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# Exsolution in potassium–calcium feldspars: experimental evidence and relationship to antiperthites and Bøggild lamellae

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**Abstract**

Fine lamellae (approximately 75 A across) and associated streaking of "a" reflections in K-exchanged plagioclase feldspars ($An_{44}Or_{56}$ to $An_{38}Or_{62}$) have been produced in samples annealed at 1050° to 1100°C for two weeks to four months. Streaking of "a" reflections was not observed in samples annealed below 1050°C or above 1100°C for periods up to four weeks. The lamellae are probably produced by exsolution involving a spinodal mechanism. Only one lamellae orientation has been observed in a given area of a grain, but two apparent orientations, $(\bar{3}01)$ and near $(1 \cdot \overline{10} \cdot 4)$, have been measured. These orientations are similar to those measured for Bøggild lamellae in an Adirondack plagioclase of average composition $An_{44}Ab_{53}Or_3$, and indicate that initial planes of minimum strain are the same for both intergrowths. The K–Ca feldspar exsolution may be related to the same miscibility gap as that for antiperthites, although the antiperthites probably exsolve by a nucleation and growth rather than by spinodal decomposition. The relationship of K–Ca feldspar lamellae to the formation of Bøggild lamellae is unclear. If Al–Si diffusion is the rate-controlling step, the small size of the experimentally produced K–Ca feldspar lamellae is consistent with the slow rate of homogenization of Bøggild lamellae.

## Introduction

A goal of studying feldspar exsolution is to place constraints on the formation conditions and the cooling histories of rock bodies containing these intergrowths. Two of the most challenging intergrowths to study are the antiperthites (intergrowths of K feldspar with plagioclase of $An_{38-50}$) and the Bøggild lamellae ($An_{45-58}$) of the intermediate feldspars. Since the composition range of these two intergrowths overlaps, and since Bøggild lamellae are not found in plagioclase with less than $Or_{1.6}$ (Nissen *et al.*, 1967), authors in earlier papers (Nissen *et al.*, 1967; Christie, 1969; Smith *in* Smith and Ribbe, 1969) suggested that Bøggild lamellae were a possible precursor to antiperthites. This idea has become less prevalent in more recent years as the nature of the Bøggild lamellae has become better known (McConnell, 1974a, b; McLaren and Marshall, 1974; Smith, 1974; Morimoto *et al.*, 1976). A detailed review by Smith (1974) suggests that antiperthites may form by more than one mechanism. Kay (1977) has shown that antiperthites in anorthosites are probably the result of exsolution involving nucleation and growth.

An important aspect in interpreting these intergrowths is to understand the phase and kinetic relationships in the subsolidus region of the ternary feldspar diagram. An attempt to begin clarifying these relations has been made by experimentally producing K–Ca feldspars and ternary feldspars with An contents from 38 to 47 and annealing these feldspars at high temperature. This paper reports the results of annealing K–Ca feldspars.

## Examination of the starting material

Three natural intermediate plagioclases were used in the exchanges to produce the K–Ca and ternary feldspars. Two samples, KI 3343 ($An_{41.4}$) and KI 3347 ($An_{37.6}$), were low structural-state plagioclases from the Kiglapait Intrusion in Labrador (Morse, 1969). The third sample, LS-1, was a low structural-state andesine of average composition $An_{44}$ but with a composition range from $An_{42-47}$ from the Adirondacks near Saranac Lake.

All three samples were examined for the presence of submicroscopic inhomogeneities, using a JEM-7A transmission electron microscope operating at 100 kV. The microscope was equipped with a tilting stage allowing seven degrees of tilt and 360° rotation of the tilt. Crushed grain samples were used to provide a series of orientations for each sample. No submicroscopic inhomogeneities were observed at this scale in the KI samples. Two sets of Bøggild lamellae were observed in LS-1, and antiperthites were observed optically.

