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Feldspars and fluids in cooling plutons

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SUMMARY. Alkali feldspars in plutonic igneous rocks vary both in their exsolution textures and in the structural state of their components. The primary factor leading to this diversity is the availability of hydrothermal fluids during their cooling history. In many plutons feldspar variation is related to degree of fractionation as indicated by rock chemistry. The variation reflects build-up of water with magmatic evolution and implies that fluids did not circulate freely in the intrusives in the temperature range of unmixing and ordering. Experimental work bearing on the role of fluids in subsolidus changes in feldspars is reviewed, and points of overlap between crystallographic studies of feldspars and stable isotope studies are discussed.

THE factors that control the striking variety of exsolution textures and differences in framework order-disorder in alkali feldspars have been the subject of a number of review articles (e.g. Smith and MacKenzie, 1961; Martin, 1974; Stewart and Wright, 1974). The stress in such treatments has been predominantly on thermal history, both with respect to temperature of crystallization and to cooling rate. In this talk, with an eye on petrologists, not feldspar specialists, I wish to concentrate on what is generally agreed to be one of the important subsidiary controls, namely the presence of aqueous fluids during the cooling of the feldspar from magmatic temperatures, and to suggest that this is pre-eminently the factor that dictates the nature of the feldspar in all but the smallest intrusive igneous bodies provided they have escaped tectonic deformation. I shall show how a few petrographic observations or simple X-ray diffraction measurements may yield a wealth of information about the distribution of fluids during the cooling of a given body of alkali-feldspar-bearing rock, and demonstrate that in many

fractionated intrusive complexes 'water' was distributed following a 'magmatic' pattern, building up with progressive fractionation, and remained essentially restricted within the evolving lithological units.

The effects of water during cooling of igneous bodies is a matter of particular concern at the present time because of the demonstration, by means of stable isotope studies (e.g. Taylor, 1974) of large-scale interactions between plutons and groundwaters. Some of the limited interactions that are demonstrated in the present review contrast strongly with the large-scale, all-pervasive water-rock interactions proposed by Taylor. The crystallographic observations to be described could, under favourable circumstances, be used to limit the thermal range in which water-rock interactions may have occurred, a factor by no means clearly defined in stable-isotope studies.

I shall draw a number of examples of feldspar-fluid interactions from one small (4×3 km stock), very intricate layered syenite pluton, the Klokken intrusion, in the pre-Cambrian Gardar province in South Greenland. The photomicrographs in the following sections illustrate the range of features of the feldspars in this one intrusive. While only limited structural and mineralogical details can be presented here (see Parsons, in preparation, *b*, for detail) it should be noted that the rocks concerned are very intimately interleaved (e.g. fig. 10) and certainly cooled together from temperatures > 850 °C into the temperature range where unmixing and framework ordering occur. The delicate sedimentary structures in the layered series of this pluton show that the intrusion has remained tectonically undisturbed since pre-Cambrian times.

Types of alkali feldspar variation

Alkali feldspars in tectonically undisturbed plutonic salic rocks show at least three types of variation. Firstly, their *bulk composition* will depend on magma composition and the P - T regime under which the feldspar grew from melt, or possibly, in some rocks, upon major subsolidus recrystallization. Rocks are familiarly classified as subsolvus or hypersolvus (Tuttle and Bowen, 1958) on the basis of whether they contain plagioclase as a discrete phase or in perthitic intergrowth only. Because of liquidus relationships in 'petrogeny's residua system' alkali feldspars in both over- and undersaturated hypersolvus rocks have a relatively narrow bulk-composition range (Tuttle and Bowen, 1958; Hamilton and MacKenzie, 1965, and fig. 2), but alkali feldspar bulk compositions in subsolvus rocks have much greater spread. The restricted compositional range of feldspar in hypersolvus rocks has some important corollaries, which are given later.

Secondly, *exsolution textures*, the perthitic intergrowths, exhibit a great diversity of morphologies (well illustrated by Smith, 1974, vol. 2), which will reflect bulk composition and 'thermal history'. Perthites may well form by processes other than exsolution, particularly by replacement (see Smith, 1974, vol. 2, for a review) and Lofgren and Gooley (1977) have produced synthetic perthite-like intergrowths by simultaneous crystallization. There is little doubt, however, that the majority of natural perthites form by exsolution, and this seems certain for the types of intergrowth discussed later.

Thirdly, the exsolved phases themselves may vary in *structural state*; by this we mean the degree of ordering of Al and Si in the tetrahedral framework, and must include within this form of variation the nature of fine-scale domain textures of which the familiar cross-hatched twinning of microcline is a large-scale relative. These features also reflect 'thermal history'. It will be shown below that within this term must be included interactions between the cooling crystals and aqueous fluids, and the term 'hydrothermal history' is perhaps more appropriate.

Hypersolvus and subsolvus rocks

Hypersolvus rocks are particularly instructive concerning subsolidus changes in feldspars because of the firm limitation that can be placed on their minimum temperature and maximum P_{H_2O} of crystal growth from the melt, and also because any large-scale totally reconstructive recrystallization (to an assemblage of two discrete feldspars) can be ruled out. The temperature of feldspar crystal-

lization is restricted by the intersection of the ternary feldspar solvus with the solidus for feldspar in salic magmatic liquids (e.g. Carmichael *et al.*, 1974, fig. 5-1). Because the restricted bulk compositional range of feldspars in hypersolvus rocks (c. $Ab_{75}Or_{25}$ to c. $Ab_{50}Or_{50}$) straddles the critical composition of the feldspar solvus ($Ab_{63}Or_{37}$, Smith and Parsons, 1974) one can display the permitted T - P 'window' for these feldspars reasonably closely on a plot such as fig. 1, and variation in feldspar Na:K will not lower minimum temperatures more than c. 20 °C.

