

ALUMINUM DISTRIBUTION  
IN AN IGNEOUS MAXIMUM MICROCLINE AND  
THE SANIDINE MICROCLINE SERIES

By

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One of the major efforts in the study of the polymorphism of the potassic feldspar group has been directed at the determination of the order-disorder relationships of silicon and aluminum and the connection of this order-disorder with lattice dimensions and physical properties. The analysis of order-disorder has been based heretofore upon the accurate measurement of the silicon oxygen bond lengths because it had not generally been thought that one could differentiate aluminum and silicon on the basis of their scattering power for X-rays. We noticed in this least squares refinement, however, that the effective scattering factor of the tetrahedral cation is a significant function of the aluminum content, as we observe anomalously low temperature factor values, where a silicon scattering factor is used for an aluminum rich site.

The difference in the ionic sizes between silicon and aluminum (often given as  $0.18 \text{ \AA}$ ) is easily measurable if a structure is fitted to a reasonably complete set of observed data by refinement procedures. Several such refinements of potash feldspars are now available in the literature, those of sanidine (Cole, Sørum, and Kennard (1949)), orthoclase (Jones and Taylor (1961)), and an intermediate microcline (Bailey and Taylor (1955)). We can now add a refinement of an igneous maximum microcline to this list and in addition make some

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comments on the results for an authigenic microcline, both of whose refinements have been done as part of the feldspar program at the University of Wisconsin.

We were fortunate at Wisconsin to have access to a sample of a suitable microcline from the collection of Dr. Julian Goldsmith of the University of Chicago. This material is a gray, coarsely perthitic microcline, largely free from the usual microcline twinning. It was collected by Eskola on Pellotsalo, an island in Lake Ladoga, in the Russo-Finnish border area. At the time of collection by Eskola the island was Finnish but is now part of Russian territory. The sample is a maximum microcline as indicated by its  $\gamma^*$  angle of  $92^\circ 14'$ , near the value of  $92^\circ 20'$  often quoted as an observed limit of obliquity for microcline.

The determination of aluminium content of a given site to 1 or 2% required that silicon-oxygen bond distances be known to about  $\pm 0.01 \text{ \AA}$ . Sufficient three dimensional reflections for this accuracy were collected from the zero levels about the  $a$ ,  $b$ , and  $c$  axes, three upper levels each from the  $a$  and  $c$  axes, and six upper levels from the  $b$  axis. Altogether 2350 observed reflections were collected, and these were measured by standard visual methods. The refinement was started from the parameters for intermediate microcline (Bailey and Taylor (1955)) and was done with the Busing-Levy least squares program for the IBM 704 computer.

### The Sanidine Microcline Series

A summary account of relevant facts derived from the work on sanidine, orthoclase and intermediate microcline follows. Table 1 is a condensation of some of the critical data.

Sanidine "C" (Cole, Sørum, and Kennard (1949)) is an artificially sanidinized specimen prepared by heating specimens of orthoclase "C" (the alphabetic designation used for feldspars from the collection of Dr. E. Spencer) at  $1075^\circ$  for 300 hours. Optically it is classed as a high sanidine with  $2V = 44^\circ$  in the sanidine (optic plane parallel to the 010) position. The corrected atomic parameters were derived from three dimensional Fourier sections and lines based upon 737 reflections. The space group of the crystal,  $C2/m$ , requires determination of parameters for two non-equivalent silicon-oxygen tetrahedra. These

non-equivalent tetrahedra have identical sizes with a tetrahedral cation-oxygen bond length of 1.642 Å.