These three plagioclases were exchanged to their K–Ca equivalents, using a technique similar to that of Viswanathan (1972). Grains in the size range 75 to 100 $\mu$m were placed in a platinum crucible with a much larger amount of reagent grade KCl and were heated at 850°C in air for two weeks. The exchanged product was checked for homogeneity by electron microprobe analysis and by monitoring the position of the ($\bar{2}01$) reflection by powder X-ray diffraction. Since the exchange proceeds in a homogeneous front, the extent of exchange can be recorded by looking at the intensity ratio of the ($\bar{2}01$) reflections for the original feldspar and the exchanged product. The exchange has gone to completion when the ($\bar{2}01$) peak of the original material disappears. Cell refinements on the exchanged plagioclases give values comparable to Viswanathan (1972) for K–Ca feldspars, and indicate that the K has gone into Na sites. Single-crystal photographs indicate that although the feldspars have been badly cracked due to coherency strain (Petrovich, 1974), the "a" and "e" reflections, and hence the essential structure of the plagioclase, have been preserved through the exchange. The K-exchanged feldspars were reexamined on the JEM-7A TEM and showed no apparent change in homogeneity or difference in the Bøggild lamellae (LS-1) from the original feldspars.

## Results of heat treatment of potassium–calcium feldspars

The K–Ca feldspars were annealed from 800° to 1200°C for two to four weeks. In addition, the KI 3343 K–Ca feldspar which had been annealed at 850°C for four weeks was annealed at 1100°C for four months. The experiments were done in platinum tubes at one atmosphere in air. Temperature control was generally ± 10°C. Samples were air-quenched.

The annealed samples were reexamined by the JEM-7A TEM to determine any changes. All three starting materials annealed at 1100°C showed streaking of "a" reflections in electron diffraction patterns. Qualitatively, the streaking appeared to be better developed in samples annealed for longer times. Some of the grains annealed at 1050°C showed faint streaking, but it was not as well developed as for samples annealed at 1100°C. Samples annealed at higher and lower temperatures showed no streaking. Feldspars annealed at 1100°C and above are probably in a high structural state since no "e" reflections were observed. The development of the streaking is consistent with a lamellar microstructure normal to the streaking. Bright-field examination on the JEM-7A revealed no evidence of a lamellar microstructure (Kay, 1975).

Subsequently, samples of KI 3343 K–Ca feldspar annealed at 850°C for four weeks and then at 1100°C for four months have been examined on a Siemens 102 transmission electron microscope operating at 125 kV at Cornell University. Crushed grains showed no microstructure at a magnification of 100,000 to 125,000× following the 850°C heating for four weeks, but after heating at 1100°C for four months a lamellar feature perpendicular to the direction of the streaking (Fig. 2) was observed. The lack of lamellae in the 850°C sample indicates that lamellae were not present in the starting material and were not produced during the exchange. The lamellae were produced during the annealing at 1100°C and are responsible for the development of streaking in the diffraction patterns of these samples. The streaking in the longer-term 1100°C annealing experiment is resolved into distinct side bands. A bright-field electron micrograph of the lamellae and the associated diffraction pattern are shown in Figure 1. The lamellae are on the order of 75 angstroms and are too small to have been resolved by the JEM-7A.

The character of the lamellae and the diffraction patterns are of the type thought to be associated with spinodal decomposition (Owen and McConnell, 1974; Yund *et al.*, 1974; Champness and Lorimer, 1976). The lamellae can be imaged in dark-field using the "a" reflections. From orientation data to be given later and the absence of "e" reflections, they cannot be associated with "e" reflections. The lamellae are generally smaller than anything that has been reported to be Bøggild lamellae, and the An contents of two samples ($An_{41.4}$ and $An_{38.8}$) are outside the range normally quoted for Bøggild lamellae.

