Alkali feldspars: ordering rates, phase transformations and behaviour diagrams for igneous rocks*

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Abstract

Homogeneous and heterogeneous phase relationships in the alkali feldspars are reviewed, and behaviour diagrams developed. Al,Si ordering is almost certainly continuous and higher order in both albite and potassium feldspar and has been established reversibly or nearly so down to below 500 °C in albite and possibly to ~ 200 °C in potassium feldspar. The degree of order in intermediate albite changes strongly over a range of ~ 75–150 °C depending on pressure, low albite being stable up to about 620–650 °C and high albite above about 725 °C at low pressure. Symmetry is broken at ~ 980 °C mainly by a cooperative shearing of the whole framework and not by Al,Si ordering alone; there is a thermal crossover near 700 °C, shearing being dominant above (high albite) and ordering dominant below (intermediate albite).

In potassium feldspar symmetry is broken by Al,Si ordering at a temperature of about 500 °C. The change in degree of order with respect to temperature has been followed easily and reversibly in sanidine from ~ 1075 to ~ 550 °C and to a lesser extent in microcline from 450 to 200 °C. Ordering rates in sanidine down to 500 °C and ordering rates in microcline between 450 and 200 °C are almost *as fast as in albite*. Ordering in sanidine at 500 °C and below slows and then stops with the development of the tweed orthoclase domain texture. The tweed texture acts as a barrier to further order because the strain energy associated with the (incipient) twin domain texture balances or nearly balances the free energy decrease resulting from ordering. Ordering stops not because of the kinetics of Al,Si diffusion, but because the total *driving force* is very small or nil. Ordering can readily proceed to completion, with the formation of low microcline, only if the domain-texture barrier is overcome by processes involving fluids or strong external stresses. There is no barrier in albite.

The symmetry-breaking process in alkali feldspar changes with composition from mainly shearing in albite to ordering in potassium feldspar. Symmetry is broken equally at a compositional crossover (metastable with respect to exsolution) near Ab_{80-75} at low pressure and progressively displaced towards Or at higher pressures. Ordering in pure albite occurs by a (nearly) one-step path which progressively becomes two-step with substitution of Or. Diagrams showing the near-equilibrium variation of the order parameters at low pressure with composition and T are given, as well as two extreme phase and *behaviour* diagrams for complete coherent and complete incoherent (strain-free) relationships. These diagrams can be used to understand feldspar relationships and microtextures in hypersolvus and subsolvus rocks, the occurrence of orthoclase, and of intermediate and low microcline.

KEYWORDS: alkali feldspars, ordering rates, phase transformations, coherency.

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Introduction

ALTHOUGH the polymorphic and subsolidus phase relationships of the alkali feldspars have been intensively studied, especially over the last 35 years, controversy still exists over many fundamental problems; nevertheless, important advances in understanding have been made in the last few years. Albite occurs in rocks almost exclusively as low albite; this is because Ab-rich feldspars are rare in rapidly cooled rocks, and in more slowly cooled rocks, ordering rates in such feldspars are fast compared to cooling rates. Potassium feldspar, in contrast, occurs in nature in several polymorphic forms known since the nineteenth century. We discuss below the reasons for this apparently different behaviour. A disordered form of albite was first unequivocally shown to exist when Tuttle and Bowen (1950) described the form, now called high albite, synthesized hydrothermally in the classic study of the system $NaAlSi_3O_8$-$KAlSi_3O_8$-H_2O by Bowen and Tuttle (1950). This discovery led to three lines of research: (*a*) the characterization of high albite and the high-low albite relationships, (*b*) the study of solid-solution series between triclinic high albite (analbite) and monoclinic high sanidine and the monoclinic-triclinic phase transformation as a function of composition, temperature, pressure and order, and (*c*) the determination of the solvus relationships. In this paper we discuss recent results for alkali feldspars and attempt to show the supposed equilibrium variation of the order parameters. We propose simple subsolidus phase diagrams for alkali feldspars and show how they can be used to understand alkali feldspar in hypersolvus and subsolvus rocks. Readers may refer to Carpenter (1988) for a review of the thermodynamics of alkali feldspars, in which intensive use is made of Landau theory.

We use the following terminology; T_10, T_1m, T_20 or T_2m are the four types of tetrahedral site in triclinic alkali feldspars. T_1 and T_2 sites are not respectively subdivided in monoclinic feldspars, when average equal Al occupancy occurs in the two sets of subsites. t_10 . . . etc., refers to the fraction of each site occupied by Al. t_10 is one in fully ordered An-free feldspars, 0.25 when fully disordered. The relevant ordering parameters of Thompson (1969) are defined as: $Y = t_10 - t_1m$, $Z = (t_10 + t_1m) - (t_20 + t_2m)$. Salje (1985) introduced $Q_{od} = (t_10 - t_1m)/(t_10 + t_1m)$.

The high-low albite transformation

This transformation has been the subject of controversy since Tuttle and Bowen (1950) first synthesized high albite, because almost all low-pressure hydrothermal experiments were not carried out so as to obtain bracketed equilibrium. Direct hydrothermal synthesis leads initially to growth of high albite at all temperatures, which orders on annealing to an extent which depends on *T* and time. By 1979 certain data (e.g. Raase, 1971; Mason, 1979) could be interpreted as pointing to an upper stability limit for low albite near 680-700 °C at low pressures (~ 0.1 GPa). The equilibrium relationships between an order-sensitive parameter, Δ131, and *T* were finally unequivocally established by Goldsmith and Jenkins (1985) at high pressures near 1.8 GPa using an NaCl pressure medium in a piston-cylinder apparatus although Salje *et al.* (1985) had shown continuous variation of the order parameters as a function of *T* from thermodynamic reasoning. Goldsmith and Jenkins measured Δ131 after quench as a function of run temperature and showed the transformation to be continuous (Fig. 1). Low albite is stable at ~ 1.8 GPa up to about 660 °C and then changes rapidly and reversibly over a *T* range of about 110 °C (intermediate albite) to high albite above 780 °C. High albite changes slowly from 780 °C to reach a steady value above 975-980 °C. They estimated that the curve should be 45-50 °C lower at low pressure, on the basis of data at intermediate pressure (Fig. 1) and from the Clausius-Clapeyron relationship.

Also plotted on Fig. 1 are those data from existing hydrothermal experiments at low *P* (mainly 0.1 GPa) which show the largest differences in order parameter from start to finish. New data in the critical region at 680 and 700 °C, 0.1 GPa, using albites synthesized by Mason (1979) as starting material, run in 2M NaOH solution, are given in Table 1 and plotted in Fig. 1. The new data are consistent with all previous data except for one run at 700 °C. This difference is outside experimental error for Δ131, but could be due to slight differences in *T*, as the precision and accuracy in the latter in long runs is not better than ±10 °C. A smooth curve has been drawn which is consistent with all the data. It is much steeper than the curve at ~ 1.8 GPa and lies at a *T* 30-70 °C lower. There is no compelling reason for suggesting a discontinuous transformation (Tuttle and Bowen, 1950; Raase, 1971; Senderov and Shchekina, 1976; Senderov, 1980; Smith, 1983; Kroll and Voll, in Ribbe, 1983). If the transformation were discontinuous it would be hard to understand why two distinct albites have never been found in ordering experiments (particularly below 700 °C) and how albite in contact with a hydrothermal fluid can order continuously to reach values of Δ131 as low as 1.5-1.3. Until