Orthoclase "C" from the ruby mines of Mogok in Burma is classed optically as orthoclase having a  $2V$  of  $44^\circ$  in a plane perpendicular to (010). This structure has been refined by Jones and Taylor (1961) using two dimensional methods including a special ( $\bar{1}10$ ) projection that eliminates most of the overlap appearing in the conventional axial projections. The space group of orthoclase is also  $C2/m$ , requiring two non-equivalent tetrahedra. The average  $Si_1-O$  distance is 1.65 Å and the average  $Si_2-O$  distance is 1.63 Å. It cannot be proven statistically that this difference is real but because of relative similarity in individual silicon-oxygen bond lengths with those of sanidine C, the good precision of the bond distances within each tetrahedra, the consistently larger size of  $Si_1$  through all stages of refinement, and the indication of the existence of ordering by comparison of the physical properties of orthoclase C with sanidine C, the authors conclude it does indicate a real difference.

Spencer  $U$  (Bailey and Taylor (1955)) is classed optically as an intermediate microcline with a  $2V$  of  $76^\circ$  in a plane perpendicular to (010). The space group for this feldspar is triclinic,  $C\bar{1}$ , requiring the specification of the parameters for four non-equivalent silicon-oxygen tetrahedra labeled after a shortened form of the notation due to Megaw (1956), as  $Si_1(0)$ ,  $Si_1(m)$ ,  $Si_2(0)$ , and  $Si_2(m)$ . This is a three dimensional refinement using 3875 reflections for the final refinement by three dimensional sections and lines. The final average cation-oxygen bond lengths for the four non-equivalent tetrahedra are  $Si_1(0)$ -1.700 Å,  $Si_1(m)$ -1.645 Å,  $Si_2(0)$ -1.614 Å, and  $Si_2(m)$ -1.611 Å.

Work on an authigenic maximum microcline ( $\gamma^* = 92^\circ 13'$ ) from the Pontiskalk limestone, Switzerland, is now in the final stages (Finney (1962)) and it will be useful to include some of these results here. The refinement was based upon 750 observed reflections. The space group is triclinic,  $C\bar{1}$ , as in intermediate microcline and one must specify four non-equivalent tetrahedra. The average silicon-oxygen bond lengths in each tetrahedra are  $Si_1(0)$ -1.734,  $Si_1(m)$ -1.612,  $Si_2(0)$ -1.621, and  $Si_2(m)$ -1.611 Å.

The Pellotsalo igneous maximum microcline may also be classed optically as such by its  $2V$  of  $85^\circ$  and its extinction angle on (001) of  $17^\circ$ . The final average bond distances in the four non-equivalent

tetrahedra are  $\text{Si}_1(0)$ -1.741,  $\text{Si}_1(m)$ -1.614,  $\text{Si}_2(0)$ -1.611, and  $\text{Si}_2(m)$ -1.611<sub>5</sub>. The refinement of the Pellotsalo microcline was carried out in two stages. First, 600 selected reflections were cycled in repeated least squares refinements until the parameter shifts became negligible, and then all 2350 reflections were employed. The average magnitude of the shifts between the two refinement stages is about 0.011 Å. This is of the same order of magnitude as the differences between the individual silicon-oxygen bonds in the Pellotsalo microcline and the Pontiskalk authigenic microcline, leading to the conclusion that the two structures are not significantly different as regards silicon-aluminum distribution.

### Distribution of Aluminum in the Five Feldspars

The aluminum distribution published for the sanidine and orthoclase *C* specimens and for the Spencer *U* intermediate microcline specimens was based upon a plot due to Smith (1954). This plot of tetrahedral cation-oxygen bond distance versus the aluminum content was based upon the best available data at that time. Data collected since the 1954 publication indicates strongly that the relation of bond lengths to the aluminum content of a tetrahedra is modified somewhat by the type of silicate in question, whether it be a framework silicate, a layer silicate, one with isolated tetrahedra, and so on. Evidently the general environment around a tetrahedron exerts an influence on the bond distances observed within the tetrahedron.