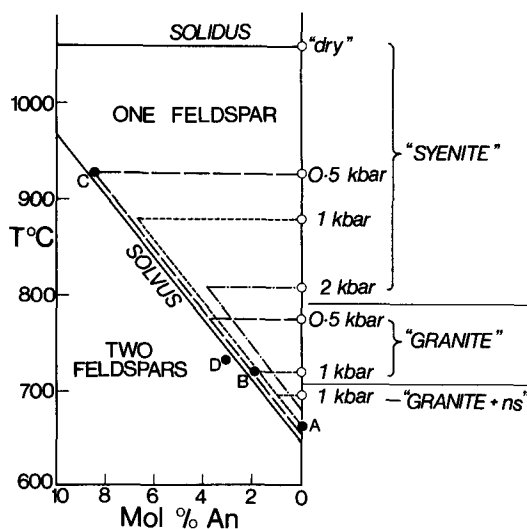


FIG. 1. Diagram illustrating the limited range of P_{H_2O} , T and mol % An over which a single feldspar phase will be the final product of crystallization for bulk compositions in the vicinity of the 'syenite' and 'granite' minima. Solidi, for the named simplified rock compositions at the labelled P_{H_2O} , are approximated by horizontal lines. Data for the solidus of 'syenite' and 'granite' is from Tuttle and Bowen (1958); 'granite + ns' is from Thompson and MacKenzie (1967), where ns is 5 wt % $Na_2Si_2O_5$. The solvus slopes steeply to higher T with increasing An; A is the critical temperature of the strain-free solvus without An (Smith and Parsons, 1974), B is for a natural starting material c. An_2 (Parsons and Smith, 1974), and C is the solvus-solidus intersection observed by Morse (1969) for a natural ternary feldspar. D shows the temperature of the piercing point in the join $(Ab-Or-Qz)_{97}An_3$ at $P_{H_2O} = 1$ kb in which James and Hamilton (1969) observed two feldspars in equilibrium with quartz, liquid, and vapour. The P dependence of the solvus is from Smith and Parsons (1974). Simplifications incorporated in this diagram are discussed in the text.

A number of simplifications are contained in fig. 1. The data on which the slope of the solvus with increasing An is based are sparse, and there are considerable difficulties in locating this surface using synthesis experiments (Smith (P.), 1974).

The Na:K ratio of the critical composition is not necessarily constant with increasing An. Little detail exists on the shape of the feldspar solidus with respect to temperature in the vicinity of the thermal minima depicted and it has been assumed to be horizontal for all liquids over the compositional range of interest; it is known to be almost flat along the Ab-Or join (Tuttle and Bowen, 1958). Despite the lack of detail the projection nevertheless shows clearly the high temperatures and low P_{H_2O} implied by relatively calcic alkali feldspars ($> 850^\circ\text{C}$ in many syenites) and the extremely low P_{H_2O} or low feldspar An contents permitted in a peralkaline granite ('granite + ns'). It is certain that homogeneous calcic alkali feldspars crystallize with a high degree of framework disorder, and probable, although less certain, that An-poor feldspars are disordered at magmatic temperatures. This aspect is further developed below.

As well as narrowing the range of feldspar crystallization temperatures in hypersolvus rocks the restricted bulk compositional variation carries the important corollary that no gross change in alkali ratio can have occurred from magmatic to lower temperatures except, perhaps, in some albized rocks. Further, it is usually assumed, although not demonstrated, that the feldspar grains in a hypersolvus rock are of one constant bulk composition. Fig. 2 shows feldspar bulk compositions for the Klokken syenite. Each analysis represents a separate microperthitic or cryptoperthitic feldspar crystal analysed by scanning with the electron microprobe from margin to margin and calculating bulk composition on the basis of accumulated counts for each major element. Each dot is a separate crystal; crystals joined by tie-lines are from the same rock sample. It is clear that variation both throughout the intrusion and within individual rocks is slight, despite the great varieties of scale and configuration of the perthitic intergrowths in these grains (examples are illustrated later) and we can assume that each feldspar has remained a closed system with respect to alkalis from magmatic to lower temperatures. O'Neill and Taylor (1967) showed that oxygen exchange in feldspars was greatly facilitated by simultaneous alkali exchange, but clearly gross alkali exchange between feldspars and solutions cannot have occurred in the Klokken example or very probably in the majority of epizonal intrusives.

The Klokken feldspars are typical of hypersolvus syenites in clustering around the thermal minimum in the feldspar system. Strictly they are *mesoperthites* (see Smith, 1974, vol. 2) but the terms *micro-* and *cryptoperthite* for optically visible and sub-optical intergrowths respectively are more

informative if we remember the restricted bulk compositional range involved.

In the crust as a whole subsolvus granites are much more common than hypersolvus types, and although total feldspar compositions tend to cover a similar restricted range (Tuttle and Bowen, 1958), bulk alkali-feldspar compositions are not so restricted because they coexist with plagioclase.

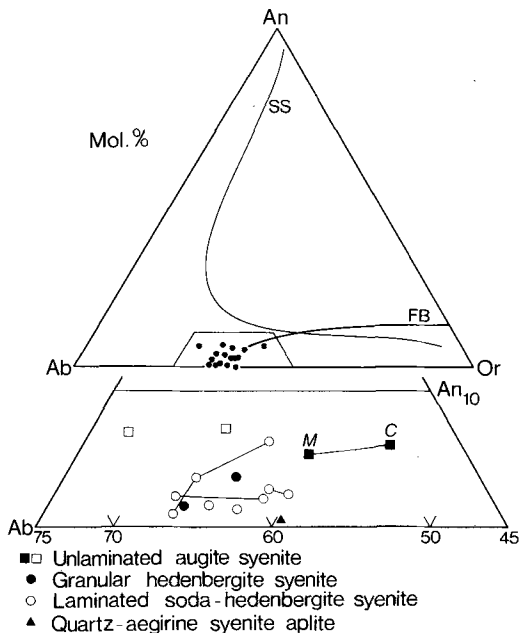


FIG. 2. Bulk compositions of crypto- and microperthitic alkali feldspars from the Klokken syenite. Each dot represents the bulk composition of a single exsolved feldspar crystal obtained by scanning with the microprobe from margin to margin. SS is the limit of feldspar solid solution suggested by Tuttle and Bowen, 1958, which is the solvus-solidus intersection for volcanic feldspars and liquids, and FB is the plagioclase-alkali-feldspar field boundary. M and C are respectively bulk compositions of micro- and cryptoperthitic regions of the large feldspar shown as fig. 3.