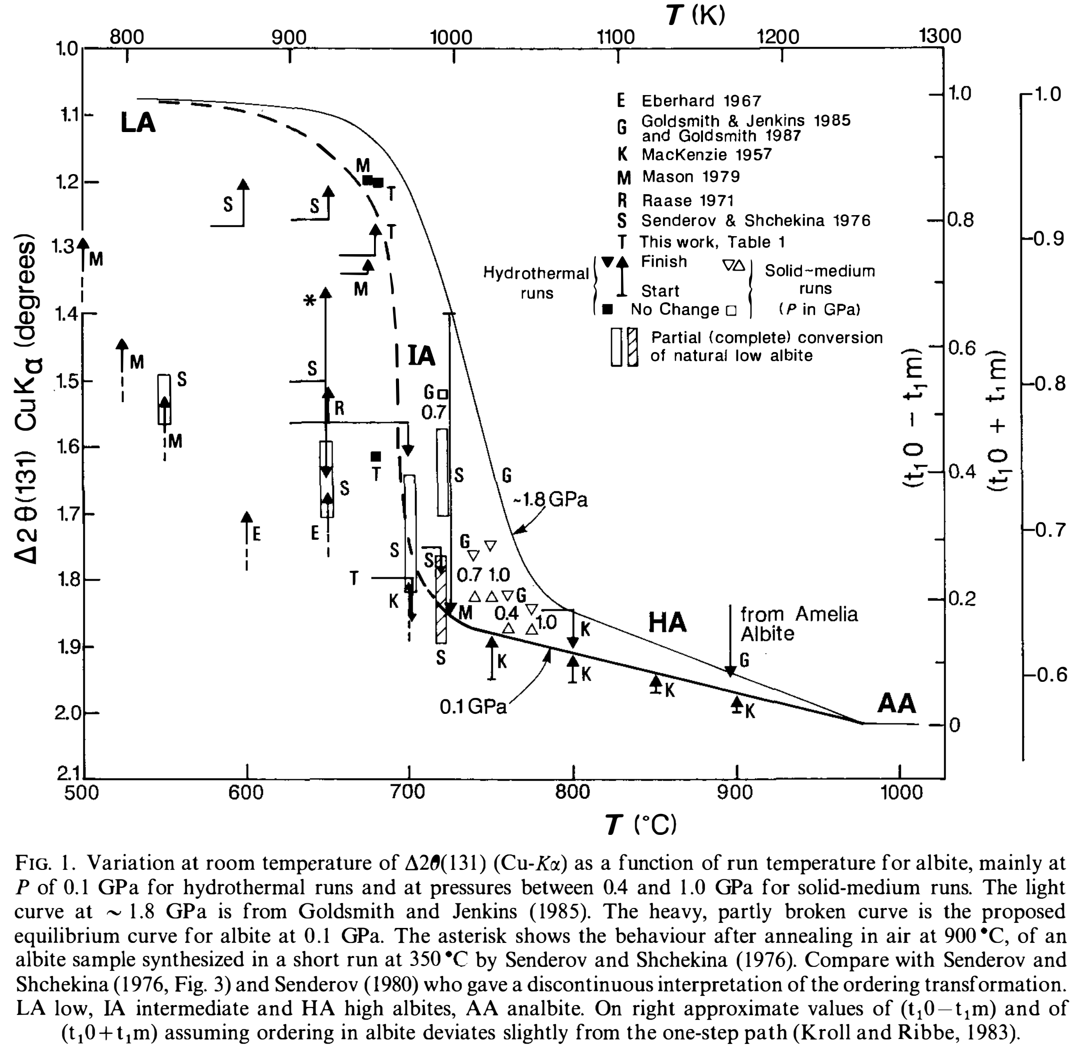

FIG. 1. Variation at room temperature of $\Delta 2\theta(131)$ (Cu-$K\alpha$) as a function of run temperature for albite, mainly at P of 0.1 GPa for hydrothermal runs and at pressures between 0.4 and 1.0 GPa for solid-medium runs. The light curve at ~ 1.8 GPa is from Goldsmith and Jenkins (1985). The heavy, partly broken curve is the proposed equilibrium curve for albite at 0.1 GPa. The asterisk shows the behaviour after annealing in air at 900 °C, of an albite sample synthesized in a short run at 350 °C by Senderov and Shchekina (1976). Compare with Senderov and Shchekina (1976, Fig. 3) and Senderov (1980) who gave a discontinuous interpretation of the ordering transformation. LA low, IA intermediate and HA high albites, AA analbite. On right approximate values of (t_10-t_1m) and of (t_10+t_1m) assuming ordering in albite deviates slightly from the one-step path (Kroll and Ribbe, 1983).

Table 1 Effect of subsequent hydrothermal treatment at a higher temperature than initial synthesis on Δ131 of synthetic albites, at 0.1 GPa

$T_{initial}$ (°C)	Δ131 (°2θ CuKα)	T_{run} (°C)	time (h)	Δ131 (°2θ CuKα)	change in Δ131
350	1.196	680	1701	1.204	+0.008
500	1.307	680	1701	1.263	-0.044
500	1.394	680	1701	1.361	-0.033
525	1.613	700	1682	1.620	+0.007
625	1.799	700	1682	1.865	+0.066

Albites initially synthesized by Mason (1979) direct proof to the contrary, the most reasonable conclusion is that the transformation is continuous both at low and high pressures. This is in accordance with the analysis by Salje *et al.* (1985). The ordering path is 'one-step' in albite, with Al migrating to $T_1 0$ sites from all other sites equally, or nearly so. Data on ordering states in Or-bearing compositions (Parsons, 1968) are inadequate and unbracketed. They suggest however, that Or-bearing high albites have very similar degrees of order to Or-free high albites down to at least 700 °C, but that they are less ordered below 700 °C and especially below 600 °C. The ordering path in such feldspars deviates more and more, with increasing Or content, from a one-step path, because significant transfer of Al from T_2 to undifferentiated T_1 sites occurs while the feldspar has monoclinic symmetry.

The kinetics of the high–low albite transformation

In all hydrothermal synthesis experiments, the ordering rates depend on T and the composition of the fluid. Maximum ordering rates in water or in the presence of sodium salts occur at T in the range 550–350 °C. The absence of a marked increase in ordering rates below 700 °C (cf. Fig. 1) is surprising, as the driving force ΔG for ordering should increase rapidly just below 700 °C. Unlike the situation at high pressure in a solid-medium apparatus (Goldsmith and Jenkins, 1985), it is probable that ordering is not homogeneous and that the rate-determining step involves a heterogeneous reaction with the fluid (Mason, 1980*a*, *b*). The marked increase in hydrothermal ordering rates below 600 °C, especially in the presence of sodium salts, is best explained as due to changes in the physical properties of the solution, in particular to an increase in ionic dissociation (Franck, 1981).

Low albite can be converted into high albite either by dry heating or hydrothermally. Disordering rates on dry heating at atmospheric pressure vary from specimen to specimen (Tuttle and Bowen, 1950; Schneider, 1957; McKie and McConnell, 1963), but are of the order of 5–10 days at 1050 °C and 150–200 days at 950 °C. Ordering has never been achieved on dry annealing at atmospheric pressure in the laboratory (compare ordering in sanidine). Goldsmith (1987) determined disordering times as a function of pressure between 0.6 and 2.4 GPa and showed that times decreased greatly as P increased, the effect levelling off above ~ 2 GPa. He suggested that hydrogen was responsible for promoting Al,Si interdiffusion. Hydrothermal conversion of low to high albite (Tuttle and Bowen, 1950; MacKenzie, 1957; Senderov and Shchekina, 1976) probably occurs by a heterogeneous solution/precipitation mechanism.

Interaction between the high–low and the monoclinic–triclinic phase transformations in $NaAlSi_3O_8$

The high–low albite transformation is slow, diffusive and continuous, and occurs between about 620 and 725 °C at low pressure (Fig. 1). Fully disordered albite transforms rapidly and displacively from triclinic analbite to monoclinic monalbite at a temperature near 980 °C (Laves, 1960; Grundy *et al.*, 1967; Winter *et al.*, 1979; Kroll *et al.*, 1980). The transformation is second-order (Salje *et al.*, 1985) and the driving force is spontaneous shearing of the framework as a whole and not Na vibration (Brown *et al.*, 1984; Salje and Kuscholke, 1984).

Salje (1985), Salje *et al.* (1985), Salje (1986), and Carpenter (1988) analysed the transformations in albite using a Landau-type free-energy expression with two parameters which are related by strain-induced coupling. One parameter (Q) describes the structural distortion during the displacive transformation between monalbite and analbite (high albite) and the other (Q_{od}) Al,Si ordering, where Q_{od} is $(t_1 0 - t_1 m)/(t_1 0 + t_1 m)$ and $t_1 0$ and $t_1 m$ are the atomic fractions of Al in the $T_1 0$ and $T_1 m$ sites. Both Q_{od} and Q vary from zero in monalbite to one in low albite at low temperature. The symmetry-breaking process, shearing of the framework as a whole, allows, under equilibrium conditions, a slight increase in order in high albite as temperatures are lowered, but only because of the existence and strain coupling of the second parameter. The order–disorder transformation *sensu stricto* alone would start at a lower temperature; a crossover (Salje *et al.*, 1985) with respect to temperature (thermal crossover) between the processes occurs. The effect on Δ131 measured at annealing temperature can be estimated from the data of Grundy and Brown (1969). The determined cell parameters at temperature for albites with a range of Al,Si order from high to low, and Δ131 values which would be observed at T for an equilibrium Al,Si distribution can be calculated (Fig. 2). T_{shear} is the temperature of the symmetry break for fully disordered albite (~ 980 °C at 0.1 MPa). By extrapolating the room-temperature curve of Δ131 against T, an apparent temperature for the symmetry break due to ordering alone (T_{ord}) of ~ 700 °C is obtained, about 280 °C lower (see, however, Carpenter, 1988). The effects of the thermal crossover are clearly seen in both curves in Fig. 2 and account for the existence of a range of stable high albites and metastable analbites.