A further interesting point can be made from the annealing experiments of the K–Ca feldspars at 1100°C. The anorthite–orthoclase phase diagram at one atmosphere determined by Schairer and Bowen (1948) indicates that compositions such as $Or_{58}An_{42}$ should be in the leucite plus anorthite plus liquid field at 1000°C. Thus a K–Ca feldspar is metastable at this temperature. Presumably, if exsolution were allowed

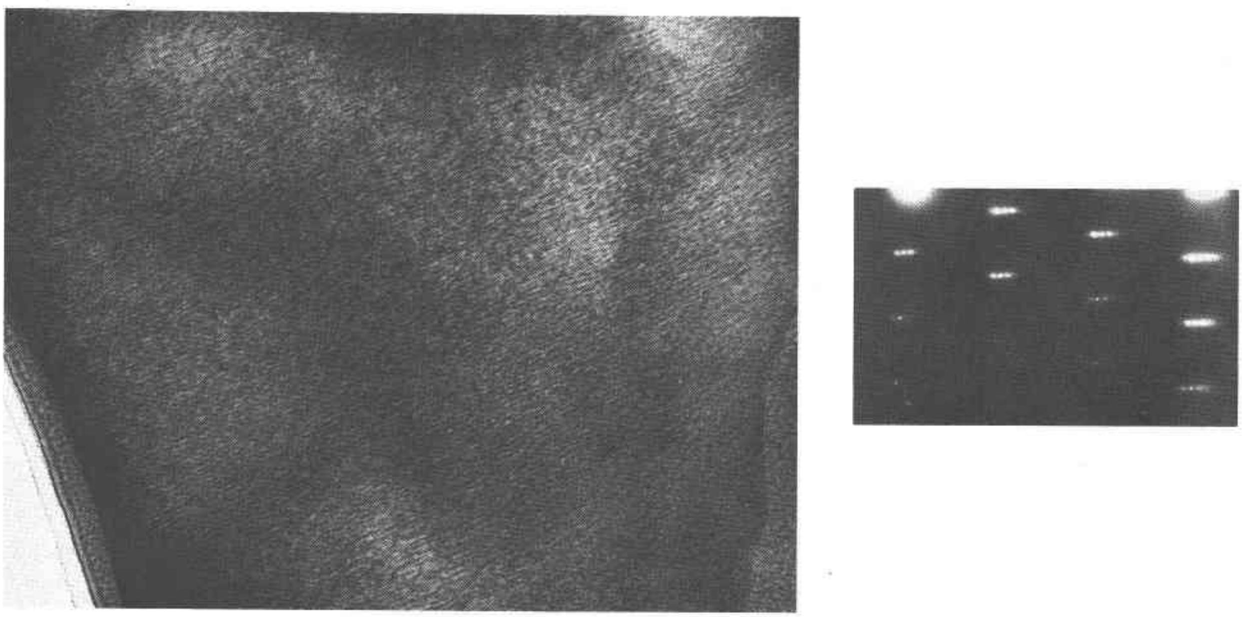

Fig. 1. (a) Bright-field electron photomicrograph of lamellae produced in sample KI 3343 heated at 850°C for four weeks and subsequently at 1100°C for four months (200,000 ×). (b) Electron diffraction pattern of the grain in Fig. 2a showing side bands associated with "a" reflections (photos by D. Kohlstedt).

to proceed to completion, an anorthite phase and an orthoclase phase would result. Melting would occur, and the final assemblage would be orthoclase plus leucite plus melt. The lack of melting in the K–Ca feldspar at temperatures above the melting point in the orthoclase–anorthite system must be related to the structure and aluminum–silicon distribution of the feldspar. The K-exchanged equivalents seem to be approximately following the melting behavior of the unexchanged plagioclase.

A further point concerns the diffraction characteristics of the exchanged LS-1 plagioclase containing Bøggild lamellae. It may be significant that no change in the diffraction characteristics was observed in exchanged samples annealed below 1050°C. If the difference in composition between the Bøggild lamellae in these samples is as great as the $An_{10-12}$ suggested by Nissen *et al.* (1973) and Cliff *et al.* (1976), the difference in the *a* cell dimension and $\alpha$ angle of the lamellae should be increased for the exchanged samples (Viswanathan, 1972). For exchanged $An_{45}$ and $An_{55}$ plagioclases, the $\alpha$ angles would differ by 50 min and the *a* cell dimensions by 0.005A. Differences as great as these should result in resolution of two diffraction lattices. Further work is being done on this, but it appears that at least in this sample the compositional differences cannot be as great as those suggested for the Lake County labradorite examined by previous workers.