Ideally compositions of coexisting discrete plagioclase and alkali feldspar grains will depend on temperature of crystallization, but Tuttle (1952) pointed out the striking textural contrast between most hypersolvus and subsolvus granites. In the former, crystal outlines are usually simple and show the crystal morphology, while in the latter grains have complex shapes, and crystal boundaries are commonly diffuse and exceptionally irregular. Tuttle explained this contrast as a result of major subsolidus recrystallization in the subsolvus rocks facilitated by the presence of volatile materials during the long cooling of these granites.

The hypersolvus character of a granite would be preserved if volatiles were used, or escaped, during crystallization.

In a general way the textural contrast between hyper- and subsolvus granites reflects the generally deeper-seated nature of the latter, and their potentially higher magmatic-water content. Extensive recrystallization implies that these fluids have remained active during cooling of the plutons. Unlike hypersolvus rocks there is no reason to presume that their alkali feldspars have maintained their original bulk composition. The earliest stages of subsolidus recrystallization (at grain boundaries) are most easily seen in undeformed hypersolvus rocks and some examples are given later.

Exsolution and coherency

Seen in thin section the sheer diversity of appearance of micropertthitic intergrowths is remarkable and immediately suggests that herein must lie a record of conditions during cooling of the feldspar. In recent years electron microscopy has revealed the beautiful details of the fine, sub-optical cryptoperthites. J. V. Smith's superb books (1974) are the best possible survey of this diversity and of the crystallographic relationships. I shall draw on specific examples of textural variation in a single hypersolvus intrusive (the Klokken intrusion) and use them as a vehicle to introduce some of the concepts concerning the mechanisms of exsolution that have emerged in recent years. A more detailed treatment of the Klokken feldspars is in preparation.

Fig. 3 shows a section through part of a large ternary feldspar crystal (at least $10 \times 8 \times 6$ cm), from a pegmatitic facies of the Klokken augite syenite. This is an appropriate example because Ussing illustrated similar features from a Gardar syenite as early as 1893. The crystal's bulk composition (analyses M and C, fig. 2) is about $\text{Ab}_{50}\text{Or}_{44}\text{An}_6$. Most of the crystal is clear in hand specimen, and shows brilliant blue iridescence, but it is traversed by cracks, which are whitened. In thin section (fig. 3) the whitened areas show coarse albite twinning, and are coarsely micropertthitic. The K-rich phase is crowded with tiny rounded cavities, which cause the cloudiness. In contrast the iridescent feldspar is clear and featureless in thin section, except for a few strain shadows around cleavages, and it requires X-ray diffraction to show that it is a cryptoperthite.

At first sight it appears that the coarsely twinned area might be due to a replacement process; in fact bulk microprobe analyses obtained by traversing along the length of a turbid band show that the micropertthitic material (M on fig. 2), is essentially

identical in bulk composition to the cryptoperthite (C). The visible difference between the two regions of the crystal is caused by a process of *coarsening* of the cryptoperthite, and in view of the turbidity and relationship to cleavages it seems unquestionable that it has been facilitated by fluids entering the crystal along fractures.



FIG. 3. Extreme contrast in coarseness of exsolution texture in a ternary alkali feldspar crystal, bulk $\text{Ab}_{50}\text{Or}_{44}\text{An}_6$. Section cut approximately normal to x . The grey, apparently structureless areas are cryptoperthitic, transparent and show blue iridescence in hand specimen. The bands showing albite twinning are coarsely exsolved micropertthite, developed along cracks, which are white and turbid. The K-rich phase in these bands is inconspicuous because of the high contrast of the albite twins in the Na-rich phase, but microprobe analysis along the length of a coarsely exsolved area shows that the crystal has essentially constant bulk composition, and these bands are caused by coarsening, not replacement (crossed nicols).

This abrupt coarsening is associated with an important structural change in the nature of the intergrowth. Such changes are best investigated using single-crystal X-ray methods or transmission electron microscopy (TEM), but even powder diffraction may yield useful information. Fig. 4 shows a series of patterns for perthitic feldspars from the Klokken intrusion, of which 1 and 2 are respectively cryptoperthitic and micropertthitic areas of the same crystal as fig. 3, separated by breaking up a thick slice. Although separation of the turbid material was imperfect the diffraction pattern shows a marked increase in the number of resolved reflections. Other coarsely micropertthitic feldspars from the complex show many more resolved peaks, in particular in the acid aplites that cut the syenite (5). Each feldspar shown may be identified as a perthite from the presence of two 201 reflections (for Na- and K-rich phases respectively, see fig. 4, pattern 5). However, certain other reflections, particularly 060 and 204 , which should

occur in pairs (as in 5), sometimes appear either as a single, broad reflection (1 and 3) or as poorly resolved doublets (2 and 4).

It is highly probable that the main factor causing these changes in the diffraction patterns is loss of *coherency* between the intergrown phases.

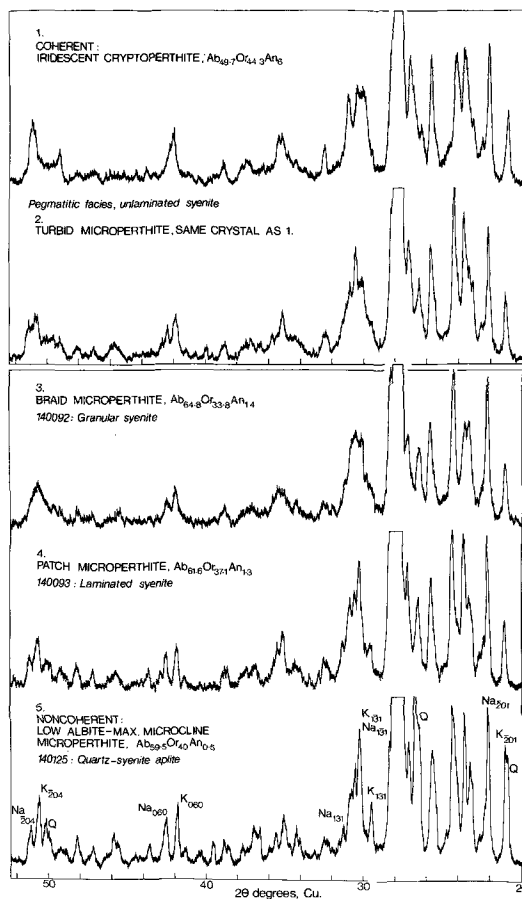


FIG. 4. X-ray diffractometer patterns showing how coherency in perthites affects the number of resolved reflections and their sharpness. Patterns 1 and 2 were obtained from cryptoperthitic and microperthitic areas of the crystal shown in fig. 3. Patterns 3 and 4 are from interbedded syenite horizons in the Klokken layered syenite (see fig. 10) and 5 is from an aplite vein cutting this series.

