THE DISORDERING OF ALKALI FELDSPARS
I. DRY HEATING OF A MICROCLINE PERTHITE

M.E. CHERRY and L.T. TREMBATH

*Department of Geology, University of New Brunswick,
Fredericton, New Brunswick E3B 5A3*

ABSTRACT

It was possible to follow the disordering path of a microcline microperthite, with bulk grain composition $Or_{61}Ab_{39}$, by calculating the Al–Si distribution from refined unit-cell parameters (obtained from X-ray powder diffraction patterns) for samples that were dry-heated at 1025°C for times ranging from 4 to 2200 hours. Dry-heating results in: (a) Na–K homogenization in less than 4 hours; (b) Al–Si disordering with retention of a triclinic cell for annealing times of 12 to 128 hours; (c) transformation from triclinic to monoclinic for annealing times of 128 to 222 hours; (d) Al–Si disordering in a monoclinic cell for annealing times greater than 270 hours. The Al–Si disordering is much more rapid in a triclinic cell (b) than in a monoclinic cell (d). The product of the triclinic-to-monoclinic transformation (c) is an ordered monoclinic feldspar, not a sanidine.

SOMMAIRE

On a pu suivre l'évolution du désordre dans un microcline microperthitique, de composition globale $Or_{61}Ab_{39}$, en calculant la distribution Al–Si à partir des dimensions affinées de la maille (obtenues par diffraction X de poudres) pour des échantillons qui furent chauffés à sec à 1025°C pendant des laps de temps variant de 4 à 2200 heures. On observe: (a) en moins de 4 heures, homogénéisation Na–K; (b) après recuit de 12 à 128 heures, désordre Al–Si dans une maille qui reste triclinique; (c) après recuit de 128 à 222 heures, transformation de triclinique en monoclinique; (d) pour tout recuit excédant 270 heures, désordre Al–Si dans une maille monoclinique. Le désordre Al–Si se produit beaucoup plus rapidement dans une maille triclinique (b) que dans une maille monoclinique (d). Le produit de la transformation (c) est un feldspath monoclinique ordonné, et non pas une sanidine.

(Traduit par la Rédaction)

INTRODUCTION

Changes in the degree of order in alkali feldspars, produced by prolonged heating under both dry (Goldsmith & Laves 1954, 1961, Baskin 1956, McKie & McConnell 1963, Müller 1969, 1970, Sipling & Yund 1974) and hydrous (Goldsmith & Laves 1954, McConnell & McKie 1960, Tomisaka 1962, Martin 1970, Sipling & Yund 1974) conditions, indicate that all structural states from complete order (maximum microcline, ordered albite) to complete disorder (high sanidine, disordered albite) are possible. Interpretations of ordering and disordering paths vary between ideal one-step and two-step processes. In a one-step process, which has been confirmed for the ordering of albites (Martin 1970), Al moves into the T_10 site equally from the T_1m, T_20 and T_2m sites. (We have used the notation in which T_10, T_1m, T_20 and T_2m refer to the tetrahedral sites and t_10, t_1m, t_20 and t_2m refer to the probability of finding Al in the corresponding tetrahedral site.) Müller (1969) disordered albite by dry-heating; his data prove the disordering to be a one-step process. In an ideal two-step disordering process, Al moves first into the T_1m site from the T_10 site until both have the same Al occupancy, after which the Al moves into the T_2 site from the T_1 site. These ideal paths are illustrated in Figure 1 on a trapezoidal plot (Stewart & Wright 1974) of the Al distribution among the tetrahedral sites of the feldspar structure. Previous studies have suggested both one-step (Müller 1969, 1970, Sipling & Yund 1974; see also Smith 1974, p. 73 and Ribbe 1975, p. R-27) and two-step (Tomisaka 1962, Stewart & Wright 1974; see also Smith 1974, p. 274) disordering paths to result from dry-heating of potassium feldspars.

EXPERIMENTAL MATERIALS AND METHODS

The feldspar used in the study is from the coarse-grained, hypidiomorphic-granular granite in the near-surface Devonian Charlotte pluton in southwestern New Brunswick. The granites in the pluton have essentially ternary-minimum-melt compositions (*e.g.*, sample 73–170A has 33.1% quartz, 28.9% orthoclase, 31.6% albite
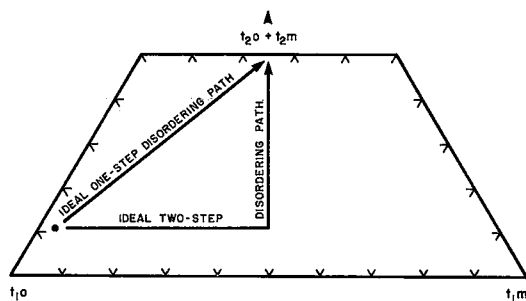
FIG. 1. Trapezoidal plot of Al occupancies (Stewart & Wright 1974) illustrating ideal one- and two-step disordering paths for alkali feldspars.

and 1.9% anorthite in its norm) and are composed of quartz, albitic plagioclase, microperthitic potassium feldspar and minor biotite (Cherry 1976, Cherry & Trembath 1978). The potassium feldspar grains contain 20% to 50% exsolved albitic lamellae. Most grains contain (1) coarse lamellae 1 mm long and 0.1 mm wide in widely spaced parallel bands and (2) fine lamellae 0.5 to 1.0 mm long and 0.01 to 0.02 mm wide in areas between the coarse lamellae. The potassium feldspar in sample 73-170A was selected for the study of disordering because of its relatively well-ordered ($t_1 0 = 0.87$) Al–Si distribution (Cherry 1976). It has a bulk grain composition, determined from refined unit-cell volume, of $Or_{61}Ab_{39}$. The perthite grains in sample 73–170A average 1.5 cm in size and are readily separated by hand-picking from a coarsely broken hand specimen. The sample material was estimated to be >95% perthite; sodic plagioclase from the granite not removed from the sample would change its composition and, hence, its cell parameters but probably does not affect the results reported for the disordering process.