### Orientation of the streaking

The orientation of the streaking of side bands was determined by indexing electron diffraction patterns and measuring the angle of the streaking against a known crystal direction. Cell parameters for indexing the diffraction patterns were obtained from the cell refinement of the LS-1 K–Ca feldspar. Orientation data from the diffraction patterns were plotted on a Wulff net, and the true orientation of the lamellae was determined by solving the apparent dip problem from a number of different orientations. Individual measurements may have errors of ± 4°. Measurement of streaking directions in all three samples were similar within this error, and the combined results are shown in Figure 2.

Most of the data fall on two great circles defining orientations for the lamellae of $(\bar{3}01)$ and close to $(1\cdot\overline{10}\cdot 4)$. There are other points which do not fit these great circles that cannot be easily explained. Although two orientations are well-defined by the data, two directions of streaking were not observed in any of the measured diffraction patterns. The reason for this is not entirely clear. The chances of observing a diffraction pattern of at least one grain with the features associated with the streaking in the proper orientations should be high, and two directions of streaking should have been observed. This strongly suggests that only one direction of the features associated with the streaking is developed in any small area of a grain, and is supported by observations on the K–Ca feldspar of KI3343 where only one orientation was observed in each grain.

### Orientation of the Bøggild lamellae

Since some of the original samples contained Bøggild lamellae and all of the exchanged samples had Al–Si compositions near the Bøggild range, the Bøggild lamellae in LS-1 were examined and the orientation measured. Two directions of Bøggild lamellae were prominent in the LS-1 sample. A bright-field photomicrograph of these lamellae is shown in Figure 3. The two sets of lamellae appear to be equally well-developed and cannot be distinguished without determining their orientation. Orientations were determined using the same methods as for the microstructure associated with the streaking, except now the orientation of the lamellae relative to the known crystallographic direction was determined from the bright-field image of the lamellae. Within the error of the measurements, no difference in orientation was

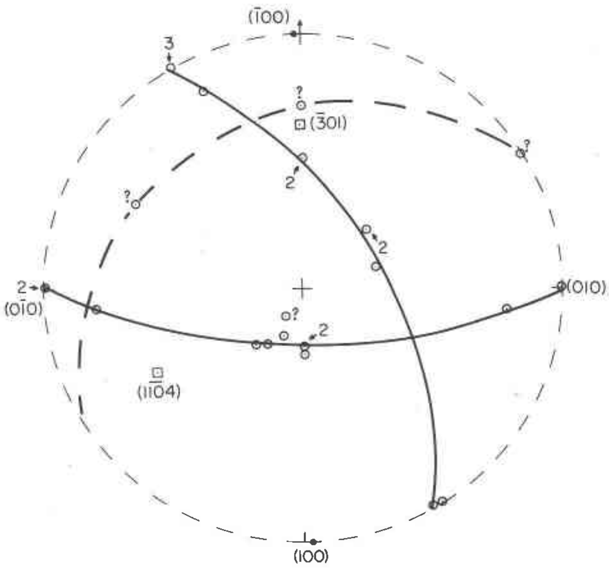


Fig. 2. Stereographic projection showing the orientations of the streaking associated with the "a" reflections in the annealed potassium-calcium feldspars. Open circles represent one measurement except where indicated by a number and an arrow. Open squares represent poles to the plane of the orientation of the lamellae. Question marks indicate unexplained measurements.