The values for the Pellotsalo microcline suggest the amount of change necessary for the 1954 curve with regard to feldspar. There has been strong presumption by most who have studied microclines from the point of view of the ordering of aluminum that maximum microcline is an end member in which the segregation of aluminum is complete, that is, all of the aluminum is to be found in one of the four nonequivalent tetrahedra. Because the variation in cell constants and optical parameters of the sanidine-microcline series reaches an observed limit in maximum microcline one intuitively suspects the aluminum segregation, which correlates with the variation in properties, reaches a limit. This segregation limit is most logically the point at which all aluminum is confined to one tetrahedron and all the silicon is in the other three tetrahedra. The use of the 1954 curve gave results indicat-

ing that the Pellotsalo microcline was about 80% ordered. In the 1954 curve the values for pure silicon-oxygen and pure aluminum oxygen bond distances are respectively 1.60 Å and 1.78 Å. If the 1954 curve is modified so that these end points are 1.61 and 1.75 Å we obtain a curve consistent with other potassic feldspar data. Using these latter values the Pellotsalo microcline is 94% ordered, consistent with theoretical expectations regarding maximum microcline. Recent data for anorthite (Megaw, Kempster, and Radoslovich (1961)) and for other feldspars show even more strongly that these latter end points are a necessary modification of the 1954 curve (Smith and Bailey (1963)).

### Correlation of Degree of Ordering with Optics and Cell Parameters

Certain quantities have been listed in Table 1 that, in addition to their ease of measurement, are sensitive to the degree of silicon and aluminum ordering. Included in Table 1 along with the data on aluminum distribution are listed: 1) the extinction angle on (001), 2) the  $\gamma^*$  lattice angles, and 3) the birefringence, " $b$ "- $\alpha$ , for five potassic feldspar polymorphs. The extinction on (001) and the  $\gamma^*$  lattice angle are quantities dependent on the degree of triclinicity of the polymorph and are fixed in value for the monoclinic members orthoclase and sanidine. The quantity " $b$ " in the birefringence " $b$ "- $\alpha$

Table 1. Optical and cell constants pertinent to aluminum distribution in five potassic feldspars

Specimen	$\gamma^*$	Extinction on (001)	" $b$ "- $\alpha$	Aluminum contents in tetrahedral sites			
				Si <sub>1</sub> (0)	Si <sub>1</sub> ( $m$ )	Si <sub>2</sub> (0)	Si <sub>2</sub> ( $m$ )
Sanidine "C"	90°	0°	.0040	0.23	0.23	0.23	0.23
Orthoclase "C"	90°	0°	.0048	0.29	0.29	0.14 <sub>5</sub>	0.14 <sub>5</sub>
Microcline "U"	90° 50'	9.0°	.0060	0.65	0.25	0.03	0.01
Pellotsalo microcline	92° 14'	17°	.0069	0.94	0.03	0.01	0.01
Pontiskalk microcline	92° 13'			0.88	0.01	0.01	0.09

refers to the refractive index of the critical ray vibrating most closely parallel to crystallographic  $b$ . In sanidine this is the  $\beta$  refractive index and in orthoclase and microcline it is the  $\gamma$  refractive index. This quantity is particularly useful since it can change with degree of order in the monoclinic feldspars as well as the triclinic. The birefringence is buffered from the effects of compositional change because it is a difference quantity, both of whose components are affected in the same direction by changes in composition while only one of these components (the "b" index) is affected by changes in aluminum-silicon order and disorder (Hewlett (1959)). As noted by Smith and Mackenzie (1961) the ordering process in igneous feldspars is usually a two step process. That is, ordering begins by segregation of aluminum in equal amounts into both members of a pair of mirror-related tetrahedra so that monoclinic symmetry is retained. At a point in this process enrichment into one member of the pair begins, changing the symmetry to triclinic. The extinction on (001) and  $\gamma^*$  are examples of parameters sensitive to this second stage since they are fixed in monoclinic symmetry. The birefringence " $b$ "- $\alpha$  is sensitive to the general development of order in both stages and is not fixed by monoclinic symmetry. Figures 1a, b, and c, show the  $\gamma^*$  reciprocal