The disordering process was followed by observing the changes in X-ray powder diffraction patterns of, and calculating the Al–Si distribution in, portions of the sample heated for different times at 1025°C. Al–Si distributions in the experimental products were calculated from refined unit-cell parameters obtained from the X-ray powder-diffraction data using the methods of Stewart & Ribbe (1969). The sample was crushed (grain size <25μ), thoroughly mixed, and portions placed in gold capsules for heat treatment. The majority of the experiments were made in crimped capsules; one was made in a sealed capsule with powder dried at 110°C to check for loss of alkalis. The annealed samples were air-quenched to room temperature in less
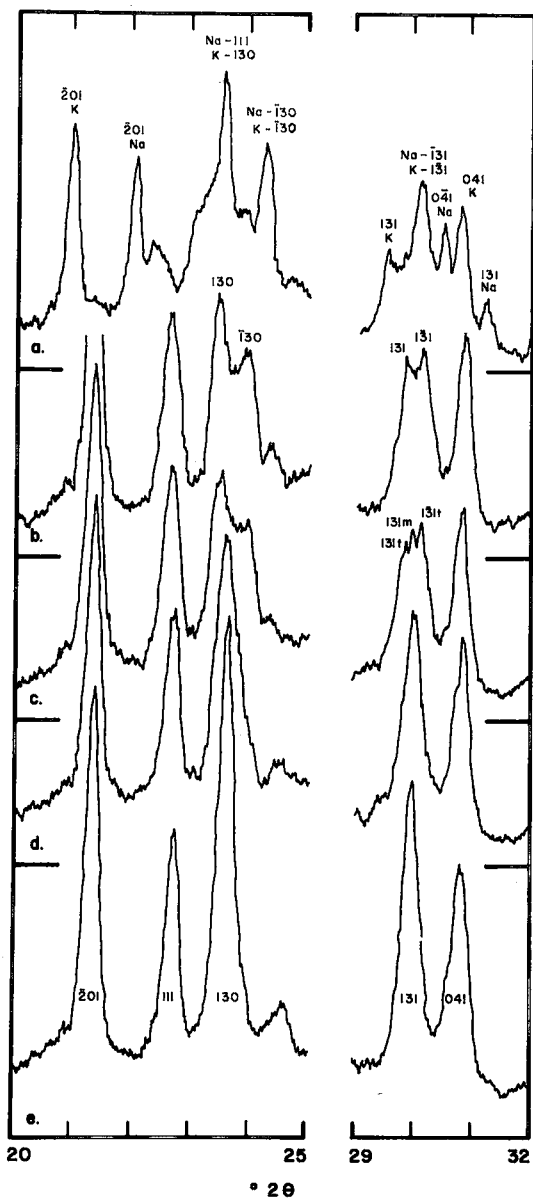

FIG. 2. Segments of X-ray powder diffraction patterns (Cu $K\alpha$) of feldspar 73–170A: (a) natural microperthite; (b) heated for 72 hours; (c) heated for 135.4 hours; (d) heated for 336 hours, and (e) heated for 672 hours. All samples were annealed at 1025°C.

than five minutes and the products then used in smear mounts for X-ray diffraction, with heat-treated CaF_2 (a 5.4626Å) as an internal standard. Three scans were made of each product from 60° to 10° 2θ at a rate of 0.25° 2θ per minute, using Cu radiation ($K\alpha$, λ = 1.54178Å

for all reflections with $2\theta < 47°$, $K\alpha_1$, λ 1.54051 Å for all reflections with $2\theta > 47°$; 40 kV, 30 mA). Mean 2θ values from the three scans were then used as input data in a cell-refinement program (Appleman & Evans 1973). The patterns were indexed using data in Wright & Stewart (1968) and in Borg & Smith (1969). Fixed indexing was used in all final refinements and unit value was assigned to all reflections.

RESULTS AND DISCUSSION

X-ray diffraction patterns

The changes in the diffraction patterns that occur with heat treatment are illustrated in Figure 2. The pattern of the natural perthitic feldspar (Fig. 2a) has separate peaks for the sodic and potassic phases; the 130, $\bar{1}30$, 131 and $\bar{1}31$ reflections of the potassic phase are sharp and the reflections in each pair are well separated. The reflections of the sodic phase are absent from the diffraction patterns of all the products heated longer than four hours, indicating rapid Na-K homogenization. The patterns of products held at 1025°C for successively longer times show a steady decrease in the separation of the 130–$\bar{1}30$ and 131–$\bar{1}31$ reflections. The 130–$\bar{1}30$ pair becomes ragged and broadened at its peak; the 131–$\bar{1}31$ pair is broadened at its peak. In addition to these changes, the diffraction patterns for products 10 (Fig. 2c), 11, 12 and 13 have an additional reflection between the 130 and $\bar{1}30$ peaks and between the 131 and $\bar{1}31$ peaks. We interpret these reflections to indicate the presence of both monoclinic and triclinic cell geometries in the products of these four experiments. Both a monoclinic and a triclinic unit-cell can be refined for the products of only these four experiments. Careful examination of all diffraction patterns after initial refinements resulted in the assignment of minor reflections on the diffraction patterns of these products to either the triclinic or the monoclinic crystal system. The diffraction patterns of experimental products 2 to 10 have reflections that can be assigned only to the triclinic crystal system and those of experiments 14 to 22 have reflections that can be assigned to the monoclinic crystal system. Each pair of refined unit-cells in products 10 to 13 has similar parameters; this is largely dictated by the use of the same strong reflections ($\bar{2}01$, 111, 041, 060, $\bar{2}04$) in the refinements of both unit-cells. Peak height-to-width ratios for these major reflections remain relatively constant on the diffraction pat-