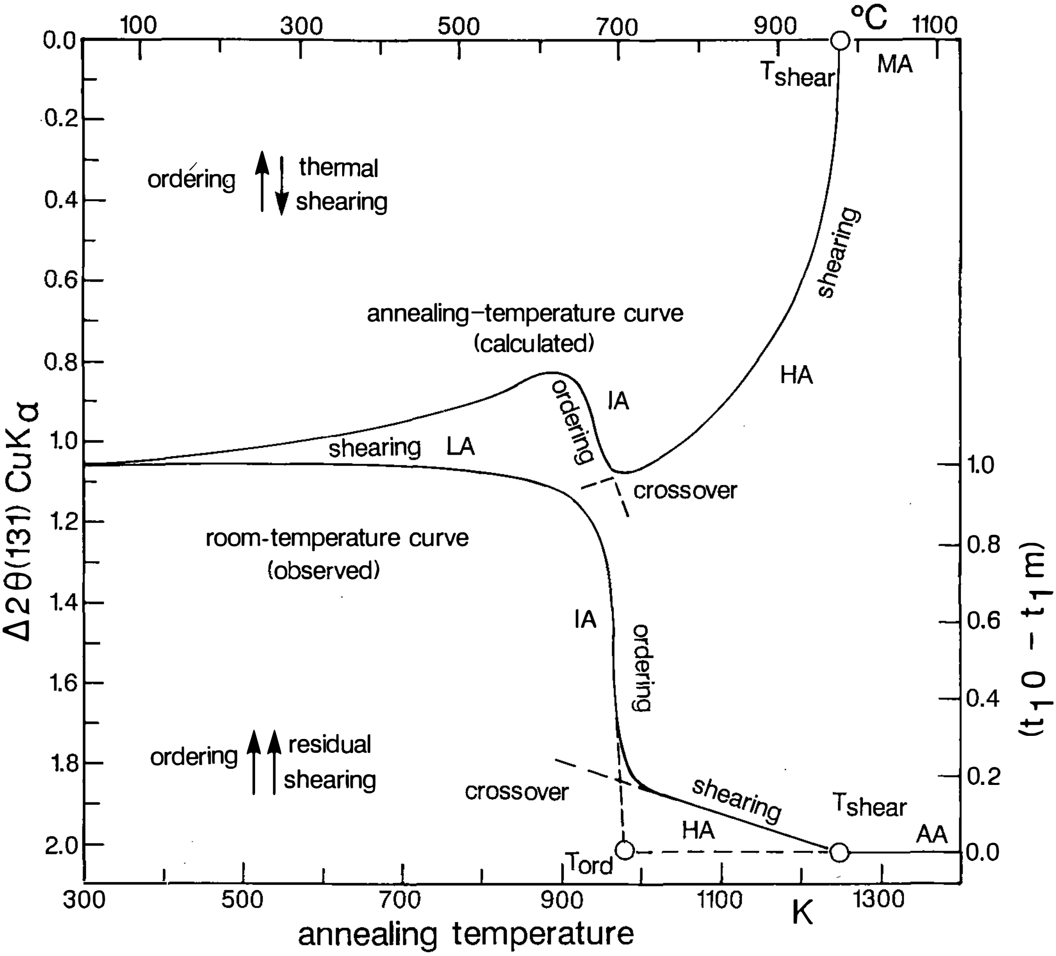

FIG. 2. Interpretation of the room-temperature (lower curve, from Fig. 1) and annealing-temperature (upper curve, calculated from Grundy and Brown, 1969) variation of the values of $\Delta 2\theta(131)$ as a function of annealing temperature for equilibrium albites at low pressure (from Smith and Brown, 1988). LA low, IA intermediate and HA high albites, AA analbite, MA monalbite. The effect of the ordering transformation is best seen in the room-temperature curve and that of the thermal shearing in the annealing-temperature curve. T_{shear}, T_{ord} and the thermal crossover are explained in the text. An increase of pressure displaces T_{ord} (cf. Fig. 1) and T_{shear} to higher temperatures (Hazen, 1976; see however Angel *et al.*, 1988). The value of (t_1O-t_1m) at room temperature is given on right.

Ordering dominates below the crossover, shearing above. Comparison of the curves of Δ131 measured at room temperature and estimated at the annealing temperature shows that the thermal-shearing effect is important in both curves but is more clearly seen in the latter curve. Similar effects are seen in the familiar plots of α and γ, α^* and γ^* or the obliquity ($\varphi = b \wedge b^*$) as a function of annealing temperature and at room temperature. Salje *et al.* (1985) showed that the true parameters of spontaneous strain are x_4 and x_6, which are approximately $\cos\alpha^*$ and $\cos\gamma$. Moreover, the fact that the macroscopic and microscopic order parameters are identical (from Raman spectra) shows that the phase transformation is homogeneous, so that domain textures do not develop, in contrast with orthoclase.

The phase transformation in $KAlSi_3O_8$ and Or-rich feldspars

Polymorphism in $KAlSi_3O_8$ has been known to exist for over 100 years but has been little understood until comparatively recently. This was due in part to difficulties in characterizing the various forms until the advent of X-ray precession methods for the study of the lattice geometry of microcline (Laves, 1950), and of transmission electron microscopy for the study of the microtextures of orthoclase and microcline (McConnell, 1965; Nissen, 1967; Eggleton and Buseck, 1980; McLaren, 1978, 1984; Fitz Gerald and McLaren, 1982). These studies have shown that the difference between orthoclase and microcline is fundamentally one of scale in the microtextures, as postulated originally by Mallard (1876), coupled, however, with differences in Al,Si order (Laves, 1950, 1960; Goldsmith and Laves, 1954). Orthoclase has a 'tweed' texture consisting of a very fine-scale alternation of partially Y-ordered and anti-ordered domains only a few unit cells thick, which retain overall monoclinic symmetry to X-rays; these correspond with the 'left' and 'right' Albite and Pericline twin domains in the coarser 'tartan' intergrowth of microcline. Our lack of understanding was and still is also due in part to the common belief (Smith, 1974; Yund, 1974) that Al,Si ordering in $KAlSi_3O_8$ is very much more *sluggish* than in albite, *whatever the structural state* of the former. The available experimental data, which we review below, show, in fact, that this is *not* the case, and that the rates of ordering in both sanidine and microcline are similar to those in albite. On the other hand ordering rates in *orthoclase* are many orders of magnitude slower, because of the development of a domain texture. Unlike albite, however, ordering in $KAlSi_3O_8$ follows a two-step path (Ribbe, 1983), so that there are two (at least) independent Al,Si order parameters. We deal below first with sanidine, then with microcline and orthoclase.

Ordering states and rates in potassian sanidine

For K-feldspars, similarly to albite, direct hydrothermal synthesis from gels or glasses leads to the disordered form, high sanidine, which orders on further annealing, especially in the presence of potassium salts (Martin, 1974*b*; Goldsmith and Newton, 1974; Senderov *et al*., 1975, 1981). As in the case of albite, ordering rates decrease as T decreases, but unlike albite, annealing after direct synthesis leads only to a maximum degree of order of $2t_1 \simeq 0.71$ at all T below 500 °C (Fig. 3). This limiting value in hydrothermal experiments is reached both at high and low pressure (Goldsmith and Newton, 1974; Senderov *et al*., 1975).

Above 500 °C the state of order has been roughly bracketed by hydrothermal crystallization or treatment of ordered starting materials (Senderov *et al*., 1981; Kroll and Knitter, 1985), $2t_1$ being estimated from cell dimensions. Brackets have also been obtained by the dry heating at atmospheric pressure of a high sanidine from the Eifel (Bertelmann *et al*., 1985; Gering, 1985), state of order being estimated from optics and neutron diffraction respectively. Times to reach the latter bracketed values during dry heating were very short, a few hours at 1050 °C to a few weeks at 750 °C, and they are very similar to the times required in hydrothermal runs both for sanidine (Senderov *et al*., 1981; Kroll and Knitter, 1985) and albite (MacKenzie, 1957). Ordering rates are thus very similar in both sanidine and albite. Moreover, evidence that the presence of Ab may affect the equilibrium state of order in sanidine (Senderov *et al*., 1981) is inconclusive. Kroll and Knitter found similar rates for an anorthoclase (Or_{28}) from the Canary Islands.

The extremely rapid variation in order in sanidine from the Eifel is possibly exceptional, other sanidines showing much less rapid variations (Priess, 1981; Bertelmann *et al*., 1985). Furthermore, the rates of change were strongly reduced by pre-annealing at 650 °C for long periods (which produced, however, no change in $2V_x$) or for shorter times at higher temperatures. Pre-annealing for even longer times caused loss of the ability to order and caused disordering rates to approach those of other sanidines (Bertelmann *et al*., 1985). The Eifel sanidine crystals are structurally very nearly perfect, with extremely low dislocation densities (Gering, 1985). The cause of the high reactivity is not known at present, but could be related to the high H_2O contents of 0.013–0.036 wt. % occurring as molecular water in the M site (Beran, 1986). Bertelmann *et al*. (1987) showed that the loss of reactivity starts from the surface of crystal slabs and proceeds inwards with time. They observed the rapid development of large, irregularly shaped 'inclusions' or pores, mainly in the (010) plane and associated with dislocations. At low temperatures condensation of a fluid or solid (ice) phase could be observed in the pores, but most were more or less empty. It is possible that these large, optically visible pores result from the exsolution of water from the feldspar, most of which is lost to the outside by diffusion along dislocation cores. It is also possible that small 'bubbles' of water might be seen by TEM as in quartz (McLaren *et al*., 1983). Ordering rates are possibly considerably lower for many natural sanidines (see for example Scott *et al*., 1971). This may be because they never were as reactive as the Eifel sanidine or more likely that they lost this property on slow cooling, like the pre-annealed Eifel sanidine.