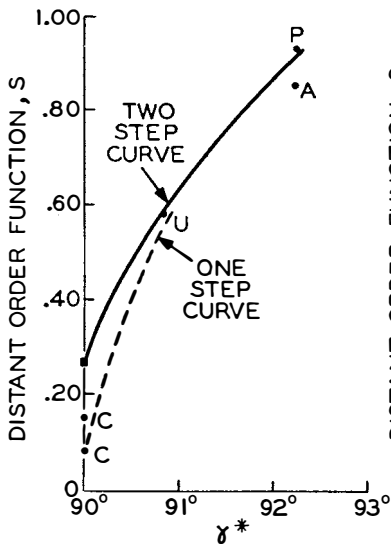


Fig. 1a

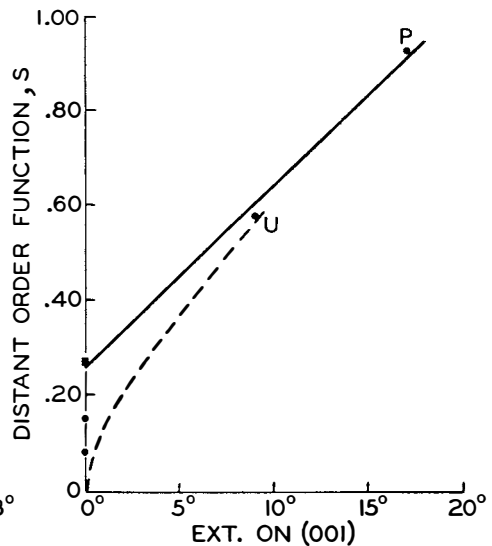


Fig. 1b

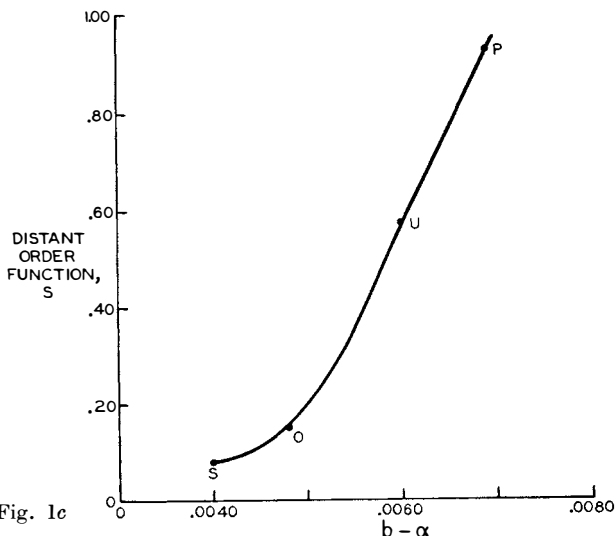


Figure 1 a, b, c. Relation of the distant order function, S, to a)  $\gamma^*$ , b) extinction angle on (001), and c) the birefringence “b”- $\alpha$ .

$$S = \sum_{i=1}^{i=4} \left( \frac{|0.25 - S_i|}{1.50} \right)$$

where  $S_i$  is the distant order,  $Al/Al + Si$  in the four different types of tetrahedra. The points on the curves are labeled such that S=sanidine C (Cole, Sørum, and Kennard (1949)), O=orthoclase C (Jones and Taylor (1961)), U=intermediate microcline (Bailey and Taylor (1955)), P=Pellotsalo maximum microcline, and A=Pontiskalk autigenic maximum microcline (Finney (1962)).