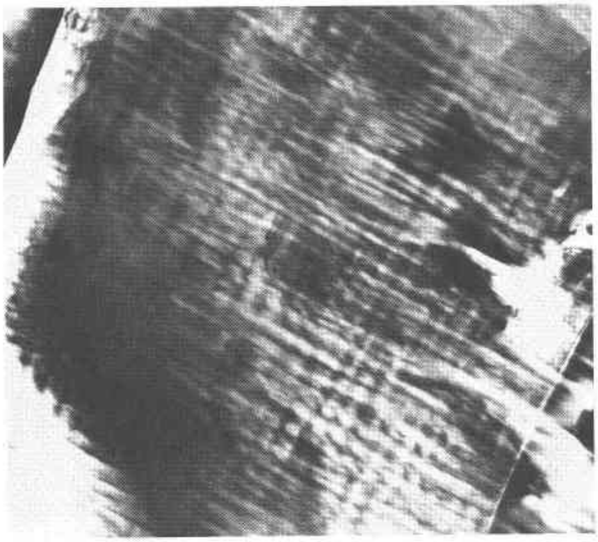

Fig. 3. Bright-field photomicrograph of two sets of Bøggild lamellae in SR-5 Adirondack plagioclase (24,000 ×).

detected for K-exchanged *vs.* non-exchanged samples or for heated *vs.* unheated samples.

The orientation data are shown in Figure 4. Most of the data lie on two great circles corresponding to orientations of $(\bar{3}01)$ and near $(1\cdot\overline{10}\cdot4)$. These two orientations correspond to those near $(\bar{3}01)$ and near $(0\bar{4}1)$ of Bøggild (1924). Several other points, marked by question marks, do not fit these great circles and cannot be easily explained. More work needs to be done to determine whether or not a third orientation is present. No bright-field photographs showed three orientations of lamellae. However, if the orientation of the third set is correct, the angles between the three planes would be such that one plane would always be out of contrast regardless of the orientation of the crystal.

The similarity in orientation between the Bøggild lamellae and the feature associated with the streaking does not necessarily indicate that the two are the same feature. The similarity does indicate that the planes of minimal elastic-strain energy are similar for the two features.

### Discussion of the K–Ca feldspar lamellae, antiperthites, and Bøggild lamellae

The most probable explanation for the microstructure observed in the K–Ca feldspars is exsolution by a mechanism of spinodal decomposition within the large ternary miscibility gap between coexisting plagioclases and alkali feldspars (Fig. 5).

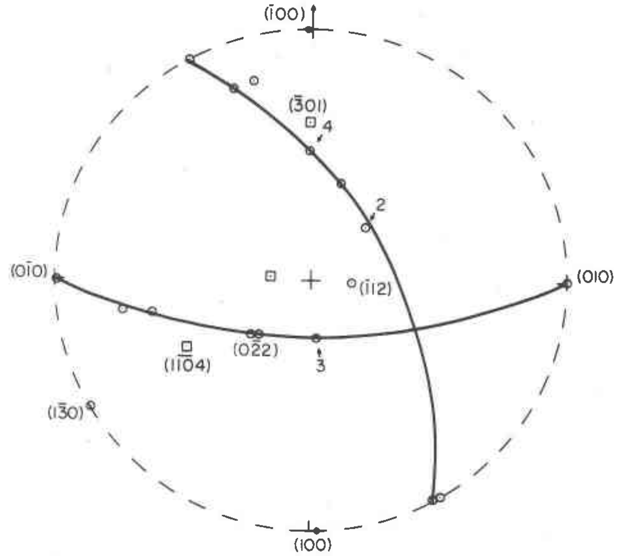


Fig. 4. Stereographic projection showing the orientations of Bøggild lamellae in sample LS-1. Open circles represent measured orientations in micrographs. Multiple measurements of the same orientation in different micrographs are indicated by a number and an arrow. Open squares represent poles to the plane of the orientation of the lamellae.

Due to constraints imposed by Al-Si diffusion rates, this exsolution would only develop at high temperatures above the coherent spinodal. The diffraction streaking is resolved into distinct side bands as growth occurs and is a consequence of the periodicity of the lamellae. A detailed discussion of exsolution mechanisms and the meaning of the coherent spinodal can be found in Hilliard (1970) and Cahn (1968). A brief summary can be found in Yund and McCallister (1970).