Ordering in microcline and the low-sanidine–microcline transformation

Direct synthesis of mm-scale single crystals of microcline was achieved by Flehmig (1977) at room temperature in alkaline aqueous solutions in an attenuated silica-gel matrix in 180 days, and authigenic low microcline occurs in sediments (Kastner and Siever, 1979). The presumption is that these microclines do not have monoclinic precursors, although Flehmig's products exhibited twinning believed to be different in type to that characteristic of cross-hatched microcline. It is generally agreed that low microcline is stable at low temperatures, but there is no concensus on the stability or otherwise of high and intermediate microclines. Although the most Or-rich feldspars which have been synthesized by hydrothermal methods have $2t_1 \simeq 0.71$, more ordered feldspars are common in igneous and metamorphic rocks. They generally have complex twin-domain textures, which were formed during the symmetry transformation from monoclinic low sanidine to pseudo-monoclinic orthoclase or triclinic microcline. Unlike albite, the symmetry-breaking process in Or-rich feldspars is ordering, except possibly at very high pressures (Hazen, 1976; see however Angel *et al.*, 1988). It starts by a continuous spinodal-like process and coarsening probably proceeds eventually by a nucleation and (partial) growth mechanism with the production of ordered and anti-ordered domains which are geometrically related to each other by complex twin-like laws (McConnell, 1965, 1971; McLaren, 1978, 1984). Orthoclase has a very fine tweed texture with $2t_1$ in the range 0.7 to 0.8 and microcline has coarser tartan twins with (t_10+t_1m) in the range 0.75–1. Once formed, tweed orthoclase, which is a common mineral even in slowly cooled rocks, persists because of the difficulty of coarsening which requires reversal of the ordering sense in adjacent domains. Eggleton and Buseck (1980) roughly calculated the strain energy involved in the tweed texture and showed that it would balance or nearly balance the decrease in volume free energy obtained by complete ordering. See also Carpenter (1988). This means that the *total* free energy change for the formation of tweed orthoclase from low sanidine is very small. Thus, the *total driving force* for ordering is very small in such a domain texture, and consequently the rate of formation of ordered domains is very low. The effect of this very low driving force has led to the widely-held view that ordering rates in Or-rich feldspars are intrinsically very low, *whatever the domain texture.* Extrinsic factors such as fluids or deformation are often invoked as a means of increasing ordering rates, whereas their main effect is to destroy, at least partially, the twin-domain texture and hence to increase the driving force. Tweed orthoclase is in a state of constrained equilibrium, where the constraint is the preservation of the domain texture. It is frequently described as being stranded or in metastable equilibrium.

Euler and Hellner (1961) claimed to have produced triclinic potassium feldspar by hydrothermal synthesis, on the basis of optical and powder diffraction data, but attempts to confirm this were unsuccessful (Martin, 1974*a*). Preliminary TEM studies on low sanidine produced at high pressure by J. R. Goldsmith did not show the presence of tweed orthoclase (unpublished data). It does not, therefore, seem to be possible to proceed further in ordering experiments using truly monoclinic precursors. Senderov and Yas'kin (1975, 1976) studied the disordering of natural low microcline, hydrothermally at T between 200 and 450 °C, together with the ordering of two 'sanidine' samples (Fig. 3). Both 'sanidine' samples were obtained hydrothermally by annealing microcline at 0.05 GPa, one for 64 h at 950 °C and the other for 53 h at 900 °C; corresponding values of $2t_1$, read from the grid of Kroll and Ribbe (1983), are 0.56 and 0.61, respectively. The two samples behaved quite differently on subsequent hydrothermal treatment. The $2t_1$ value of the more disordered 950 °C sample increased only slightly to ~ 0.66 even after 120 days at 350 °C. The behaviour of the less-disordered 900 °C sample was quite different. Run products were either microcline (plus kalsilite with or without residual 'sanidine') or, in one case with less concentrated KOH, sanidine alone. The highest values reached were 0.89 at 450 °C and 0.915 at 200 °C, and are shown on Fig. 3, along with the results for the two low microcline starting materials. The unannealed, less ordered microcline samples showed virtually no change at 350 and 450 °C, whereas at 550 and 650 °C, they showed very large changes to values which fall within the band defined by ordering in sanidine. The more ordered microcline samples showed slight increases in disorder at 350 and 450 °C. The approximate values of (t_10-t_1m) can also be deduced from the lattice parameters of Senderov and Yas'kin (1975, 1976) and are given in Fig. 3. Moderately to strongly triclinic microclines were obtained at T of 450 °C and below, whereas at 550 and 650 °C the run products were monoclinic. Unfortunately, the precision in the lattice parameters is not high.

Senderov and Yas'kin (1975) suggested that the different behaviour of the two 'sanidine' samples was due to the preservation of triclinic domains in the 900 °C sample, but not in the 950 °C sample. This seems to be the most probable explanation

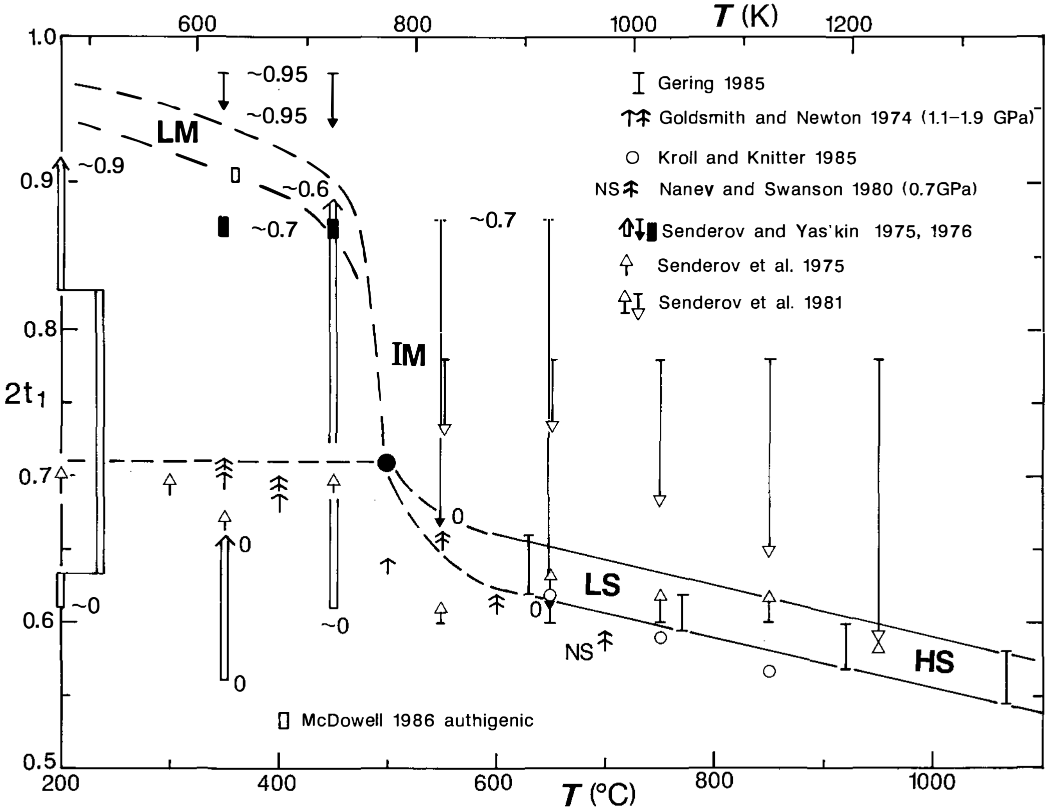

FIG. 3. Variation of $2t_1$ as a function of annealing temperature for Or-rich feldspars. Heads of arrows show final values in all cases, tails show starting values for experiments of Senderov and Yas'kin (1975, 1976) and Senderov *et al.* (1981). Double-headed arrows indicate Or-rich feldspars coexisting with Ab-rich ones, and which are therefore Na-bearing. The three broad arrows indicate changes in 'sanidines' produced initially by hydrothermal treatment of natural microcline. Solid rectangles indicate samples which did not change with time. The open rectangle is for a sample recovered from a borehole at 360 °C in the Salton Sea geothermal field. Numbers show approximate values of $(t_1 0 - t_1 m)$ for triclinic feldspars. LM low, IM intermediate microcline (including high microcline); LS low, HS high sanidine. Curved bands (widths indicating uncertainty) show supposed equilibrium variation of $2t_1$ for $KAlSi_3O_8$ and Or-rich feldspars. Solid circle is approximate position of monoclinic–triclinic transformation. Horizontal dashed line gives approximate limit of order reached in synthetic Or-rich feldspars because of development of a domain texture (orthoclase). Compare with Senderov and Yas'kin (1976) who showed a first-order transformation.

and it is supported by a dry-annealing study of the disordering of low microcline by Blasi *et al.* (1984); they showed that it occurred by a one-step path and that triclinic symmetry was still detected in specimens whose *b–c* values would imply a $2t_1$ value of ~ 0.62. Such triclinic starting materials are particularly suitable for approaching equilibrium in microcline from either side, because there is no domain-texture barrier to overcome. Although they involve metastable states of order, this is unlikely to affect significantly the final states of order in experiments of long duration. A systematic study of ordering in microcline using such starting materials is highly desirable.

The above experiments may be considered to give reasonable brackets on the value of $2t_1 = (t_1 0 + t_1 m)$ at temperatures of 350, 450 and 550 °C (Fig. 3). When combined with data for ordering in sanidine between 650 and 1075 °C, it is possible to draw a curve or band taking account of all data on Or-rich feldspars, which is sigmoidal in shape and very similar to that for albite (Fig. 1), but with the steep part displaced to lower *T*. Also shown is the $(t_1 0 + t_1 m)$ value deduced from $2V_x$ from an authigenic microcline occurring at 360 °C in a borehole in the Salton Sea geothermal field (McDowell, 1986) which is consistent with the experimental data. We conclude that low microcline is stable up to 450 °C and low sanidine above about 550 •C. Only unbracketed experimental data exist between these two T. Goldsmith and Laves (1954) obtained partial conversion of a microcline from Madagascar by hydrothermal treatment at ~ 0.06 GPa in 24 h at 525 °C and no conversion at 500 °C in 500 h. They showed that conversion occurred by solution and reprecipitation. Tomisaka (1962) hydrothermally annealed an impure perthitic low microcline ($An_{1.6}Ab_{29.9}Or_{68.5}$) at various pressures and showed that Δ131 was effectively unchanged at Tup to ~ 450 °C and that it decreased at T 500 °C. Steady-state values were not reached in times up to 1000 h.