angle, the extinction angle on (001), and the “b”- $\alpha$  birefringence respectively plotted against the distant order function. This function is defined by:

$$S = \sum_{i=1}^{i=4} \left( \frac{|0.25 - S_i|}{1.50} \right),$$

where  $S_i$  is the ratio  $Al/Al + Si$  in the four different types of tetrahedra (Smith and Mackenzie (1961)). The values for aluminum contents of tetrahedra are derived from the modified curve of Smith and Bailey (1963). These curves are of a necessarily preliminary nature because so few points are available to define them. On the plots of extinction on (001) and  $\gamma^*$  vs. the distant order function two lines are dashed in between the value observed for intermediate microcline and the

limiting values of the monoclinic feldspars. This is to illustrate the possible differences between a two step sanidine-orthoclase-microcline ordering process and a one step sanidine-microcline process. The two step curve intercepts the ordinate at about 0.27, which Smith and Mackenzie (1961) suggest as a possible limit of segregation in orthoclase. The “ $b$ ”- $\alpha$  birefringence is probably affected by the total amount of order rather than by the degree of triclinicity and would not therefore change greatly between one and two step ordering processes.

Smith and Mackenzie (1961) suggest that there is reason to believe that the optic axial angle is a function of the general development of order, while the rotation of the optic axial plane from the positions with monoclinic symmetry is a measure of the unbalance of order between the pairs of tetrahedra related by symmetry in the monoclinic feldspars. Therefore the extinction on (001), a function of the rotation of the optic plane, and  $\gamma^*$ , also related to this rotation, are perhaps better described as functions of the difference of aluminum contents in  $\text{Si}_1(0)$  and  $\text{Si}_1(m)$ . In Figure 2 this difference is plotted against  $\gamma^*$  and extinction on (001).

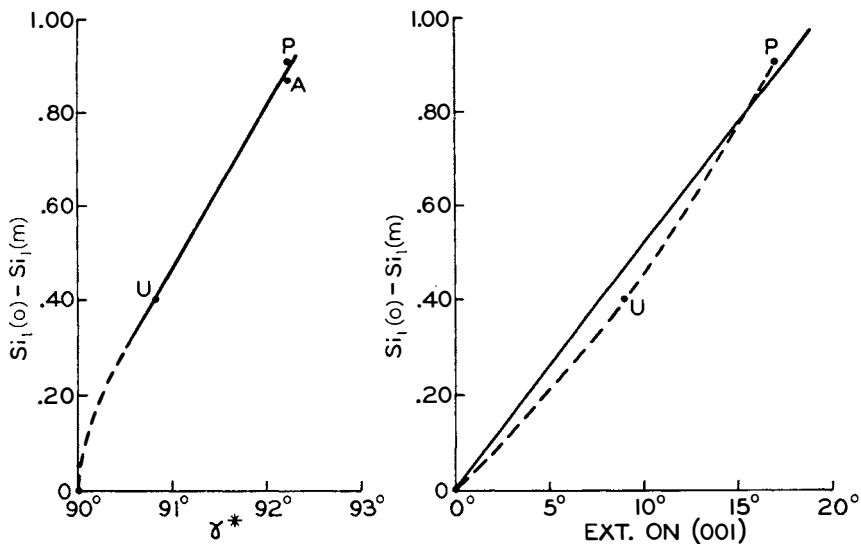


Figure 2. The difference in aluminum content in the  $\text{Si}_1(0)$  and  $\text{Si}_1(m)$  tetrahedra plotted against two measures of triclinicity,  $\gamma^*$  and the extinction angle on (001), for three microclines.



### Correlation of Degree of Order with the Intensities of Selected Reflections

In the monoclinic feldspars intensities of type  $hkl$  are equivalent to those of type  $h\bar{k}l$ , and those of type  $\bar{h}kl$  are equivalent to  $h\bar{k}l$ . In the triclinic feldspars this equivalence is lost and the departure of a formerly equivalent pair from mutual equality of intensity is a measure of the degree of triclinicity and ordering that has taken place. The relative degree of change in the equivalence of former mirror related reflections is another measure of the degree of order in the second step, orthoclase to microcline, of the two step process. Ratios of the form  $I(hkl)/(h\bar{k}l)$  can be calculated for the triclinic polymorphs and such a set of ratios has been plotted on Figure 3 using the monoclinic value of unity, the values from Spencer U, and the values from the Pellotsalo maximum microcline as the data points. The ratios have been arranged in every case so that the numerator is larger than the denominator and all the values can then be represented using the same coordinate axes.