terns of the experimental products with triclinic unit-cell geometries and the reflections do not exhibit splitting or broadening (Fig. 2). The $\bar{2}01$ reflection shifts markedly from $\sim$21° 2θ in the perthite to $\sim$21.4° 2θ in the homogenized feldspar; other reflections have smaller shifts in their positions. The diffraction patterns of products of experiments 14 to 22 (Figs. 2d and 2e) show only minor changes in peak positions and are consistent with a monoclinic unit-cell. However, the reflections in these patterns become sharper with increased duration of annealing. The $\bar{2}01$, 060 and $\bar{2}04$ reflections on these patterns have relatively constant peak height-to-width ratios but the 111, 130, $\bar{1}12$ and 131 reflections have increased height-to-width ratios with longer annealing times. These changes in the diffraction patterns of the annealed feldspars with monoclinic geometry probably reflect increasing domain size and homogeneity within the feldspar as annealing time is increased.

Refined unit-cell parameters

The refined unit-cell parameters of the experimental products are given in Table 1. The accuracy and precision of refined unit-cell data have been discussed by Stewart (1975), who cautioned against overinterpretation of data obtained from X-ray powder diffraction methods which undoubtedly give results for an 'average' structure composed of a number of domains with different degrees of Al-Si order. We acknowledge the limits to interpretation imposed by the techniques but consider the systematic changes we have observed to be interpretable.

The refined unit-cell data are plotted on b – c and α^* – γ^* diagrams (Stewart & Wright 1974) in Figures 3 and 4, respectively. Alkali homogenization, which occurs in less than four hours, results in a shift from the cell dimensions of the potassic phase of the perthite (experiment 1). There is, however, little if any Al-Si migration for annealing times less than 48 hours (experiments 2 to 5). The products of these experiments have larger Δa values ($\Delta a = a_{obs} - a_{est}$: Stewart & Wright 1974) than does the perthite; these Δa values probably represent 'strain' brought about by the alkali homogenization. Appreciable Al–Si migration occurs during experiments of 72 to 128 hours duration (experiments 6 to 9) and satisfactory refinements based on a triclinic unit-cell can be obtained. The decrease in degree of order during these experiments is accompanied by a decrease in the 'strain' in the feldspar as indicated by Δa