Goldsmith (1988, and pers. comm. 1987) investigated the 'dry' disordering rates of an authigenic microcline and a K-exchanged low albite at 750̂900 •C. As in albite, disordering rates are greatly enhanced at high pressures and were similar for the two microclines. Goldsmith reported the length of time to convert the microclines into sanidine with a sharp monoclinic pattern, but the exact structural state of the product was not known. Below 1.3 GPa at 800 °C, 1.5 GPa at 850 °C and up to at least 2.5 GPa at 900 °C, the potassium feldspar disordered considerably more slowly than Clear Creek albite and the effect is particularly marked below ~ 1 GPa when disordering rates of the microclines decreased sharply. At higher pressures the microcline converted to sanidine slightly more rapidly than low albite disordered. Goldsmith suggested that a change of diffusion mechanism occurs in K-feldspar in the region of 1 GPa, perhaps because transient re-coordination of Al in the framework, or formation of OH groups, may be inoperative below that pressure. More data are required on the nature of the transformation, and the textural changes, in these experiments.

The monocliniĉtriclinic phase transformation, whatever its nature, must lie between 550 and 450 °C at low P. There is a large change in $2t_1$ from ~ 0.65 at 550 °C to ~ 0.9 at 450 °C and it is possible to draw either a smooth curve (Fig. 3) or a sharp break (Senderov and Yas'kin, 1976). As is the case for albite, there is no compelling reason to suggest the presence of a sharp break with a first-order transformation. By analogy with albite, the transformation may be close to tricritical (Carpenter, 1988). We thus propose that the degree of order in potassium feldspar varies strongly and continuously with T at temperatures just below ~ 500–525 °C near the start of triclinic ordering at $2t_1 \simeq 0.7$–0.71 (Fig. 3). The continuous nature of this transformation has also been called in doubt by Kroll and Voll (in Ribbe, 1983, pp. 29–30) who proposed a first-order transformation between low sanidine and highly ordered microcline at ~ 450 and 500 •C. This difference of interpretation arises, we believe, because of the formation and stranding of tweed orthoclase and confusion between *stability*, *attainability* and *preservation* of intermediate microclines. In the absence of conclusive experiments between 450 and 550 °C in which the transformation has been accomplished reversibly, we can draw, like Kroll and Voll, only on the evidence of feldspars in rocks. Many studies of subsolvus igneous rocks, reviewed by Smith (1974), Parsons (1978*a*), and Kroll and Ribbe (1983) have shown that the Or-rich feldspar is almost always either orthoclase or nearly low microcline with a high degree of order, or *mixtures* of the two, often demonstrably within the confines of a single crystal grain. Intimate mixtures of tweed orthoclase and tartan microcline have been imaged using TEM by Fitz Gerald and McLaren (1982), though the exact geometrical relationships may differ from straightforward M twinning. Studies of 'transformation isograds' in metamorphic regions (e.g. Bambauer and Bernotat, 1982; Bernotat and Bambauer, 1982) also show the common coexistence of optically monoclinic feldspar and low microcline. Krause *et al.* (1986) determined the Al occupancy of the T_10 site in Pericline-twinned microcline lamellae coexisting with orthoclase using electron channelling enhanced microanalysis in an electron microscope (ALCHEMI, Taftø and Buseck, 1983). They obtained a value for t_10 of approximately 0.56; the corresponding values of (t_10+t_1m) and (t_10-t_1m) were not determined but could be in the ranges 0.8–0.9 and 0.3–0.2 respectively, hence showing that the lamellae consist of high to intermediate microcline. The coexisting orthoclase has a value for $2t_1$ of ~ 0.88 derived from X-ray powder diffraction. This value is high compared with a value for $2t_1$ of 0.71 for a Madagascar gem orthoclase (Taftø and Buseck, 1983), which was presumably free of microcline lamellae.

McLaren and Fitz Gerald (1987) combined another new electron-beam technique, convergent beam electron diffraction (CBED), with ALCHEMI. They showed that for a high sanidine devoid of microstructure and a low microcline with coarse, cross-hatched twin microstructure, there was excellent agreement between $2t_1$ values obtained from X-ray diffraction and from ALCHEMI. CBED can be used to obtain the symmetry of very small volumes of crystals; in this case, McLaren and Fitz Gerald obtained patterns from regions with a diameter of *c.* 50 nm in a 'tweed orthoclase' (previously illustrated by Fitz Gerald and McLaren (1982) and with monoclinic symmetry from normal selected-area diffraction), corresponding to an average of about 10 modulations of the tweed pattern. The symmetry of these small volumes was triclinic. ALCHEMI, on regions of *c.* 100 nm diameter, gave $2t_1$ of 0.67 ± 0.02 (S.D.), and, at this scale the sample is an intermediate microcline. Further work of this type on carefully selected suites of samples is desirable in order to understand details of the orthoclase-microcline transformation.

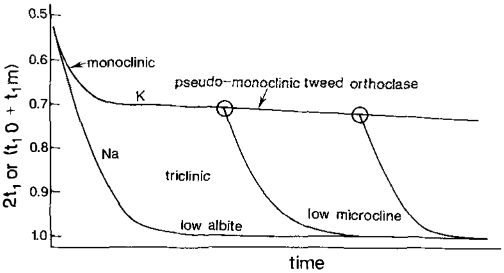

FIG. 4. Schematic variation of the degree of order in Ab and Or-rich feldspars as a function of time at a *T* near the upper limit for low microcline or during slow cooling in rocks. In albite ordering proceeds to completion, whereas in Or-rich feldspars it is blocked at orthoclase, unless some 'unzipping' event (such as interaction with fluids or external stresses) intervenes (circles).

On the face of it, the common natural occurrence of two coexisting K-feldspars supports the hypothesis of a discontinuous transformation. However, intermediate microcline was first described in Or-rich crystals by MacKenzie (in Adams, 1952) and there have been many subsequent descriptions (e.g. Mergoil-Daniel and Chevalier, 1984; Stewart and Wright, 1974). It occurs in coherent cryptoperthites (Brown and Parsons, 1984*a*, *b*) and intergrown with orthoclase (Krause *et al.*, 1986). These observations are not easily reconciled with a discontinuous transformation (cf. discussion on albite). We suggest that the comparative rarity of intermediate microcline is a result of the relative *rapidity* of Al,Si ordering, once the barrier of tweed is overcome. This is shown schematically in Fig. 4 in which ordering is compared in albite and potassium feldspar during slow cooling. At the beginning of cooling, potassium feldspar is assumed to order only slightly more slowly than albite, but ordering slows down dramatically near $2t_1 \sim 0.7$, because of the reduction in driving force resulting from the build-up of strain energy associated with the twin-domain texture. If, however, this texture can be by-passed, by some process that allows nucleation and growth of microcline, then ordering can again proceed rapidly. Tweed may coarsen to tartan in response to interactions with deuteric fluids (e.g. Parsons, 1978*a*) or to deformation (see Smith 1974, vol. 2, p. 384). If intermediate microcline had no stability field, coarsening of tweed orthoclase under these circumstances would lead directly to low microcline. If on the other hand intermediate microcline has a stability field, coarsening should occur by way of intermediate microcline as in the specimen studied by Krause *et al.* (1986). If ordering rates are, as we suggest, rapid, it would not be preserved except under special cooling conditions.

In coherent (or semicoherent) intergrowths (see below) the nature of the Or-rich phase depends on the *bulk* composition of the intergrowth (Brown and Parsons, 1984*b*). Brown and Parsons (1984*a*) discussed the development of different perthite morphologies and the presence of intermediate microcline with respect to cooling in strain-controlled coherent cryptoperthites in a compositional range around $Ab_{60}Or_{40}$; their conclusions are summarized in Fig. 5. For intermediate microcline to develop, rather rapid cooling rates in a limited range between C and C′ are required. Intermediate microcline occurs in these coherent intergrowths, rather than tweed orthoclase, because of coherency strain imposed by the intergrown Ab-rich phase; there is no barrier to the formation of microcline. Orthoclase on the other hand forms only in Or-rich or in Ab-rich compositions where coherency strain is much less; dislocations develop to relieve coherency stress. For more Or-rich bulk compositions we have at present not even a semi-quantitative estimate of cooling rate. Parsons and Brown (1984) reviewed the rather fragile petrological evidence for the upper temperature limit of the microcline field; it is in rough agreement with but at slightly lower *T* than in Fig. 3.

In conclusion, we believe that the ordering transformation in $KAlSi_3O_8$ is very probably continuous in nature and similar in part to that in albite. Carpenter (1988) has suggested that it may be tricritical. High-to-low sanidine and high-to-low microcline are stable phases characterized by different degrees of Al,Si order, whereas orthoclase is a thermodynamically metastable (or constrained stable) configuration. It is common in nature because it is a kinetically stranded domain texture which requires the intervention of appropriate geological events to overcome the energy barrier to domain coarsening. Intermediate microclines are rare (as are intermediate albites!) because their temperature range of stability is small and ordering rates very fast geologically; their preservation may require a particular limited range of cooling rates in the absence of interactions with deuteric fluids.