Coherency occurs in feldspars because the segregation of Na and K ions takes place in an AlSi_3O_8 framework that may remain continuous across the interface between the perthitic lamellae. Yund (1975) has provided a comprehensive review of the subject and discussed mechanisms of exsolution. Lattice planes normal to a coherent interface will have the same spacing in both phases, and since the

interface is commonly $(\bar{6}01)$ in cryptoperthites a single reflection will be observed for planes such as 060 . The adjustment of such planes means that the structure is subject to elastic strain, and neither phase will have the cell dimensions of the same phase occurring as a separate crystal or in a non-coherent or 'strain-free' intergrowth. Such strained intergrowths are in no way transient—the example given has an age of 1159 Ma (Blaxland and Parsons, 1975). The effect of coherency on planes more nearly parallel to $\bar{6}01$, such as 201 , may be to increase the separation of the diffraction maxima for the respective phases. Thus 201 reflections, commonly used for obtaining the composition of homogeneous alkali feldspars (e.g. Orville, 1963), may indicate 'impossible' compositions with > 100 or $< 0\%$ Or, the case with pattern 1 (fig. 4). This feature of certain perthites was explained by Smith, 1961, as a result of the need for the cell volumes of the coherent units to remain approximately constant. Procedures have been suggested (Robin, 1974; Tullis, 1975) for correcting the cell dimensions of feldspars in coherent intergrowths so that diffraction patterns can be used to obtain 'true' phase compositions. Such procedures are needed in experimental studies of coherent exsolution, but are of less value to petrologists studying plutonic rocks, in which phase compositions probably vary little and usually approach end-member low albite (although it may be calcic in many hypersolvus rocks) and a K-feldspar, either monoclinic orthoclase or triclinic microcline, in the range Or_{83} to Or_{100} (see Brown and Willaime, 1974).

The orientation of lamellar intergrowths in crypto- and fine microperthites is variable, changing from $(\bar{6}01)$ in many fine cryptoperthites to $(\bar{6}\bar{6}1)$ in cryptoperthites that exhibit a diamond-shaped intergrowth (see e.g. transmission electron micrographs in Brown and Willaime, 1974). These may coarsen ultimately to optically visible 'braid' microperthites, which are probably still partly coherent (fig. 5A). The dividing line between intergrowths that are *possibly* coherent and those that are *largely* non-coherent corresponds very approximately to that between crypto- and microperthites (Yund, 1975). Really coarse microperthites (fig. 5B) are usually irregular in texture (patch perthites), are non-coherent, and often bear little or no record of any earlier coherent stage.

The orientation changes that occur during coarsening of *coherent* intergrowths have been elegantly explained using calculations of coherent elastic energy by Willaime and Brown (1974). The lamellar interface develops so that the elastic energy is at a minimum, and it must change direction in response to symmetry changes as temperature falls. Further coarsening involves loss of

coherency and is not necessarily constrained crystallographically to fixed orientations of interface although many coarse perthites do inherit interface orientations from an earlier coherent stage. Water plays an essential role in this stage of coarsening, best understood after discussion of phase equilibrium relationships.

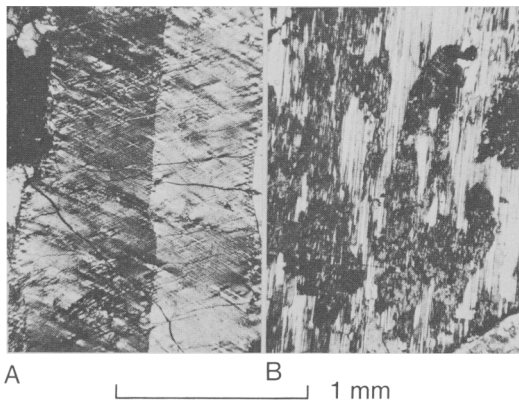


FIG. 5. Contrasting exsolution textures in feldspars from adjacent horizons in the Klokken layered series (fig. 10) (crossed nicols). A, Carlsbad twinned braid microperthite crystal (from granular syenite giving diffraction pattern 3, fig. 4). Such intergrowths may maintain a high degree of coherency and probably represent the extreme of coarsening by coherent exsolution. B, very coarse patch microperthite crystal (from laminated syenite) showing albite twin lamellae in the Na-rich phase. The K-rich phase is albite and pericline twinned microcline, but is turbid. Such intergrowths are probably largely or wholly incoherent; the irregular shape of K-rich areas is in striking contrast to the regular lamellae in A.

Solvus curves

Initially, exsolution probably proceeds by spinodal decomposition, the mechanism favoured by Lorimer and Champness (1973), Owen and McConnell (1971), and Sipling and Yund (1976) although not unequivocally proven (see Yund, 1975, for a review). In this process lamellae of a characteristic, temperature-dependent wavelength became progressively more different in composition. At temperatures just below the temperature of inception of unmixing compositional fluctuations will be large in wavelength but low in compositional contrast. In crystals annealed at lower temperatures the initial wavelength is shorter and the compositional contrast greater.

Experiments published to date do not wholly rule out coherent nucleation as a mechanism for phase separation, and there are differences in behaviour observed in the Sipling-Yund and Owen-McConnell studies, in which annealing was

respectively 'dry' and hydrothermal. Whatever the mechanism, however, the phase compositions eventually reach equilibrium values, which define a solvus curve called the *coherent solvus* (fig. 6), which lies inside the *strain-free solvus*. The latter is the solvus normally depicted in phase diagrams. The two curves differ because when coherency exists a term for strain energy has to be added to the normal Gibbs energy curves for the crystalline solution. The coherent solvus can be calculated from the strain-free solvus if strain energy is accommodated in thermodynamic models of the solvus (Robin, 1974).

