12 October 1972

Name: Sr-Labradorite

Location: Synthetic

λ = 0.7107 A°

Lattice Parameters:

(mm.) a^*= 11.33/2 b^*= 6.55/2 c^*= 6.67

α^*= 90° β^*= 64° 10′ γ^*= 90°

(A°) a = 8.361 b = 13.020 c = 7.107

α = 90° β =115° 50′ γ = 90°

Film #	μ (°)	Film advance $F\lambda d^*$	screen radius r_s	screen distance r_α	exposure time	Drum setting	
1	20	-	15	-		188.4°	a*c*plane k = 0
2	20	-	15	-		278.4°	⊥ to a*c*
3	20	3.31	20	39mm.	7 hrs.	188.4°	a*c*plane k = 1
4	20	6.6	25	37mm.	57 hrs.	188.4°	a*c*plane k = 2

Specimen No. 2 **Date**: 23 January 1973

Name: Sr-Labradorite

Location: Synthetic

λ = 0.7107 Å

Lattice parameters:
(mm.) a*= 11.33/2 b*= 6.55/2 c*= 6.67
α*= 90° β*= 64° 10' γ*= 90°
(Å) a = 8.361 b = 13.020 c = 7.107
α = 90° β = 115° 50' γ = 90°

Film #	μ (°)	Film advance $F\lambda d^*$	screen radius r_s	screen distance r_α	exposure time	Drum setting	
1	20	-	15	-	1 hour	121.5°	a*c*plane k = 0
2	20	-	15	-	4 hrs.	211.5°	⊥ to a*c*
3	20	-	15	-	44 hrs.	121.5°	a*c*plane k = 0
4	20	-	15	-	48 hrs.	211.5°	⊥ to a*c*
5	20	3.3	20	39mm.	49 hrs.	121.5°	a*c*plane k = 1
6	20	6.6	20	29mm.	80 hrs.	121.5°	a*c*plane k = 2 Zr filtered

Specimen No. 3 **Date:** March 1973

Name: Sr-Labradorite

Location: Synthetic

$\lambda =$ 0.7107 A°

Lattice parameters:
(mm.) $a^* = 11.33/2$ $b^* = 6.55/2$ $c^* = 6.63$

$\alpha^* = 90°$ $\beta^* = 64° 10'$ $\gamma^* = 90°$

(A°) $a = 8.361$ $b = 13.020$ $c = 7.143$

$\alpha = 90°$ $\beta = 115° 50'$ $\gamma = 90°$

Film #	μ (°)	Film advance $F\lambda d^*$	screen radius r_s	screen distance r_α	exposure time	Drum setting	
1	20	-	15	-	-	280.3°	⊥ to a*c*
2	20	-	15	-	-	190.3°	a*c*plane k = 0
3	20	-	15	-	-	190.3°	a*c*plane k = 0 Zr filtered
4	20	-	15	-	-	280.3°	⊥ to a*c* Zr filtered