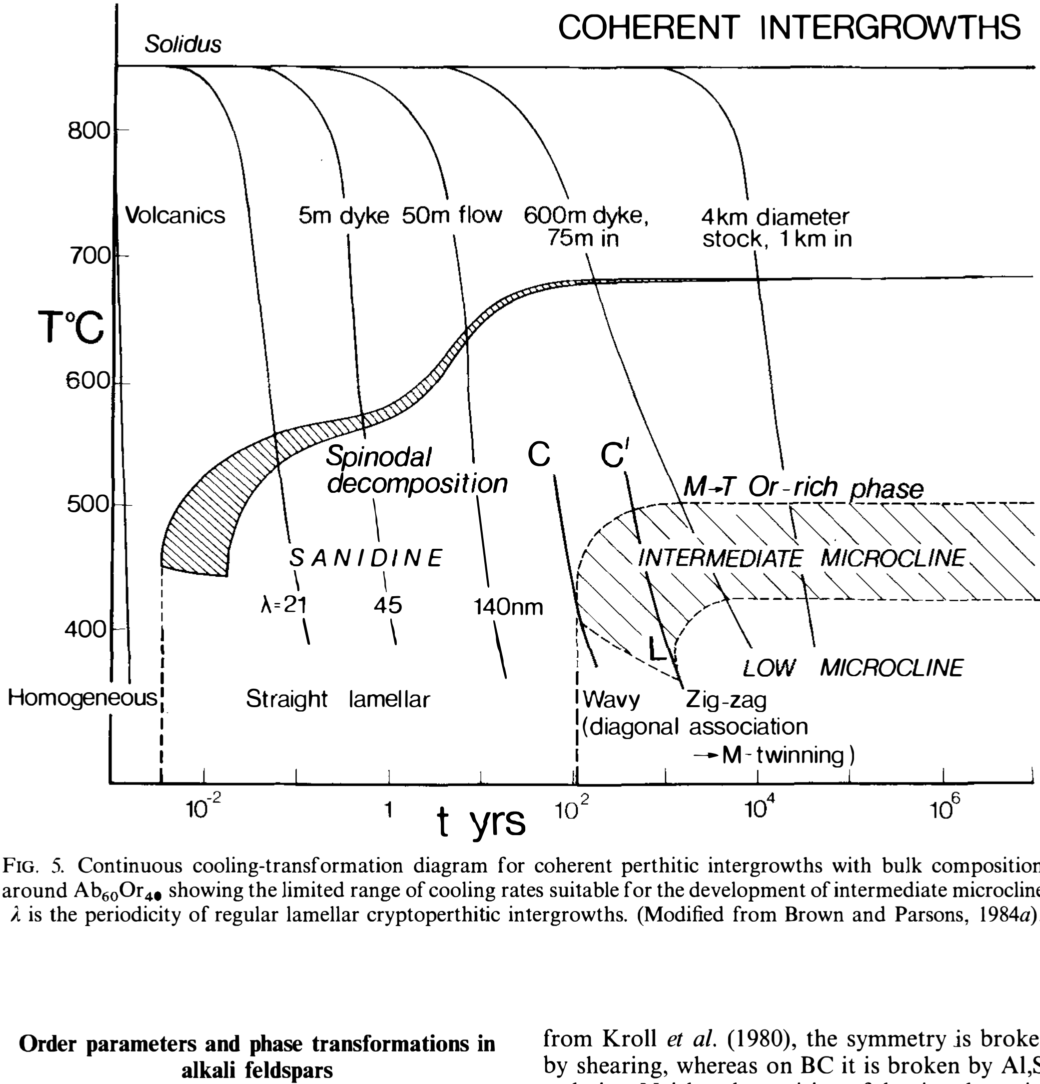

FIG. 5. Continuous cooling-transformation diagram for coherent perthitic intergrowths with bulk compositions around $Ab_{60}Or_{40}$ showing the limited range of cooling rates suitable for the development of intermediate microcline. λ is the periodicity of regular lamellar cryptoperthitic intergrowths. (Modified from Brown and Parsons, 1984*a*).

Order parameters and phase transformations in alkali feldspars

Alkali feldspars at equilibrium are monoclinic at high temperatures and triclinic at low temperatures. The symmetry-breaking process is shearing in albite (Fig. 2) and Al,Si ordering in potassium feldspar. If the phase transformation is continuous, there can be only one line which crosses the Ab–Or–*T* diagram separating monoclinic from triclinic feldspars. As the symmetry can be broken only once, the symmetry-breaking process must change from shearing to ordering at a point on this line. Fig. 6 shows the proposed constrained equilibrium relationships in the alkali feldspars, where the feldspars are considered to be homogeneous (cf. Carpenter, 1988). The symmetry-breaking line is ABC, A being at 980 °C and C taken at ~ 500 °C. On the segment AB, taken from Kroll *et al.* (1980), the symmetry is broken by shearing, whereas on BC it is broken by Al,Si ordering. Neither the position of the singular point B, where symmetry is broken equally by shearing and ordering nor that of the line BC is known with certainty. The position of BC depends on the way the Na/K ratio is supposed to affect equilibrium Al,Si ordering, and this is also not well known. Most authors consider that Na,K mixing favours Al,Si disorder, so that lines of equal order are shown sloping inwards from both sides (MacKenzie and Smith, 1961; Wright, 1964; Parsons, 1968; Senderov, *et al.*, 1981) or an inward-sloping binary loop is drawn which implies the same thing (Wright, 1967; Luth *et al.*, 1974; Martin, 1974*b*; Smith, 1974). Laves (1952; 1961, in discussion to MacKenzie and Smith, 1961) suggested that the ratio had little effect on Si,Al order; only Zyrianov (1977), Thompson and Hovis

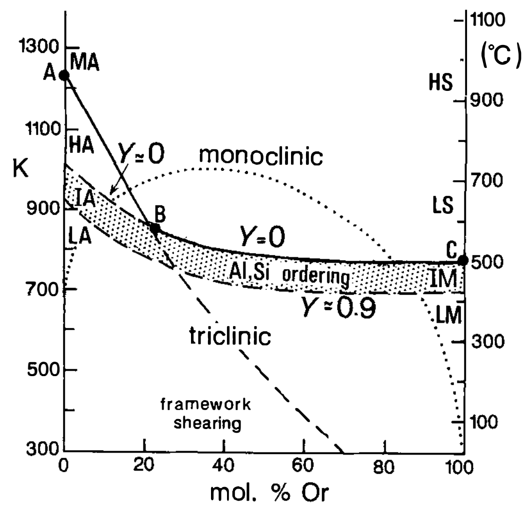

FIG. 6. Diagram showing supposed equilibrium variation of symmetry-breaking line (ABC) as a function of *T* and composition (modified from Smith and Brown, 1988). The stippled band shows region of rapid *Y* ordering. Along AB symmetry is broken by shearing and along BC by ordering. At B a thermal and compositional cross-over occurs at which symmetry is broken equally by shearing and ordering. MA monalbite, HA high, IA intermediate, LA low albite; HS high, LS low sanidine; IM intermediate, LM low microcline. Dotted curve is solvus from Fig. 8.

(1979) and Carpenter (1988) proposed diagrams in which Ab favoured order in $KAlSi_3O_8$.

Above about 700 °C the Na/K ratio appears to have little effect on non-convergent Al,Si ordering (Figs. 1 and 3; see Parsons, 1968, and Senderov *et al.*, 1981), whereas this is not so below 700 °C. The major departure from horizontal is near the Ab end member because significant ordering occurs at a higher *T* in albite (due to the displacive transformation) than in potassium feldspar. Thus a stippled band is shown in Fig. 6 which occurs at about 650–720 °C on the Ab side (intermediate albite) and slopes down rather steeply towards B to become nearly horizontal towards Or (intermediate microcline). This downward slope is based on a comparison of data which is partly non-equilibrium for albite at low pressure. At high pressure it is deduced from data in Goldsmith and Jenkins (1985) for pure albite and Goldsmith and Newton (1974) for potassian albite coexisting with a potassium feldspar. The band is shown horizontal on the Or-rich side of the diagram for want of any convincing evidence to the contrary (see e.g. Thompson and Hovis, 1979; Carpenter, 1988). It is, moreover, likely that substitution of the smaller sodium ion in Or-rich feldspar will have less effect on framework order than the substitution of potassium in Ab-rich feldspars. Feldspars below the dotted solvus (see next section) are metastable relative to exsolution.

The stippled band in Fig. 6 corresponds with rapid *Y* ordering with decreasing *T*. It crosses the line AB and its dashed continuation (Brown *et al.*, 1984) at the point B and below; see, however, Carpenter (1988). Compared to Fig. 2, there is both a thermal and a compositional crossover at B. From A to B, shearing is dominant, whereas from B to C, *Y* ordering is dominant. The stippled band in Fig. 6 corresponds to values of *Y* of zero (or nearly zero) and ~ 0.9. Finally, possible variation of *Z* is shown in Fig. 7, lines of equal *Z* being horizontal at higher *T* but sloping inwards from the Ab side below ~ 700 °C.