Antiperthites such as those found in anorthosites are related to the same solvus and probably exsolve by a nucleation and growth mechanism, between the spinodal curve and the strain-free solvus (Kay, 1977). The difference in exsolution mechanism between the antiperthites and K–Ca feldspars is thus related to their K content. As shown in Figure 6, on cooling, K–Ca feldspars intersect the spinodal curve at very high temperatures, and hence exsolution occurs by a spinodal mechanism. Antiperthites, on the other hand, intersect the spinodal at lower temperatures and exsolution occurs by nucleation and growth, since they enter the miscibility gap at high temperatures where Al-Si diffusion is still relatively rapid.

The Bøggild lamellae are also thought to be formed by exsolution involving a mechanism of spinodal decomposition (McConnell, 1974b; Champness and Lorimer, 1976). This exsolution could be associated with the intersection of the ternary miscibility gap with the An–Ab join. Since the Bøggild lamellae are not found in plagioclases with less than $Or_{1.6}$ (Nissen *et al.,* 1973), the miscibility gap could terminate before reaching the Ab–An join. If so, there must be a spinodal which extends from the An–Or join across the ternary field to the composition range of the Bøggild lamellae near the Ab–An join. Since antiperthites form by nucleation and growth, the spinodal surface would have to extend below this composition at lower temperatures. The Bøggild lamellae would thus have to form at lower temperatures than antiperthites in plagioclases containing both.

Alternatively, the Bøggild lamellae could be associated with a separate miscibility gap along the Ab–An join. Like the Bøggild lamellae, peristerites and Huttenlocher lamellae result primarily from the redistribution of Al, Si, Ca, and Na. Smith (1972), among others, associates these two intergrowths with separate miscibility gaps intersecting the Ab–An join, but of unknown ternary extent. If the Bøggild intergrowths are associated with a third miscibility gap along the Ab–An join, they could form spinodally at a temperature above or below the temperature-of-formation of antiperthites. The surface of the spinodal associated with the formation of the Bøggild lamellae would not be related to and need not be

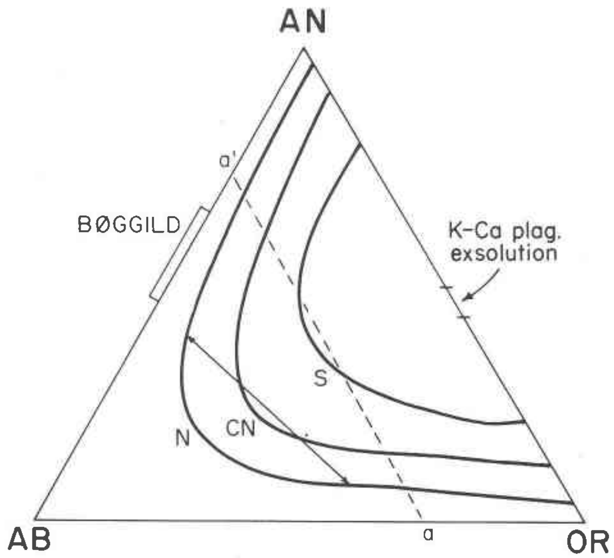


Fig. 5. Ternary diagram showing the schematic position of the coherent spinodal (S), the coherent solvus (CN), and the strain-free solvus (N) at 1100°C. The composition interval of the Bøggild lamellae along the An–Ab join is shown. The double-arrowed line represents a sample tie-line between a plagioclase and an alkali feldspar.

continuous with the spinodal surface of the ternary miscibility gap.

A third possibility is that Bøggild lamellae are the result of a disordering phenomenon as suggested by Smith (1972).