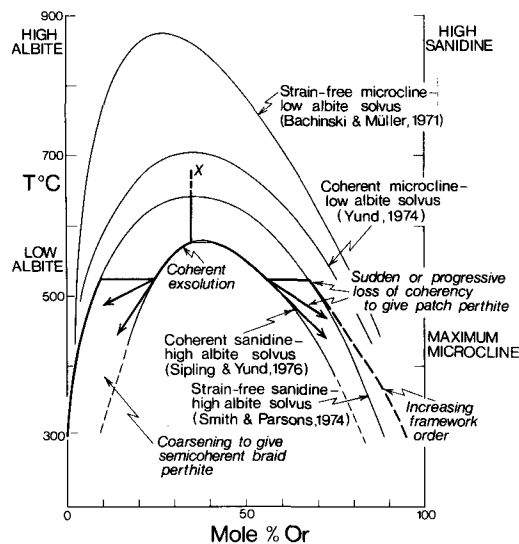


FIG. 6. Experimentally determined solvus curves for the alkali feldspar system (thin lines). To aid comparison the curves have been adjusted to 1 bar pressure assuming the temperature dependence of the solvus on pressure is $16\text{ }^{\circ}\text{C}/\text{kb}$. Heavy lines indicate alternative exsolution paths for crystals like those in figs. 5 and 7. The approximate temperature ranges of the polymorphs of the end-members are shown; it is probable that solid solutions of the bulk composition (\times) shown are strongly disordered with respect to Al and Si when Na-K unmixing begins, and that framework ordering occurs in step with unmixing.

Different types of experiment are needed to determine the two types of solvus curve. Coherent solvi are determined by using relatively large crystal fragments, which are either homogeneous at the outset and are caused to unmix by heating below the top of the coherent solvus, or are coherent intergrowths, which may be partially or completely homogenized at various temperatures. Strain-free solvi are determined either by homogenizing mechanical mixtures of compositionally contrasting feldspars, or by direct crystallization of

two-feldspar assemblages from amorphous gel or glass starting materials.

The first determination of a coherent solvus seems to have been carried out unwittingly by Smith and MacKenzie (1958). They heated cleavage fragments of a sanidine cryptoperthite for long periods and measured the two-phase compositions using cell angles obtained by single-crystal X-ray means. Some difficulties were experienced in explaining the curve obtained, which lay well inside the 'synthesis' solvus curve then available (Bowen and Tuttle, 1950). Sipling and Yund (1976) have recently determined a coherent solvus using a series of disordered alkali feldspars obtained by ion-exchanging a high sanidine (actually an annealed adularia) with molten alkali chloride mixes, and using single crystal X-ray means and TEM to detect the inception of unmixing. Their curve is quite similar to Smith and MacKenzie's curve, and it is clear that the earlier experiments had, by their nature, located a coherent solvus.

The position of the coherent solvus also depends on the degree of framework order and Yund (1974) has determined a coherent microcline-low-albite solvus (fig. 6). Except at low temperatures such a curve will be metastable with respect to framework ordering. Even in plutons alkali feldspars are very probably strongly disordered with respect to Al and Si when unmixing begins, so that exsolution will begin when the feldspar intersects the coherent solvus (or the coherent spinodal, see Yund, 1975) for *disordered* frameworks and phase compositions will move out towards the 'ordered framework' coherent solvus as ordering and exsolution proceed together. Apparently some coherent perthites are also highly ordered (see e.g. Brown and Willaime, 1974) but more commonly loss of coherency accompanies exsolution and ordering, and this will lead, via a variety of paths (fig. 6) to phase compositions defined by a strain-free solvus appropriate for the degree of framework order attained.

Yund (1975) has suggested that it may not be unreasonable to extend existing experimental work on coherent coarsening to lower temperatures and geologically interesting cooling rates, and this might prove valuable in plutons with coherent perthites of the type I shall describe later. He also suggests that the critical temperature (the 'crest' or 'top') of the coherent solvus of a cryptoperthite may also be a measure of the degree of coherency. In practice the An-content and degree of framework order of the cryptoperthite will have a pronounced effect on both coarsening rates and on the position of the solvus, so that interpretation of such curves for natural examples is not straightforward.

The strain-free solvus, depicting the composition

of coexisting feldspar grains in contact but not in crystallographic continuity, has been tackled by many workers at pressures up to 15 kb (Goldsmith and Newton, 1974). Most studies involve direct crystallization of two phases, as separate suites of K- and Na-rich crystals, from gels in the presence of water, the composition of the phases being obtained from the $\bar{2}01$ spacing. Superficially this would seem to be a relatively straightforward experimental problem, but consistency between the various solvus determinations has been poor. Recent determinations at 1 kb using equilibrium reversals by P. Smith and the writer (1974) and by Lagache and Weisbrod (1977), are in extremely good agreement, and also fit well with the high-pressure reversal study of Goldsmith and Newton (1974) if a linear dependence of the critical temperature on pressure of 16 °C/kb is assumed (Parsons, 1978). The solvus most widely applied to a number of petrological problems is that obtained by Thompson and Waldbaum (1968) by a thermodynamic treatment of data of Orville (1963) and Luth and Tuttle (1966). It agrees to within 2 mole% on the sodic limb, but is about 10 mole% too potassic on the potassium-rich limb (see Parsons, 1978). Much of the scatter in other determinations can be ascribed to the phenomenon of partial exchange equilibrium (Thompson and Waldbaum, 1968) in which the two phases reach a metastable exchange equilibrium via the fluid in the capsule and take long periods to reach complete crystal-crystal equilibrium (Smith and Parsons, 1974; Parsons, 1978). Any effects of non-stoichiometry in the starting materials, as suggested by Luth and Tuttle (1966), and possible effects due to framework ordering during synthesis experiments with excess alkali (Martin, 1974) must be disentangled from partial equilibrium effects before they can be accepted as fact. Feldspar solvus diagrams purporting to show sudden breaks due to framework ordering processes (Luth *et al.*, 1974; Martin, 1974) should be treated with caution, since neither the writer (Parsons, 1978), Lagache and Weisbrod (1977), nor Goldsmith and Newton (1974) have been able to detect effects due to ordering even in relatively long experiments.