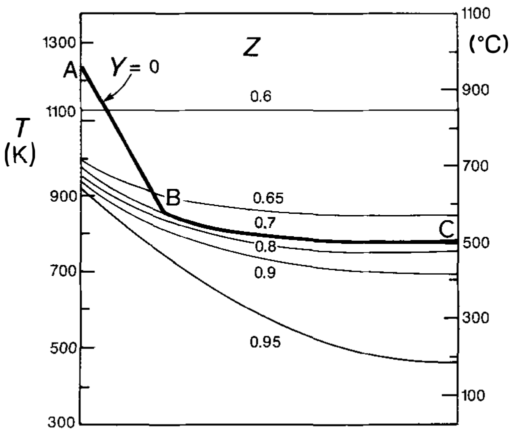

FIG. 7. Supposed equilibrium variation of *Z* in alkali feldspars as a function of *T*. Above line ABC (from Fig. 6) feldspars are monoclinic. Ordering follows a one-step ordering path (or a near one-step path) in Ab_{100} whereas it is two-step for other alkali feldspars.

Solvus relationships and possible partial and complete stable equilibrium alkali feldspar phase diagrams

In this section we discuss briefly the various types of solvi and the relationship between the monoclinic–triclinic transformation line and the solvi. The solvi vary in position with respect to degree of Al,Si order, occurring at higher *T* in more ordered feldspars (Müller, 1971). They also depend on the nature of the interface between the phases. In coherent intergrowths the framework is continuous and strained by coherency stresses;

incoherent phases have separate frameworks and are unstrained ('strain-free') i.e. there are no coherency stresses. The coherent solvus lies at lower *T* than the corresponding strain-free solvus (see Yund and Tullis, 1983, for a review).

In principle, if the solvi intersect a phase transformation line or even a temperature zone representing the rapid onset of Al,Si ordering (Fig. 6), there is likely to be some change of slope (e.g. Laves, 1960; Bambauer *et al.*, 1974). However, there are serious practical problems in interpreting solvus data. Most studies of the strain-free solvus have involved data which were not bracketed (see Parsons, 1978*b*); refined treatment of such largely invalid data (as carried out by Martin, 1974*a*, and Merkel and Blencoe, 1982) cannot locate subtle changes of slope, and only closely reversed data should be used for this purpose. Even then we come up against a severe observational problem: the *Y*-ordering band (Fig. 6) intersects the strain-free solvus near its crest on the Ab-rich limb at temperatures around 600 °C (at 0.1 GPa), and above this temperature it is extremely difficult to measure phase compositions because the X-ray diffractions are poorly resolved (see Smith and Parsons, 1974). Special high-resolution techniques (e.g. synchrotron radiation) might solve this problem, but at present this has not been done. Reversed experiments at high *P* (Goldsmith and Newton, 1974) do not extend to high enough temperatures to locate any likely intersection (see Parsons, 1978*b*, Fig. 3). We conclude that no data-set exists at present which can be used to demonstrate the existence or non-existence of changes in slope on any solvus at the monoclinic-triclinic transformation, and although we expect that high quality work could demonstrate such changes, we have drawn smooth curves on the diagrams in the following section. Merkel and Blencoe (1982) gave a complete review of possible relationships between the strain-free solvus and spinodal, and the symmetry transformation, but the data are not of sufficiently high precision to enable a choice to be made.

The strain-free and coherent solvi for equilibrium ordered feldspars

The many attempted determinations of the 'strain-free' alkali feldspar solvus at low *P* have been reviewed by Parsons (1978*b*). However, all these curves are likely to be metastable to a large extent with respect to Al,Si order on the Ab-rich limb, and are certainly so on the K-rich limb at low *T*. At high *P*, stable equilibrium may have been nearly reached on the Ab-rich limb (see Goldsmith and Newton, 1974), but the crest of the solvus is truncated by melting if small amounts of water are present. On Fig. 8*a* we therefore show a composite, probable stable-equilibrium solvus at low *P* from Brown and Parsons (1984*a*) constructed from the solvi obtained in homogenization experiments by Müller (1971), using feldspar starting materials with known degrees of order. We also show (Fig. 8*a*, *b*) the phase transformation line and a band of rapidly changing *Y* order from Fig. 6. A coherent solvus representing equilibrium with respect to Al,Si order has also not been obtained. We show a coherent solvus on Fig. 8*b* constructed on the basis of the temperature difference between the disordered strain-free solvus of Smith and Parsons (1974) and the disordered coherent solvus of Sipling and Yund (1976) near the solvus critical temperature, and the ordered strain-free solvus of Bachinski and Müller (1971) and ordered coherent solvus of Yund (1974) on the limbs. Although not fully satisfactory, we consider that these two curves are the best presently available estimates for complete 'strain-free' and coherent thermodynamic equilibrium, which take into account both the most reliable experimental data and theoretical considerations. A direct determination of these curves using reversed data points would be a formidable task.

Alkali feldspars in magmatic rocks: phase and behaviour diagrams

Fig. 8*a*, and *b* represent two extremes which are rarely found in feldspars in rocks, except over restricted *T* ranges. Fig. 8*a* is a *normal phase diagram* which shows supposed-equilibrium relationships of separate but coexisting feldspars whose compositions lie on the strain-free solvus; each feldspar is a single crystal which is homogeneous at every *T* and acts as a perfect open system. Alkali exchange occurs only between crystals and there are no fine-scale intergrowths. Furthermore, the homogeneous feldspars are supposed to contain no microstructures resulting from the monoclinic–triclinic phase transformation, i.e. they change symmetry essentially as single crystals without developing complex twin microtextures. Fig. 8*b* represents the other extreme. Crystals act essentially as *closed systems*, alkali exchange occurring only within and not between crystals. Moreover, all feldspars below the heavy line consist of complex twin and/or intergrowth microtextures which are fully coherent. Labelled fields within the solvus refer to *bulk compositions* and not phase compositions. Fig. 8*b* is thus *not* a phase but a *behaviour* diagram. It is possible to combine parts of these diagrams to show behaviour in common rocks which may be either essentially

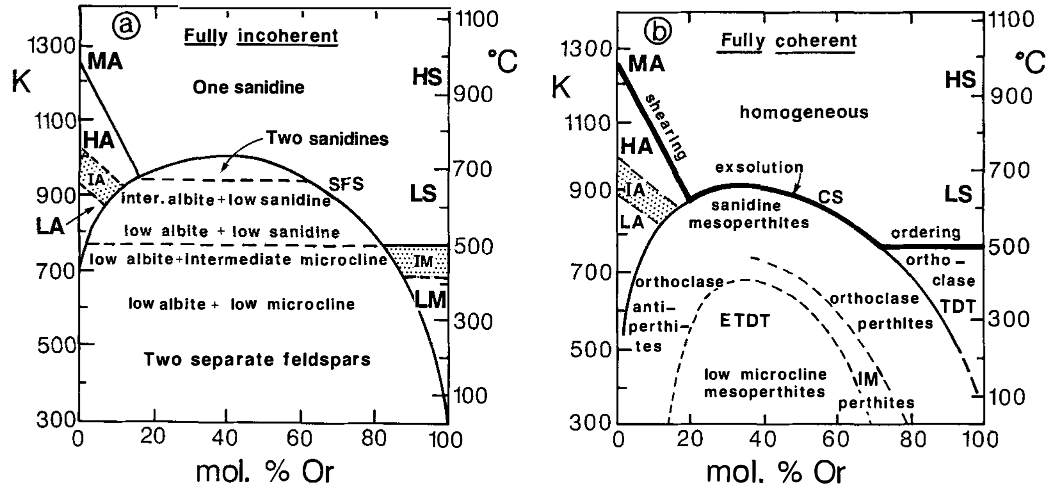

FIG. 8. (*a*) Diagram showing phase relationships for An-free alkali feldspars under complete (incoherent) equilibrium. Outside the strain-free solvus (SFS) all feldspars are homogeneous and devoid of any exsolution or twin domain textures. For bulk compositions inside the strain-free solvus, two phases coexist whose compositions are given by the solvus at any T and are independent of bulk composition; each feldspar is devoid of domain textures and the interfaces between them are stress-free (no strain energy). (*b*) *Behaviour* diagram showing different constrained equilibrium states as a function of *bulk composition* and T for completely coherent intergrowths (below heavy line). TDT twin-domain microtexture; ETDT exsolution and twin-domain microtexture. Inside the coherent solvus (CS) the microtextures depend on the proportions of the phases and thus on the bulk compositions (dashed lines are purely schematic). Low microcline occurs only in mesoperthites whose bulk composition is in the region $Ab_{60}Or_{40}$, whereas orthoclase occurs in more Ab or more Or-rich bulk compositions. MA, HA, IA, LA, HS, LS, IM and LM as in Fig. 6.

hypersolvus or subsolvus, depending on rock composition and crystal growth conditions.