TABLE 1. REFINED UNIT-CELL PARAMETERS OBTAINED FROM X-RAY DIFFRACTION DATA FOR HEAT-TREATED SAMPLES OF FELDSPAR 73-170A

Expt.	Time	a	b	c	α	β	γ	α^*	γ^*	Volume	% Or	t_10	t_1m	t_20[1]	Δa	n
1	0	8.590(6)	12.977(6)	7.211(3)	90.63(6)	116.03(4)	87.99(5)	90.28(5)	91.93(4)	721.9(5)	97.0	0.87	0.02	0.04	0.00	28
2	12	8.419(12)	12.966(8)	7.206(4)	91.07(6)	116.07(6)	88.05(7)	89.76(6)	91.65(7)	706.1(9)	60.1	0.86	0.03	0.06	-0.08	18
3	16	8.428(16)	12.963(10)	7.209(5)	91.01(12)	116.07(8)	88.09(11)	89.81(11)	91.63(10)	707.0(1.2)	61.9	0.86	0.05	0.04	-0.08	15
4	24	8.436(15)	12.963(9)	7.204(4)	90.85(10)	116.05(7)	88.23(10)	89.91(10)	91.55(9)	707.5(1.1)	62.8	0.81	0.07	0.06	-0.04	15
5	48	8.416(18)	12.962(11)	7.206(5)	90.96(11)	116.10(9)	88.18(12)	89.82(13)	91.56(10)	705.6(1.4)	59.2	0.83	0.06	0.05	-0.06	16
6	72	8.428(18)	12.963(10)	7.198(5)	90.87(9)	116.00(8)	88.43(11)	89.80(9)	91.32(11)	706.4(1.3)	60.7	0.75	0.09	0.08	-0.02	18
7	96	8.426(14)	12.961(8)	7.197(4)	90.79(7)	116.03(7)	88.48(8)	89.86(7)	91.31(8)	706.0(1.0)	59.9	0.74	0.10	0.08	0.00	18
8	120	8.424(17)	12.969(10)	7.200(5)	90.84(8)	116.06(8)	88.49(10)	89.81(8)	91.27(10)	706.3(1.2)	60.5	0.73	0.11	0.08	-0.06	18
9	128	8.425(19)	12.966(11)	7.200(5)	90.81(9)	116.09(9)	88.54(11)	89.81(9)	91.23(11)	706.2(1.4)	60.3	0.73	0.12	0.08	-0.04	17
10	135.5	8.453(13)	12.973(8)	7.198(4)	90.50(8)	116.10(6)	88.74(9)	90.06(8)	91.16(8)	708.6(9)	65.0	0.67	0.15	0.09	-0.03	14
		8.464(12)	12.973(10)	7.196(5)	90.00	116.02(7)	90.00	90.00	90.00	710.0(1.0)	67.9	0.40	0.40	0.10	-0.02	11
11	144	8.423(14)	12.956(9)	7.194(4)	90.34(16)	116.07(7)	89.05(16)	90.09(14)	90.89(13)	705.1(1.2)	58.2	0.61	0.23	0.08	0.00	12
		8.454(16)	12.978(17)	7.199(7)	90.00	116.18(10)	90.00	90.00	90.00	708.9(1.4)	65.6	0.41	0.41	0.09	-0.07	15
12	168	8.433(12)	12.972(7)	7.191(4)	90.56(13)	116.00(6)	89.93(14)	89.90(10)	90.92(10)	706.9(9)	61.7	0.61	0.17	0.11	-0.02	11
		8.435(8)	12.965(5)	7.191(3)	90.00	115.96(4)	90.00	90.00	90.00	707.1(6)	62.1	0.40	0.40	0.10	+0.02	7
13	222	8.438(7)	12.976(7)	7.195(3)	90.35(6)	116.03(4)	89.39(8)	89.92(5)	90.52(7)	707.8(7)	63.4	0.52	0.27	0.10	-0.01	15
		8.437(5)	12.970(5)	7.192(2)	90.00	116.00(3)	90.00	90.00	90.00	707.4(5)	62.6	0.39	0.39	0.11	+0.01	12
14	270	8.438(5)	12.969(5)	7.191(2)	90.00	115.94(3)	90.00	90.00	90.00	707.6(5)	63.0	0.39	0.39	0.11	0.00	10
15	315	8.445(5)	12.974(7)	7.190(3)	90.00	115.97(3)	90.00	90.00	90.00	708.2(5)	64.2	0.38	0.38	0.12	0.00	14
16	336	8.434(10)	12.995(13)	7.187(5)	90.00	116.01(6)	90.00	90.00	90.00	707.9(1.0)	63.6	0.35	0.35	0.15	-0.09	16
17[2]	524	8.435(8)	12.986(5)	7.188(2)	90.00	116.08(4)	90.00	90.00	90.00	707.2(6)	62.2	0.36	0.36	0.14	-0.04	11
18	672	8.441(5)	13.010(5)	7.181(2)	90.00	116.09(4)	90.00	90.00	90.00	708.4(5)	64.6	0.31	0.31	0.19	-0.11	18
19	840	8.455(10)	13.008(6)	7.182(3)	90.00	116.09(5)	90.00	90.00	90.00	709.4(8)	66.7	0.31	0.31	0.19	-0.09	14
20	1008	8.452(8)	13.015(4)	7.180(2)	90.00	116.12(4)	90.00	90.00	90.00	709.1(6)	66.0	0.30	0.30	0.20	-0.12	16
21	1347	8.445(5)	13.013(3)	7.177(2)	90.00	116.14(3)	90.00	90.00	90.00	708.0(4)	63.8	0.29	0.29	0.21	-0.09	20
22	2231	8.447(5)	13.020(3)	7.172(2)	90.00	116.06(4)	90.00	90.00	90.00	708.6(4)	65.0	0.26	0.26	0.24	-0.09	12

Time is given in hours; cell dimensions are given in angstroms and degrees; composition is given as mol % Or, calculated using the formula in Stewart & Wright (1974); t_10, t_1m and t_20 calculated using the formulae in Stewart & Wright (1974); [1] $t_20 = t_2m$; n = number of reflections used in the cell refinement; [2] expt. done in sealed capsule, all others done in crimped capsules. The numbers in parentheses give the standard error of the cell dimension calculated in the cell refinement program.

(Table 1). There seems to be a range of structural states in the products of experiments of 135.5 to 222 hours duration (numbers 10 to 13). Details of peak broadening and splitting, as previously described, suggest that there is a discontinuous step with both monoclinic and triclinic cell geometries present. It was possible to refine a reasonable unit-cell with either monoclinic or triclinic symmetry restrictions for these four products. At the least, there is a range of structural states present in them; at best, there are two main structural states. Only a monoclinic unit-cell geometry was evident in the products of experiments longer than 270 hours (numbers 14 to 22), with the $b-c$ plot indicating a gradual change of Al–Si order from highly ordered to disordered monoclinic feldspar, parallel to the maximum microcline – high sanidine edge of the plot. The slight trend toward the dimensions of high sanidine probably reflects loss of sodium from the crimped capsules during experiments of longer duration. The structures of these highly disordered feldspars are 'strained' as indicated by Δa.