Water and exsolution

The role of water (and possible solutes) in the two types of exsolution process is different and its role in coherent exsolution is not wholly clear. Ideally coherent exsolution involves only Na:K migration through a continuous defect-free framework and is therefore amenable to study as a pure volume-diffusion process. Studies of alkali diffusion in feldspars, using radioactive tracers, have been carried out by Petrovic (1974), Lin and Yund

(1972), and Foland (1974); there are quite large differences in the experimental results, probably indicating the difficulty of ensuring that starting materials are of such quality that only true volume diffusion occurs, and that diffusion down microfractures is minimized. Experiments under 'dry' and 'hydrothermal' conditions (Petrovic, 1974; Lin and Yund, 1972) appear to show that water makes no difference to volume diffusion rates of alkalis, but Foland (1974) suggests that molten-salt experiments are not necessarily 'dry' and that oxygen defects or the catalytic effect of an H_2O species cannot be excluded.

Whether water is at all important in the earliest stages of coherent exsolution is thus a moot point. However, as coarsening proceeds coherency is lost because dislocations are developed at lamellar interfaces. As Brown and Willaime (1974) point out, the activation energy for creation and migration of dislocations will be lowered if water is present and loss of coherency will be facilitated by presence of fluids. They illustrate the presence of relatively regular dislocations in a cryptoperthite using TEM.

The regularity of braid textures in many crystals (e.g. fig. 5A) suggests that water at grain boundaries had only a minimal role at this stage of exsolution, and that if water does affect coherent exsolution rates, then water included in the crystal and relatively homogeneously distributed must be invoked. There is some evidence (presented later) that coarseness of exsolution textures in some cryptoperthites and braid micropertthites increases with the degree of fractionation of the magma from which they form, and this might be accounted for by 'water-bearing' dislocations inherited at the stage of crystal growth. Alternatively it may represent subtle changes in An-content.

There is no doubt, however, that exsolution under two different regimes is shown by fig. 3, and also by fig. 7. In the latter case a Klokken feldspar (c. $Ab_{62}Or_{37}An_1$) has exsolved to a regular braid perthite (approximately as coarse as fig. 5), which then abruptly coarsens to irregular patch perthite around the margins and throughout the crystal at one end. The majority of other crystals in the section are coarse perthites, but this relic of braided texture is convincing evidence that all these crystals initially passed through a coherent exsolution stage. It is also indicative of a catastrophic loss of coherency as a result of fluid interactions, and the K-phase in the coarsely exsolved area is turbid while the braided relics are clear. It seems reasonable to deduce that this particular feldspar-fluid interaction took place substantially below the top of the coherent solvus, perhaps as low as $< 400^\circ C$. It is highly likely that the stage in cooling at which

fluids become active in facilitating loss of coherency (various paths are suggested on fig. 6) is a major factor in the evolution of diversity in appearance of micropertthites. It is certainly more important than cooling rate because closely adjacent lithologies in the same intrusive may have quite different perthite morphologies (e.g. fig. 5).

It is difficult to envisage the mechanism of this abrupt coarsening stage. The locus of the changes must depend on the mechanical condition of the crystal, and coarsening around margins is to be expected. A possible mechanism is that envisaged by O'Neill and Taylor (1967) in their series of experiments on simultaneous oxygen and alkali exchange. They suggested a series of minute solution-redeposition steps along an advancing fluid film. In the natural example the situation may differ because there is no evidence for a large overall compositional contrast (with respect to Na:K) between fluid and crystal (see earlier section), although such contrasts might exist on a local scale. Whatever the mechanism it must maintain or increase the degree of framework order, since feldspar-fluid interactions in rocks normally tend to increase Al-Si order (see later).

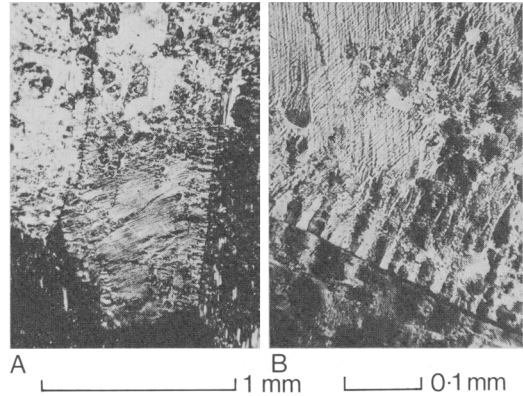


FIG. 7. Development of patch perthite from braid perthite (crossed nicols). A, crystal with relics of braid texture in rock (laminated syenite) in which most crystals show only patch perthite texture. B, detail of part of same crystal showing the relatively sudden coarsening of the exsolution around the braid perthite. Numerous small spherical inclusions can be seen in the coarsened areas, particularly at the braid-patch boundary. Away from the boundary the braided areas are inclusion-free.

Although sudden invasions of a rock mass by hot fluids could explain textures like figs. 3 and 7, it should be remembered that the solubility of the crystals and the properties of the fluids are changing with falling temperature. Synthetic feldspars crystallized in the presence of alkaline solutions give sharper X-ray diffraction patterns and faster

equilibration rates with respect to the strain-free solvus (Parsons, 1978). The effects of such fluids on ordering rates in albite change dramatically with falling temperature (Mason, 1977) as they become less molecular and more ionic in character. Lagache and Weisbrod (1977) have recently shown that the properties of alkali chloride solutions in equilibrium with two feldspars change with falling temperature. Changes of this type may have important roles to play in the textural evolution of natural feldspars.

Systematic variation in exsolution textures

Exsolution textures are difficult to describe in a satisfactory way and their diversity is enormous (see Smith, 1974, vol. 2). This stems partly from variations in bulk chemistry. Within the restricted compositional range of hypersolvus rocks one commonly valid generalization is that exsolution textures coarsen in parallel with indices of igneous fractionation. This is well shown in the Gardar province where several mineralogically well-understood intrusions range from larvikitic augite syenites to either alkali granite residua (e.g. Nunarssuit, Anderson, 1974; Klokken, Parsons, in preparation) or nepheline syenite residua (e.g. S. Qoroq, Stephenson, 1976; N. Qoroq, Chambers, 1976). Strongly alkaline pyroxenes or amphiboles normally coexist with coarsely exsolved microperthites, usually with readily seen albite and microcline-type twinning, while in the less-fractionated larvikitic syenites cryptoperthites are the common feldspar. Cooling rate is not the important control since large augite syenite plutons (e.g. the 20-km diameter Nunarssuit syenite) may contain crypto- and fine microperthite while minor, cross-cutting alkali granite residual members contain coarsely exsolved, highly ordered microperthites. In the Oslo province Oftedal (1948) notes that cryptoperthites are common in biotite, green amphibole, or augite-bearing nordmarkites, but that coarse microperthite predominates where aegirine and alkali amphibole are the mafic phases.