Hypersolvus rocks contain only one alkali feldspar which crystallized from a magma with low water content (Tuttle, 1952; Tuttle and Bowen, 1958). The compositions of the alkali feldspar in such rocks are limited to the centre of the diagram (e.g. Brown *et al.*, 1983), generally in the range Or_{20}–Or_{80} (Fig. 9*a*). Once the alkali feldspar has crystallized from the magma, there is usually little exchange between crystals through diffusion in such dry rocks. On further cooling exsolution will occur *within* each crystal below the coherent solvus, usually by spinodal decomposition, which gives rise to extremely regular, fully coherent cryptoperthitic or microperthitic exsolution microtextures (Brown *et al.*, 1983; Brown and Parsons, 1984*a*, *b*). Such microtextures occur homogeneously throughout all the crystals of a given rock sample and are independent of defects in the crystal. Each crystal acts as a perfect closed system at this stage, and should continue to do so down to lower and lower T, as diffusion slows. The microtextures which develop depend on the *bulk composition* of the crystal, as does the structural state of the Or-rich phase. Low microcline occurs only in crystals whose bulk composition lies close to the centre of Fig. 9*a*, whereas intermediate microcline and orthoclase occur in more Or-rich bulk compositions; this is because of the effect of the coherency stresses, which vary with the relative amount of the Ab-rich phase (Brown and Parsons, 1984*b*). Such coherent perthites and mesoperthites are common even in large, slowly cooled hypersolvus igneous intrusions.

They may be considered to be in constrained equilibrium, where total coherency is the imposed constraint. Such microtextures may change only if some way is found to overcome coherency. Parsons (1978*a*) discussed various ways in which this may occur and showed that water was the main agent in igneous rocks, though external stresses may act in the same way. The coherent interfaces became 'unzipped' and 'catastrophic' coarsening may occur irregularly within a rock or within alkali feldspar crystals during the deuteric or hydrothermal stage. The very regular coherent cryptoperthitic microtextures may be locally preserved (e.g. Moreau *et al.*, 1987) and should be carefully looked for even in the most altered rocks. The catastrophic coarsening consists of an abrupt, often more than thousandfold increase in the scale

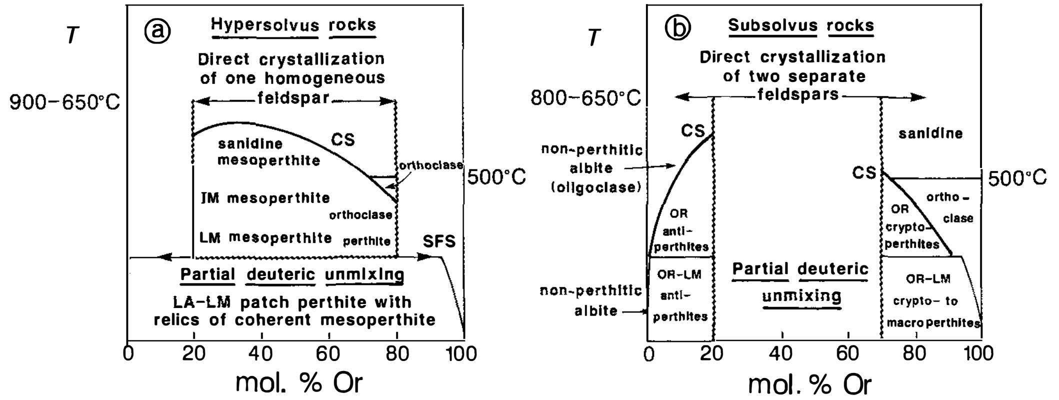

FIG. 9. Diagrams showing approximate ranges of feldspar compositions and microtextures in slowly cooled igneous rocks. Temperatures depend directly on An-content, which raises strain-free and coherent solvi. (*a*) Hypersolvus rocks. Only one bulk feldspar occurs. (*b*) Subsolvus rocks. Two bulk feldspars coexist due to intersection of solidus and solvus. After crystallization feldspar crystals behave essentially as closed systems and develop complex microtextures, except at low *T* where deuteric or hydrothermal alteration has occurred.

of the textures, with very marked phase separation. This is shown schematically at the bottom of Fig. 9*a*. Microprobe analyses of such coarsened textures would give two extreme compositions, one almost pure albite (Ab $\geqslant 98$) and the other very Or-rich (Or_{95-98}), whereas the clear cryptoperthitic areas, with exsolution textures considerably finer than the probe beam, would give bulk-compositions near the centre (Brown *et al.*, 1983; Moreau *et al.*, 1987).

Subsolvus rocks contain two separate feldspars which crystallized directly from the magma, either because of the presence of An which raises the solvus or because of the presence of dissolved H_2O which lowers the solidus (Tuttle, 1952; Tuttle and Bowen, 1958). The compositions of the two feldspars lie towards the Ab and Or ends with a central portion of very variable width unoccupied by bulk feldspar compositions. In some hypabyssal rocks this gap is almost closed (Henderson and Gibb, 1983), but in most typical subsolidus granitic suites, the gap is quite wide (Fig. 9*b*). The two feldspars are usually an Or-rich alkali feldspar and an An-poor plagioclase in the albite or oligoclase range. In markedly subsolvus rocks the Or content of the plagioclase may be < 5 mol % and it is generally not perthitic.

The Or-rich feldspar is (perthitic) orthoclase with a very fine tweed texture. It arises during the monoclinic–triclinic ordering transformation and may be preserved, even in slowly cooled igneous and metamorphic rocks, unless the coherent microtexture can be bypassed in some way. Such orthoclase may have a value of $2t_1$ (derived from a *b–c* plot) which exceeds 0.71 and may reach 0.8–0.85 from X-ray powder diffraction (e.g. Guidotti *et al.*, 1973; Stewart and Wright, 1974). Ab-rich plagioclase, developed following coherent exsolution, is generally insufficient in amount to allow coarser microcline to develop by coherency stresses (Brown and Parsons, 1984*b*). Because orthoclase has a very fine coherent tweed texture, it has no place on a phase diagram for total incoherency such as Fig. 8*a*. Again, as in hypersolvus rocks (Fig. 9*a*), the coherent orthoclase microtexture may be catastrophically unzipped at low *T* through the action of fluids or external (local) stresses giving rise to coarse, cross-hatched low microcline. Large volumes of intermediate microcline formed by coarsening of orthoclase within crystals can arise only under unusual conditions where the unzipping occurs in the stability field of intermediate microcline (Fig. 8*a*) under conditions in which the unzipping agent (water, or stress) does not persist into the low microcline field. Most Or-rich alkali feldspar crystals in subsolvus rocks consist of relics of orthoclase with coarsened low microcline (e.g. McLaren, 1984) giving a typical bimodal distribution in the obliquity index. Coarsening therefore almost always occurs or continues in the low microcline stability field.

Conclusions

Although much further research is required to establish fully equilibrium homogeneous and heterogeneous phase relationships in the binary alkali feldspars, it is now possible to resolve many of the problems concerning the alkali feldspars. At high temperatures disordered alkali feldspars are monoclinic. On slow cooling, they order and transform to triclinic symmetry. The most significant difference between Ab and Or-rich feldspars lies not in the kinetics of Al,Si ordering as such, but in the nature of the symmetry-breaking process. In albite symmetry is broken by a long-range cooperative shearing of the feldspar framework (displacive transformation) which is 'instantaneous' and reversible. There is no barrier to the symmetry transformation and the relatively coarse twin-domain texture which may, but does not necessarily, develop, is also not a barrier to ordering. The high-low order/disorder transformation can be established experimentally and to a large extent reversibly, the only problem being the time required to reach equilibrium below ~ 700 °C at low to moderate pressures. Intermediate and low albites are stable below ~ 700 °C, the former having a narrow stability range of ~ 75 °C at low pressure, and a wider one of ~ 150 °C at 1.8 GPa.

In Or-rich feldspars, the symmetry-breaking process is Al,Si ordering, and the symmetry change occurs at a temperature of about 500 °C. Above that T ordering in sanidine occurs homogeneously, does not break the symmetry and occurs reversibly and about as rapidly as in albite. Further ordering does not occur so readily once the symmetry has been broken, because of the very fine-scale domain texture which develops, the so-called 'tweed' orthoclase texture. Ordering in tweed orthoclase proceeds only slowly and partially, not because ordering rates are intrinsically slow in triclinic microcline, but because the driving force in tweed orthoclase is very slight. This arises because the strain energy in the tweed texture, which is always positive, counter-balances the free-energy reduction due to ordering in the triclinic microcline domains. Ordering in microcline devoid of small tweed domains is very rapid and can be achieved hydrothermally and reversibly at temperatures down to ~ 200 °C. As in the case of albite, Al,Si ordering in $KAlSi_3O_8$ is continuous and occurs, in the absence of the tweed domain texture, mainly over a small temperature range of ~ 100 °C below 500-525 °C.

The symmetry-breaking process in alkali feldspars changes from shearing in albite to Al,Si ordering in Or-rich feldspars; a compositional crossover between the two (metastable with respect to exsolution) occurs at about $Ab_{80-75}Or_{20-25}$. Homogeneous alkali feldspars intermediate in composition exsolve readily on lowering T and more rapidly than they order, because Na,K interdiffusion is much more rapid than Al,Si diffusion. As in the case of the tweed orthoclase texture, strain energy is involved in the exsolution microtextures, which may vary from fully coherent to largely incoherent. Exsolution in alkali feldspars most frequently occurs by spinodal decomposition and the resulting fully, or almost fully coherent microtextures are independent of defects and very regular; this is also the case for tweed orthoclase. If coherency is disrupted by external factors, the textures become strongly dependent on defects (both original and induced) and nearly complete strain-free relationships may apply. Phase and behaviour diagrams have been presented which can be applied to alkali feldspars in hypersolvus and subsolvus rocks and which adequately explain the occurrence of the natural forms of Or-rich feldspars.

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