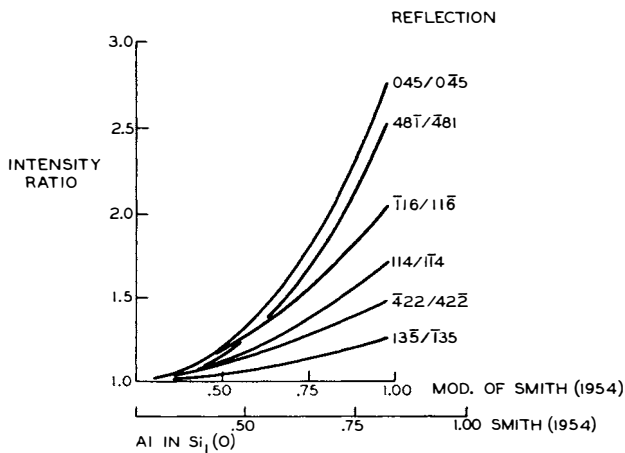


Figure 3. Plot of intensity ratios of selected reflections from the Pellotsalo maximum microcline and Spencer U intermediate microcline.

### The Segregation of Aluminum and the Twinning of Microcline

Structural analyses of feldspars show a consistent tendency of aluminum enrichment into the  $Si_1$  tetrahedra and aluminum migration

out of the  $\text{Si}_2$  tetrahedra. Certain spatial and charge balance factors are probably influential in promoting migration of aluminum from the  $\text{Si}_2$  to the  $\text{Si}_1$  tetrahedra. The  $\text{Si}_2$  positions are connected by a common oxygen atom,  $\text{OA}_2$ , that lies on the mirror plane in monoclinic feldspar and serves to link the chains of fourfold rings sideways across the mirror plane or the approximation to a mirror that remains in the triclinic types. Expansion of the  $\text{Si}_2$  sites by entrance of aluminum in place of silicon would tend to force the chains away from this common oxygen, or alternatively to force the  $\text{Si}_2$  cations into the already closely packed chains. In contrast the  $\text{Si}_1$  positions are positioned so that they can expand relatively easily into the spacious potassium cavities. Ferguson, Traill, and Taylor (1958) point out that charge balance considerations appear to be significant in influencing distribution of aluminum. The strengths of the positive bonds reaching each oxygen should total two and therefore the total positive bond strength for each tetrahedron of four oxygens should total eight. The charge distribution in sanidine, as calculated by Ferguson, et al. is actually  $\text{Si}_1 = 8.05$  and  $\text{Si}_2 = 7.94$ . The slightly positive nature of the  $\text{Si}_1$  tetrahedra will facilitate the exchange of trivalent aluminum for quadrivalent silicon. The further segregation of aluminum into half of the  $\text{Si}_1$  tetrahedra in the triclinic potash feldspars is usually ascribed to the reduction in internal energy consequent to the complete segregation of aluminum into one set of equivalent tetrahedra. There are eight  $\text{Si}_1$  tetrahedra in the conventional unit cell of the potash feldspars. We can be perfectly general if four of these tetrahedra related in the monoclinic feldspars by the mirror plane and the center of symmetry, and consequently designated as  $\text{Si}_1(0000)$ ,  $\text{Si}_1(m000)$ ,  $\text{Si}_1(m00c)$ , and  $\text{Si}_1(000c)$ , are considered. These sites are all equivalent environmentally in the monoclinic members and each may with equal probability contain an aluminum atom. As further segregation takes place with the consequent inversion to triclinic symmetry the resulting orientation of the triclinic axes of a given domain depends on which of the four sites becomes dominant in accepting aluminum. Figure 4 shows the relative orientations of triclinic domains produced by aluminum migration into the four sites with the orientation of the original monoclinic host held constant. Such orientation domains can enlarge in the monoclinic host but as they do they will remain related by the original monoclinic symmetry elements as shown by Laves (1950). The growth of