Disordering path and Al occupancy

The multistep character of the disordering path is best illustrated on a trapezoidal plot (Fig. 5) of calculated Al occupancies of the tetrahedral sites (Stewart & Wright 1974). The alkali homogenization obvious on the $b-c$ and $\alpha^*-\gamma^*$ plots (Figs. 3 and 4) is not evident on the Al occupancy plot because it occurs without a change in Al–Si order. The step in which Al moves from the T_10 site into all three of T_1m, T_20 and T_2m is shown on Figure 5 by experimental products 5 to 13. A least-squares linear-regression fit for experiments 1 to 9 and the triclinic refinements of experiments 10 to 13 is drawn on Figure 5; this line is parallel to, although offset to higher T_2 occupancies than, the band of microclines from a suite of metamorphic rocks plotted by Stewart & Wright (1974). This suggests similar relative rates of Al–Si migration during the ordering of the potassium feldspars in the metamorphic rocks discussed by Stewart & Wright (1974) and the disordering of the perthite from granite sample 73–170A; Al migrated from T_10
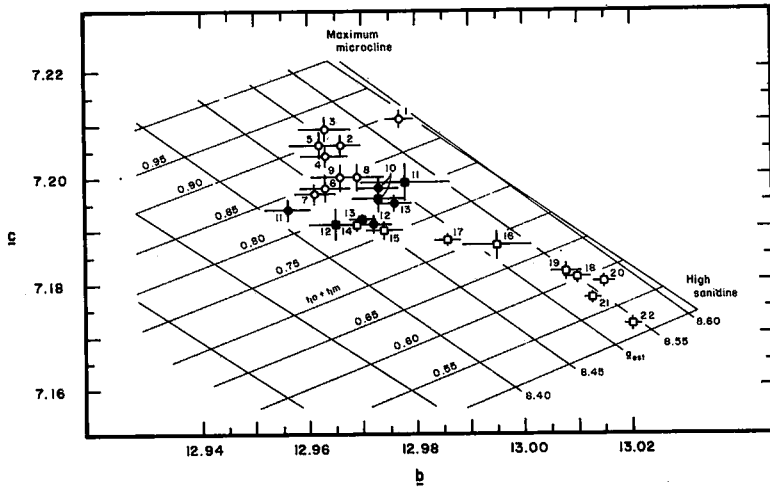
FIG. 3. Refined $b - c$ unit-cell dimension diagram (Stewart & Wright 1974) for heat-treated samples of feldspar 73–170A. Experiment numbers are as in Table 1. Circles are experimental products with triclinic refined unit-cells; squares are experimental products with monoclinic refined unit-cells. Filled symbols indicate the experiments for which both a monoclinic and a triclinic refined unit-cell were obtained. Error bar lengths are twice the standard error calculated by the cell-refinement program.
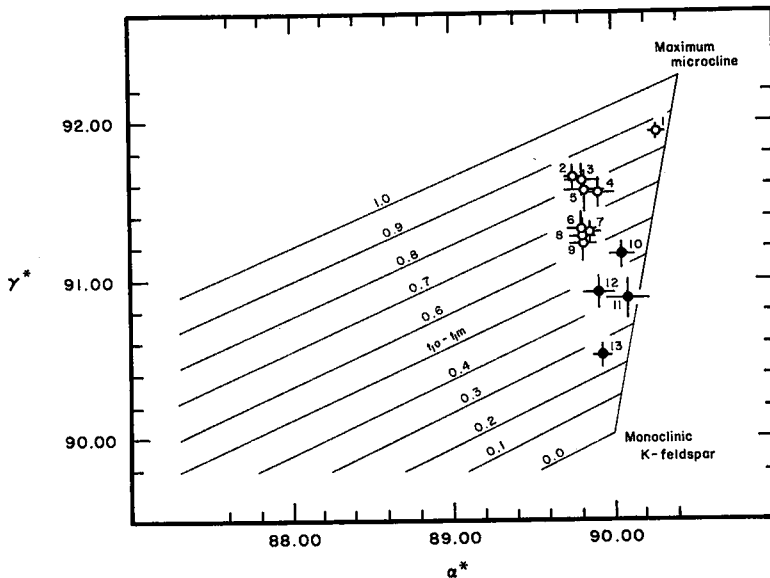
FIG. 4. Refined α^* — γ^* dimension diagram (Stewart & Wright 1974) for experimental products with triclinic refined unit-cells. The symbols are as for Figure 3.

into T_1m approximately four times as rapidly as into the T_2 sites. A gap is present on the Al occupancy plot (Fig. 5) and on the $\alpha^* - \gamma^*$ plot (Fig. 4) between the most disordered triclinic feldspar and the most ordered monoclinic feldspar. Attempts to fill this gap resulted in experimental products with both monoclinic and triclinic cell geometries. The products of these experiments, as shown on Figure 5, have approximately the same Al content in the T_2 sites of
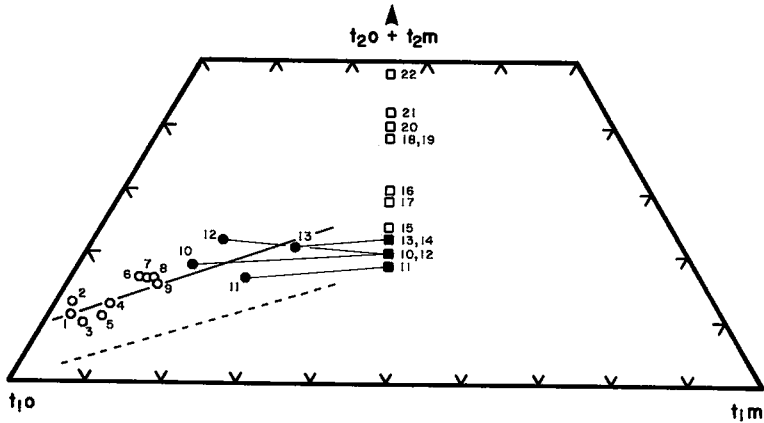
FIG. 5. Trapezoidal plot of calculated Al occupancies of the tetrahedral sites in the experimental products. The symbols are as for Figure 3. The light solid lines join monoclinic and triclinic refined unit-cells for experiments 10 to 13. The heavy solid line is a least-squares linear regression fit for experiments 1 to 9 and the triclinic refined unit-cells of experiments 10 to 13. The dashed line is the trend of intermediate microclines plotted by Stewart & Wright (1974) for a suite of metamorphic feldspars (Guidotti *et al.* 1973).
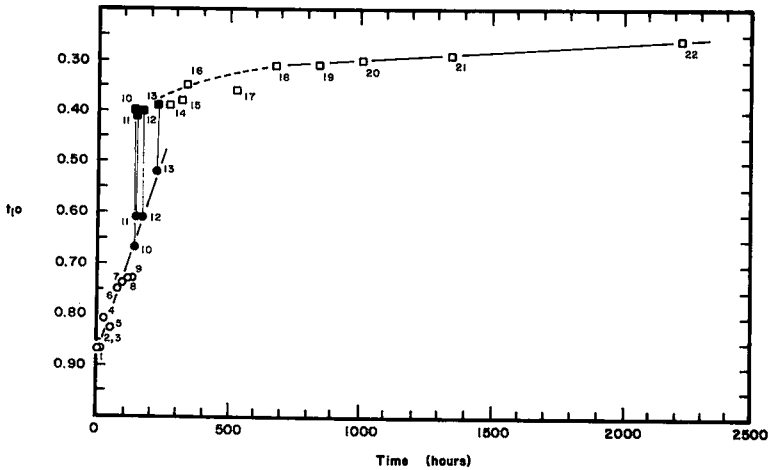