While choosing among the above possibilities is difficult, arguments can be made against Bøggild lamellae being the precursors of antiperthites. Electron microscopy on Adirondack plagioclases containing both antiperthites and Bøggild lamellae indicates that there is no tendency for the Bøggild lamellae to be depleted or absent in the regions of the K-feldspar blebs. No size gradation appears to exist between the Bøggild lamellae and the smallest K-feldspar blebs, as would be expected if Bøggild lamellae are the precursors of antiperthites. Lastly, while not a sufficient criterion, the orientations of antiperthites and Bøggild lamellae are not parallel.

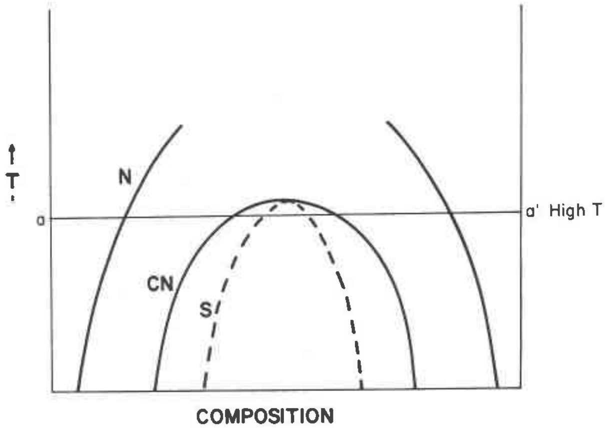


Fig. 6. Vertical cross-section parallel to the An–Or join in composition-temperature space for the ternary feldspars showing the strain-free solvus (N), the coherent solvus (CN), and the coherent spinodal (S). Line labeled "high T" shows the schematic relations along *a–a'* in Fig. 5.

### Role of potassium in Bøggild lamellae

The role of the K in the Bøggild lamellae remains a problem. Champness and Lorimer (1976), among others, believe the K may be a catalyst in the exsolution of Bøggild lamellae. However, Smith (1974) points out that many samples not containing Bøggild lamellae have 1 percent Or, which should be sufficient for catalysis. Observations on natural Bøggild lamellae and their K-exchanged equivalents provide no explanation for the necessity of a minimum K content. Possibly the Or content in these plagioclases is simply a reflection of the environment of formation of plagioclases containing Bøggild lamellae, rather than an integral factor in the development of Bøggild lamellae. As pointed out by Sen (1959), plagioclases crystallized and cooled slowly at high temperatures are more likely to contain K in their structure than plagioclases formed at lower temperatures. Bøggild lamellae are commonly found in anorthosites and layered basic intrusions where crystallization temperatures are postulated to be quite high and cooling rates are slow. They have not been reported in metamorphic rocks formed at lower temperatures.

### Heating of Bøggild lamellae

The actual temperature of the formation of Bøggild lamellae is not known. Nissen *et al.* (1967) found that dry heating at 1160°C for seventy days produced no change in the color or intensity of the iridescence of a plagioclase containing Bøggild lamellae. Hydrothermal heating of Bøggild lamellae at 1000°C by McConnell (1974a) produced no change in spacing or development. These results are consistent with the production of the K–Ca lamellae in this study. If heating a highly metastable feldspar at 1100°C for four months produces lamellae only in the size range of 75A, it is not surprising that Bøggild lamellae which may be 1000A across were not destroyed under the conditions imposed on them by Nissen *et al.* (1967) and McConnell (1974a). If Al–Si diffusion is the rate-controlling step, it is too slow to homogenize Bøggild lamellae in laboratory times. These data suggest that Bøggild lamellae must form from plagioclases cooled slowly at high temperatures. Since antiperthites require greater redistributions of aluminum and silicon than Bøggild lamellae, they may form at a higher temperature than the Bøggild lamellae.

### Conclusions

Clearly, there are many aspects of the ternary feldspar subsolidus diagram and of Al–Si diffusion which are poorly understood. This study is just a beginning, but it does demonstrate that feldspars with plagioclase Al–Si distributions can be exsolved under laboratory conditions. Further experiments on other compositions will help to answer some of the complex questions associated with the feldspars.

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