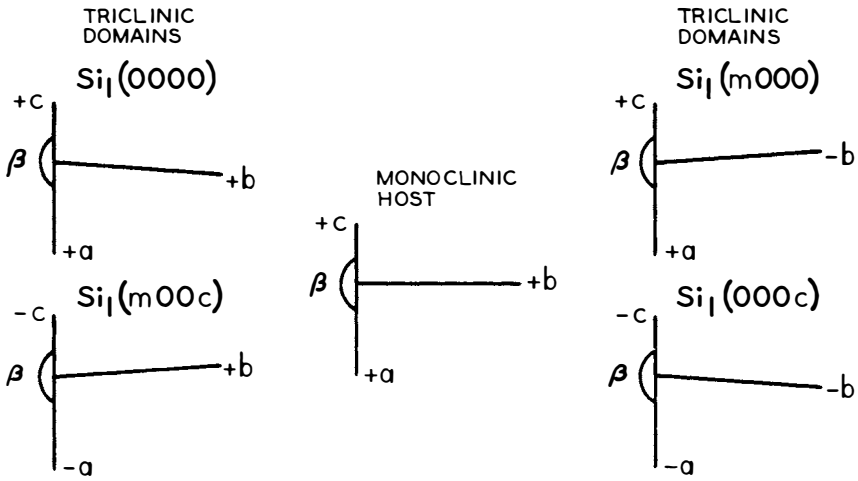


Figure 4. Relative orientations of triclinic domains produced by aluminum migration into  $Si_1(0000)$ ,  $Si_1(m000)$ ,  $Si_1(m00c)$ , and  $Si_1(000c)$ .

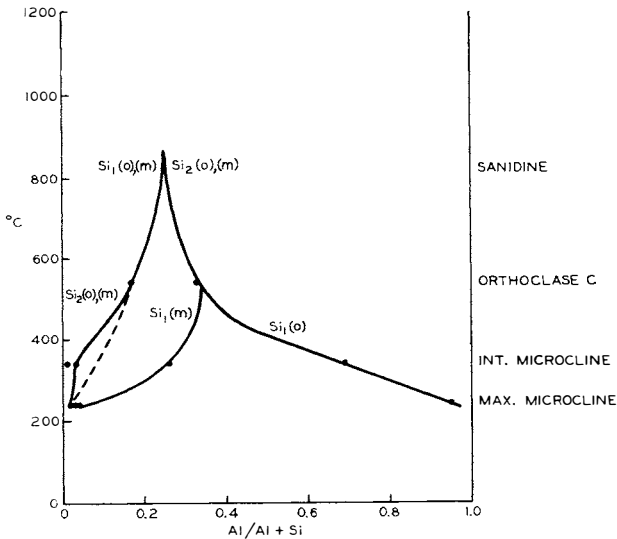


Figure 5. A possible course of aluminum segregation following the data from orthoclase (Jones and Taylor (1961)), intermediate microcline (Bailey and Taylor (1955)), and the Pellotsalo maximum microcline.

these domains in a triclinic crystal can result in the cross hatch albite-pericline twinning or finer scale phenomena as discussed by Smith and Mackenzie (1961).

### The Course of Aluminum Segregation

By adding the data for orthoclase C to the original diagram of Laves (1960), Smith and Mackenzie (1961) have shown the sequence of aluminum segregation into  $\text{Si}_1(0)$  during ordering. A diagram similar to the (1961) diagram of Smith and Mackenzie is given in Figure 5, showing how the Pellotsalo microcline may be fitted to the curves. The dashed portion of the  $\text{Si}_2(0,m)$  curve indicates the course proposed for this tetrahedron by Smith and Mackenzie. The solid line indicates the probable course as indicated by the Pellotsalo microcline data.

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