FIG. 6. Rate of movement of Al from the $T_1 0$ site in the experiments. The symbols are as for Figure 3. Light solid lines join monoclinic and triclinic refined unit-cells for experiments 10 to 13. The heavy solid lines are least-squares linear regression fits for experiments 1 to 9 and the triclinic refined unit-cells of experiments 10 to 13, and for experiments 18 to 22. The dashed line is a visually estimated fit for experiments 14 to 18 and the monoclinic refined unit-cells of experiments 10 to 13.

both the monoclinic and the triclinic refined unit-cells; this Al distribution ($2t_2 \simeq 0.20$) may be an upper limit for the existence of a triclinic structure. The final stage of the disordering process involves a slower movement of Al into the T_2 sites from the T_1 sites, illustrated on Figure 5 by experiments 14 to 22.

Rate of Al–Si migration

The rate of change in Al occupancy of the $T_1 0$ site is shown on Figure 6. An 'incubation' period of approximately 24 hours is apparently needed before Al and Si can sensibly migrate through the feldspar structure. This contrasts

with the initial rapid change in order parameters reported by Sipling & Yund (1974) for $<44\mu$ samples of Hugo microcline (Or_{89}) and its K-exchanged equivalent annealed at 1070°C. Disordering occurs rapidly after the incubation period (experiments 4 to 9) until monoclinic cell geometries appear when $t_10 + t_1m \simeq 0.80$. There follows a period during which both monoclinic and triclinic cell geometries are present (experiments 10 to 13) and apparently an interval of intermediate rate of Al–Si migration in experiments with only monoclinic geometry (experiments 14 to 18) until $2t_1 \simeq 0.60$. These are followed by a slower migration of Al and Si at a constant rate (experiments 18 to 22) until disordering is complete.

Nature of 'strain' in the feldspar

As would be anticipated, the microperthitic natural potassium feldspar exhibits no evidence of 'strain' as indicated by Δa. A significant degree of 'strain' becomes apparent following alkali homogenization in experimental products retaining a triclinic cell geometry and a high degree of Al–Si order. This 'strain' decreases as the Al–Si order decreases and the products of experiments resulting in both monoclinic and triclinic cell geometries are 'unstrained'. Experiments resulting in monoclinic cell geometries are initially 'unstrained' but become increasingly 'strained' as annealing times are increased. In itself, the 'strain' may not be an important part of the disordering process, but it may have an appreciable effect on the rates of Al–Si migration among the tetrahedral sites or on the nature of a subsequent transformation. With increased duration of heat treatment, the Al–Si disordering occurring within a triclinic cell geometry coincides with an apparent decrease in 'strain', suggesting that the Al–Si order is adjusting to the Na–K distribution.

Nature of the triclinic–monoclinic transformation in alkali feldspars

Most studies of order–disorder relationships in the alkali feldspars have been concerned with following the process for end-member compositions. We have used a feldspar with a grain composition of $Or_{61}Ab_{39}$. Although the appreciable sodium content of the feldspar introduces an extra complication into order–disorder considerations, we think that this grain composition is representative of conditions of formation of microclines in many igneous environments. As the microperthitic microcline is homogenized in the first few hours, the subsequent dry-heating

disordering experiments would be characteristic of a highly ordered triclinic feldspar with a grain composition of about 60 mole % Or.

Experiments 2 to 9 (Fig. 5) represent a continuous disordering process with only a triclinic unit-cell geometry evident. The Al content of the $T_10 + T_1m$ sites in the feldspar is initially approximately 0.89 and remains at approximately 0.88 during alkali homogenization. It then decreases to approximately 0.84 while triclinic geometry is retained. The disordering path of Figure 5 indicates a more rapid transfer of Al from T_10 to T_1m than to the T_2 sites, consistent with an intermediate two-step disordering path, as distinct from the one-step path proposed by Sipling & Yund (1974) for the Hugo microcline. As only one triclinic cell geometry is apparent, we consider this early stage of the disordering process to be a homogeneous transformation.

Stewart & Wright (1974) noted a minimum $t_10 + t_1m$ occupancy of 0.70 and a gap in $t_10 - t_1m$ values from 0.40 to 0.65, implying that certain degrees of order are not achieved or, at least, are not retained. In our annealed material, the minimum $t_10 + t_1m$ occupancy attained while retaining triclinic unit-cell geometry was 0.84. Attempts to extend the $t_10 + t_1m$ occupancy (Fig. 3) to lower values and to fill the gap in $t_10 - t_1m$ values (Fig. 4) resulted in experimental products (numbers 10 to 13) with both monoclinic and triclinic unit-cell geometries rather than a single intermediate geometry. We interpret this second stage as a discontinuous transformation with both monoclinic and triclinic geometries present. The transformation requires time to initiate but once started the change in geometry takes place rapidly and is not accompanied by an appreciable transfer of Al out of the T_1 sites. This break in geometry would be consistent with a discontinuous transformation requiring nucleation and coarsening of domains.