Two factors compete to control this relationship between perthite coarsening and igneous fractionation. In general An-content in hypersolvus alkali feldspars decreases with igneous fractionation and this is demonstrably the case in several Gardar plutons (e.g. fig. 2 and Stephenson, 1976). The ternary feldspars with the highest An-contents in these complexes are cryptoperthites except where specific localized interactions with fluids can be shown (e.g. fig. 3). The effect of Ca on exsolution rates has not been explored experimentally; at first sight one might expect that Ca would promote exsolution because of the steep rise with respect to

T of the ternary solvus tunnel (fig. 1) and because exsolution would begin at higher temperatures where diffusion is faster. Working against this is the need to break framework bonds to maintain charge balance as Ca diffuses. In coarse ternary intergrowths (fig. 3) microprobe analyses show that Ca follows Na; how precise this connection is in cryptoperthites is not so clear, but single crystal studies (see Smith, 1974, vol. 1) confirm that Ca is in the Na-rich phase. In this case the rate-limiting factor for exsolution may be Si and Al diffusion, known to be relatively slow (Sipling and Yund, 1974).

'Water' in magmas is generally believed to increase in amount with igneous fractionation, and the high temperatures implied for feldspar crystallization in larvikites, the presence of augite, fresh olivine, and high-temperature Fe-Ti oxide pairs (Parsons, in preparation) all imply that such magmas are comparatively 'dry' and water-under-saturated. In contrast the residual intrusive phases of such plutons may be amphibole-bearing, often drusy, alkali granite bodies and the parent melts are certainly relatively water-rich and also peralkaline (within the limitations imposed by low P_{total}) even if not water-saturated at the beginning of crystallization. Systematic perthite coarsening may therefore reflect water build-up, and when such systematic coarsening persists even when variations in An-content are small (e.g. the Klokken layered series, see Parsons, in preparation) it seems likely that fluids are the primary factor.

The idea that exsolution textures reflect build-up and retention of magmatic water is not new (e.g. Tuttle and Bowen, 1958) or restricted to feldspars. In their celebrated paper on the Fe-Ti oxide geothermometer, Buddington and Lindsley (1964, p. 324) pointed out that temperatures obtained departed most markedly from reasonable magmatic temperatures in rocks from magmas of increasing H_2O content, and stated, 'there is a possibility that H_2O has persisted in the subsolidus rock somewhat in proportion to its content in the magma and facilitated external granule "exsolution" at successively lower ranges of temperature. This is a problem for future study.'

Crystal boundaries

Related to exsolution textures, and providing additional evidence for the passage of fluids along grain boundaries, is the intricacy of feldspar-feldspar interfaces. Fig. 8A shows the boundaries between cryptoperthitic grains in a Klokken augite fayalite syenite; they are extraordinarily simple and regular, curiously unfamiliar when compared to boundaries in a typical subsolvus granite, as is the

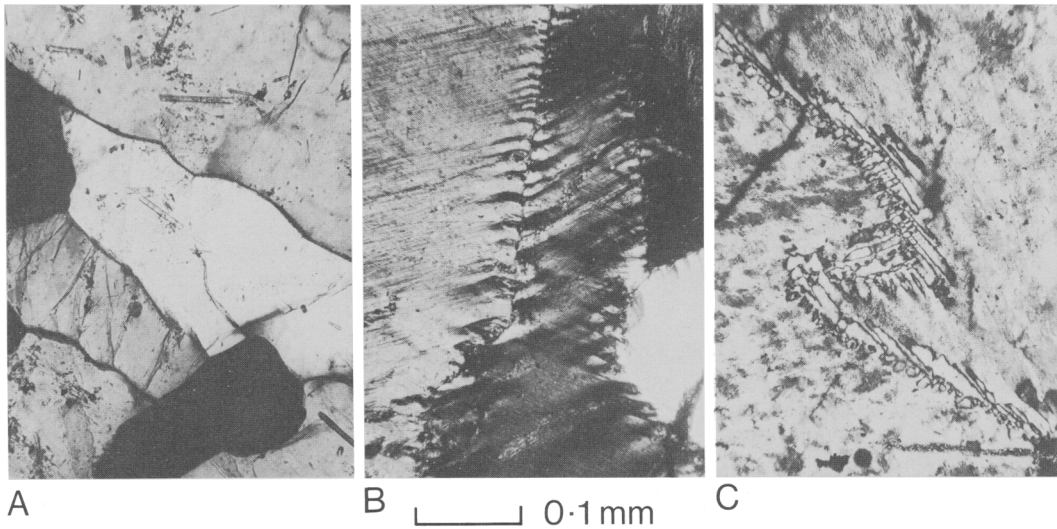


FIG. 8. Contrasting alkali-feldspar crystal boundaries in a series of fractionated syenites (crossed nicols). A, simple boundaries between cryptoperthite crystals, which are free of turbidity. Included prisms are apatite. B, pleated boundaries to braid micropertthite. C, sutured boundaries to patch micropertthites. Turbidity is visible in the K-rich phase. Increasing fractionation indicated by associated mafic phases is described in the text.

transparency of these completely inclusion-free feldspars. This is an example of a pristine plutonic igneous rock, as little affected by post-crystallization hydrothermal activity as one is likely to encounter. Fig. 8B is from an adjacent, chemically more fractionated, hedenbergite syenite; the feldspar is a braid micropertthite and crystal boundaries have a 'pleated' appearance. Fig. 8C is a boundary between coarse patchy micropertthites in a sodic hedenbergite syenite, extremely intricate and interlocking. Grain-boundary modifications of this type were discussed by Voll (1960) and Ramberg (1962). They may be extreme in mildly deformed rocks (e.g. the Loch Ailsh complex, Parsons, 1965), but are not in themselves indicative of deformation, which has certainly not occurred at Klokken. Bulk-chemical differences between these feldspars are negligible (fig. 3 and Parsons, in preparation), yet the exsolution textures and the crystal boundaries correlate perfectly with indices of magmatic fractionation (particularly well shown by the coexisting pyroxenes, Parsons, in preparation). The only reasonable explanation is that water built up in the fractionating magma, and was retained along crystal boundaries within the cooling units until temperatures fell below the coherent solvus, subsequently facilitating grain-boundary modifications.