The product of the discontinuous transformation has a monoclinic geometry and retains a high degree of Al–Si order with $2t_1 = 0.78$. We could not establish the presence of intermediate triclinic geometries but we could establish that the resulting monoclinic material is highly ordered. It is quite possible that a triclinic Al–Si distribution is also retained although X-ray powder-diffraction techniques could not establish this. It should be observed that this T_1 occupancy approximates the most commonly observed degree of monoclinic order for natural specimens (Stewart & Wright 1974). This degree of order is also similar to values determined

from structural analyses of orthoclase (Spencer C) and adularia (Spencer B) suggested by Colville & Ribbe (1968) to have "as low a structural state as is observed in 'monoclinic' potassium feldspars." In experiments of longer duration (numbers 14 to 22) the monoclinic feldspar goes through a second continuous disordering stage involving a transfer of Al from the T_1 to the T_2 site. This is a comparatively slow process approaching completion for annealing times greater than 2000 hours. We regard this as a second homogeneous reaction.

In summary, the sequence of events observed with dry-heating of a triclinic alkali feldspar ($Or_{61}Ab_{29}$) at $1025°C$ is: (1) Sodium – potassium homogenization. (2) Al–Si disordering with triclinic unit-cell geometry. Al migrates from $T_1 0$ to $T_1 m$ and, to a lesser extent, to $T_2 0$ and $T_2 m$. (3) Transformation from triclinic to monoclinic unit-cell geometry. The result of this transformation is a highly ordered monoclinic feldspar, not a sanidine. (4) Al–Si disordering with monoclinic unit-cell geometry. Al migrates from T_1 to T_2 at a much slower rate than during the triclinic disordering.

The disordering process is at least a two-step process and differs from that of the albite endmember, which has been shown (Müller 1969) to be a continuous one-step process.

Applications to natural alkali feldspars

Interpretations of order–disorder processes and of the monoclinic–triclinic transformation in alkali feldspars based upon the structural states of naturally occurring potassium feldspars are hindered by the complexities of the host-rock petrogenesis, including such commonly accepted controls of the structural state as the crystallization and cooling rates of igneous rocks, the heating and cooling rates of metamorphism, the temperatures of igneous intrusion and extrusion and of metamorphism, the presence or absence of fluid phases and the composition of fluid phases. We suggest that the common structural states in the potassium feldspars reflect, in part at least, the multistep order–disorder process outlined in the previous section. The most rapid step in this process is the change from maximum microcline to intermediate microcline during disordering (or, conversely, the change from intermediate microcline to maximum microcline during ordering). The slowest step is the change from ordered monoclinic feldspar to sanidine. The discontinuous character of the triclinic–monoclinic transformation is indicated by a lack of intermediate triclinic

structural states with $t_1 0 + t_1 m < 0.80$, which is reflected in gaps on $\alpha^* - \gamma^*$ plots (Fig. 4; Stewart & Wright 1974, p. 370) and on Al occupancy plots (Fig. 5; Stewart & Wright 1974, Fig. 8).

A paucity of intermediate microclines in comparison to the abundance of maximum microcline and monoclinic potassium feldspars was indicated by Dietrich's studies (1961, 1962) of the triclinicity (Goldsmith & Laves 1954) of potassium feldspars from different geological environments and, more recently, has been noted by Stewart & Wright (1974) in their extensive compilation of refined unit-cell parameters of potassium feldspars. The presence of both monoclinic and triclinic phases within single potassium feldspar grains is common (MacKenzie 1954, Emeleus & Smith 1959, Smith & MacKenzie 1959, Wright 1964, 1967, Crosby 1971). The triclinic phase in these occurrences has been described, with one exception (Wright 1967), as intermediate microcline, commonly with a variable structural state; the monoclinic phase has been described as orthoclase. Refined unit-cell parameters for these intermediate microclines reveal, however, that with few exceptions they have $t_1 0 + t_1 m > 0.80$ and do not fill the gaps on the $\alpha^* - \gamma^*$ and Al occupancy plots. In fact, the only suite of potassium feldspars known to us to have such intermediate Al occupancies is the suite of metamorphic feldspars described by Guidotti *et al.* (1973) and included in Stewart & Wright (1974, Fig. 7). The lack of intermediate microclines with $t_1 0 + t_1 m < 0.80$ and the occurrence of monoclinic and triclinic unit-cell geometries within single grains of potassium feldspar would be consistent with a discontinuous transformation.

The rates of movement of Al from the $T_1 0$ site during the disordering process indicated on Figure 6 are also compatible with the relative abundances of potassium feldspar polymorphs (Dietrich 1961, 1962, Stewart & Wright 1974). The most abundant polymorphs should be a monoclinic feldspar with $2t_1 \simeq 0.60 - 0.80$ in rocks that cooled relatively rapidly in volcanic or contact metamorphic environments, and a microcline with $t_1 0 > 0.80$ in more slowly cooled rocks such as plutonic igneous or regional metamorphic environments.

Application of the order–disorder process that we have described is limited by the anhydrous character of our experiments. Similar experiments must be done in H_2O-undersaturated and saturated conditions to determine the effects of H_2O upon the process.

REFERENCES

APPLEMAN, D.E. & EVANS, H.T., JR. (1973): Job 9214: Indexing and least-squares refinement of powder diffraction data. *U.S. Geol. Surv. Comp. Contr.* 20.

BASKIN, Y. (1956): Observations on heat-treated authigenic microcline and albite crystals. *J. Geol.* 64, 219-224.

BORG, I.Y. & SMITH, D.K. (1969): Calculated X-ray powder patterns for silicate minerals. *Geol. Soc. Amer. Mem.* 122.

CHERRY, M.E. (1976): *The Petrogenesis of Granites of the St. George Pluton, Southwestern New Brunswick.* Ph.D. thesis, Univ. New Brunswick, Fredericton, N.B.

———— & TREMBATH, L.T. (1978): Structural state and composition of alkali feldspars in granites of the St. George pluton, south-western New Brunswick. *Mineral. Mag.* 42, 391-399.

COLVILLE, A.A. & RIBBE, P.H. (1968): The crystal structure of an adularia and a refinement of the structure of orthoclase. *Amer. Mineral.* 53, 25-37.

CROSBY, P. (1971): Composition and structural state of alkali feldspars from charnockitic rocks on Whiteface Mountain, New York. *Amer. Mineral.* 56, 1788-1811.

DIETRICH, R.V. (1961): Comments on the "Two-feldspar geothermometer" and K-feldspar obliquity. *Inst. "Lucas Mallada", Curs. Conf.* 8, 15-20.

———— (1962): K-feldspar structural states as petrogenetic indicators. *Nor. Geol. Tidsskr.* 42, 394-414.

EMELEUS, C.H. & SMITH, J.V. (1959): The alkali feldspars. VI. Sanidine and orthoclase perthites from the Slieve Gullion area, Northern Ireland. *Amer. Mineral.* 44, 1187-1209.

GOLDSMITH, J.R. & LAVES, F. (1954): The microcline-sanidine stability relations. *Geochim. Cosmochim. Acta* 5, 1-19.

———— & ———— (1961): The sodium content of microclines and the microcline-albite series. *Inst. "Lucas Mallada", Curs. Conf.* 8, 81-96.

GUIDOTTI, C.V., HERD, H.H. & TUTTLE, C.L. (1973): Composition and structural state of K-feldspars from K-feldspar + sillimanite grade rocks in northwestern Maine. *Amer. Mineral.* 58, 705-716.

MACKENZIE, W.S. (1954): The orthoclase–microcline inversion. *Mineral. Mag.* 30, 354-366.

MARTIN, R.F. (1970): Cell parameters and infrared absorption of synthetic high to low albites. *Contr. Mineral. Petrology* 26, 62-74.

McCONNELL, J.D.C. & McKIE, D. (1960): The kinetics of the ordering process in triclinic NaAl Si₃O₈. *Mineral. Mag.* 32, 436-454.

McKIE, D. & McCONNELL, J.D.C. (1963): The kinetics of the low → high transformation in albite. I. Amelia albite under dry conditions. *Mineral. Mag.* 33, 581-588.

MÜLLER, G. (1969): *Die Abhängigkeit der Gitterkonstanten und der Mischkristallbildung der Na- und K-Feldspäte vom Ordnungszustand.* Dipl.-Min. dissertation, Technische Univ., Karlsruhe.

———— (1970): Der Ordnungs-Unordnungs-Übergang in getemperten Mikroklinen und Albiten. *Z. Krist.* 132, 212-227.

RIBBE, P.H. (1975): The chemistry, structure, and nomenclature of feldspars. *In* Feldspar Mineralogy (P.H. Ribbe, ed.), *Mineral. Soc. Amer. Short Course Notes* 2, R1-52.

SIPLING, P.J. & YUND, R.A. (1974): Kinetics of Al/Si disordering in alkali feldspars. *In* Geochemical Transport and Kinetics (A.W. Hofmann, B.J. Giletti, H.S. Yoder, Jr. & R.A. Yund, eds.), *Carnegie Inst. Wash. Publ.* 634, 185-193.

SMITH, J.V. (1974): *Feldspar Minerals. I. Crystal Structure and Physical Properties.* Springer-Verlag, New York.

———— & MACKENZIE, W.S. (1959): The alkali feldspars. V. The nature of orthoclase and microcline perthites and observations concerning the polymorphism of potassium feldspar. *Amer. Mineral.* 44, 1169-1186.

STEWART, D.B. (1975): Lattice parameters, composition and Al/Si order in alkali feldspars. *In* Feldspar Mineralogy (P.H. Ribbe, ed.), *Mineral. Soc. Amer. Short Course Notes* 2, St1-22.

———— & RIBBE, P.H. (1969): Structural explanation for variations in cell parameters of alkali feldspar with Al/Si ordering. *Amer. J. Sci.* 267A, 444-462.

———— & WRIGHT, T.L. (1974): Al/Si order and symmetry of natural alkali feldspars, and the relationship of strained cell parameters to bulk composition. *Soc. Franç. Minéral. Crist. Bull.* 97, 356-377.

TOMISAKA, T. (1962): On order-disorder transformation and stability range of microcline under high water vapour pressure. *Mineral. J. Japan* 3, 261-281.

WRIGHT, T.L. (1964): The alkali feldspars of the Tatoosh pluton in Mount Rainier National Park. *Amer. Mineral.* 49, 715-735.

———— (1967): The microcline-orthoclase transformation in the contact aureole of the Eldora stock, Colorado. *Amer. Mineral.* 52, 117-136.

———— & STEWART, D.B. (1968): X-ray and optical study of alkali feldspar. I. Determination of composition and structural state from refined unit-cell parameters and 2V. *Amer. Mineral.* 53, 38-87.