Framework ordering

Generalized studies of feldspar framework ordering are more numerous than attempts to

generalize about perthites, presumably because data based on X-ray diffraction can be presented in a numerical form. In some coherent cryptoperthites it is not possible to characterize degree of framework order except by single-crystal means. There are great complexities: some cryptoperthites, for example, contain two sodium-rich phases in different twin relationships, with different structural states (Smith, 1974, vol. 1). In coarser, non-coherent perthites rock-to-rock variation in structural state is essentially restricted to the K-phase since the Na-rich phase is invariably low-albite. Structural-state variation in such K-feldspars can be tackled by powder X-ray diffraction. Early workers (e.g. Dietrich, 1962; Parsons and Boyd, 1971) concentrated on the monoclinic or triclinic nature of the feldspar ('orthoclase' or microcline—the reader should see Smith, 1974, for the tortuous history and present understanding of the former term). When triclinic the departure of the α and γ angles from 90° could be estimated, and quoted as 'obliquity' or 'triclinicity' by measuring the separation of certain pairs of reflections (e.g. $131-1\bar{3}1$; $130-1\bar{3}0$; $111-1\bar{1}1$), which form single reflections when the crystal is monoclinic. In perthitic feldspars from hypersolvus rocks (particularly coherent examples) most of these reflections are obscured by albite reflections (fig. 4) but the K-feldspar can be identified by looking for the 131 microcline peak at 29.5° (Cu-radiation) or the 131 reflection of orthoclase at 29.8° . Many feldspars contain both monoclinic and triclinic K-feldspar so

that the reflections are diffuse, and Parsons and Boyd (1971), in common with several other authors, devised a ranking scheme based on the relative intensities of the reflections for monoclinic and triclinic symmetry.

More recent studies have used cell dimensions refined by computer from powder diffraction data, and the variation is reported in terms of b and c cell dimensions and α^* and γ^* cell angles (Wright and Stewart, 1968). These studies appear to be more informative and less qualitative than older techniques, because Stewart and Ribbe (1969) have related the b - c cell dimensions to Al occupancy of T_1 sites and the $\alpha^*\gamma^*$ angles to Al distribution between T_1O and T_1m . (In high sanidine Al is equally distributed between T_2 and between T_1 sites, which are in pairs related by mirror symmetry. In microcline one T_1 site (T_1O) is favoured by Al and hence the mirror plane is lost.) Thus estimates of 'degree of order' in terms of Al distributions are now often quoted (e.g. Stewart and Wright, 1974). This straightforward interpretation of cell dimensions may be incorrect for intermediate K-feldspars with domain textures (Smith, 1974, vol. 1).

In a sense this attention to numerical estimates of 'degree of order' may tend to obscure the most important feature of K-feldspar variation in plutonic rocks. The computer will refine cell dimensions for a triclinic or monoclinic cell, but not both simultaneously, and it is the writer's experience (Parsons and Boyd, 1971) and also that of J. V. Smith (1974, vol. 1) that most plutonic rock samples contain both monoclinic and triclinic material (even on the scale of fragments suitable for single-crystal X-ray work). It is certainly essential to record the nature of symmetry-sensitive reflections before embarking on cell-dimension refinement (see also Wright and Stewart, 1968).

The reason I believe that this qualitative feature of the X-ray patterns should be stressed stems from the nature of the orthoclase \rightleftharpoons microcline transition itself. Both types of X-ray study lead to the same conclusion: on the basis only of symmetry, most plutonic rocks contain a monoclinic feldspar, a highly oblique microcline (near to maximum microcline), or mixtures of the two. The ' b - c plot' studies (Stewart and Wright, 1974) suggest a preponderance of highly oblique, highly ordered microcline (90 to 100% Al in T_1 sites) or less-ordered monoclinic feldspar (c. 80% Al in T_1 sites). Thus, once conditions are suitable for the formation of microcline, the process appears to lead direct to maximum microcline without the development of intermediate forms. As Smith (1974, vol. 1) explains, orthoclase appears monoclinic to X-rays because any regions it contains in which Al has a preference for one T_1 site over the other are small;

microcline is triclinic because Al prefers one site (T_1O) over large regions of structure—visible optically as microcline 'tartan' twinning. The step from monoclinic to triclinic, as it appears in rocks, is essentially a *coarsening process*, which requires substantial Al-Si diffusion if the left- or right-handed sense of small domains must be changed to allow their accommodation in larger domains. These ultimately emerge as albite and pericline twin individuals. In rocks, K-feldspars giving triclinic X-ray diffraction patterns nearly always reveal 'tartan' twinning under the microscope, although in hypersolvus rocks careful inspection of crystals in a number of orientations may be needed. In geological settings, as the coarsening barrier is overcome, any Al remaining in T_2 sites diffuses to T_1 and the final product is maximum microcline. Qualitative assessments of proportions of orthoclase or microcline in mixed samples are thus a measure of the success or otherwise of this coarsening process.

Phase-equilibrium studies on framework ordering

The difficulty of domain enlargement in a grossly monoclinic structure is probably the reason why microcline has not been synthesized. Studies of disordering of microcline (Sipling and Yund, 1974) under 'dry' conditions are not a reversal of ordering (Al seems to diffuse from T_1O sites into the other three sites at an equal rate), but they do demonstrate that pure volume diffusion of framework cations is extraordinarily slow at low temperatures. Under hydrothermal conditions microcline disorders by a solution-redeposition mechanism and Sipling and Yund (1974) state that an effect for water in volume Al-Si diffusion has not been demonstrated. Oxygen exchange experiments (Yund and Anderson, 1974) show that oxygen diffuses much faster under hydrothermal as against 'dry' conditions and considerably faster than any cation in the feldspar structure.

Most data on ordering in alkali feldspars comes from studies of albite, which is triclinic at all temperatures up to 980 °C and does not suffer the problem of overcoming domain textures. MacKenzie's (1957) work first showed that a continuum of 'supposed equilibrium forms' of albite could be made at different temperatures, and twenty years later his careful use of words has borne fruit because R. A. Mason (1977) has shown clearly that different suites of 'supposed equilibrium forms' can be made in different fluids. He has to conclude that the temperature range of the stable equilibrium forms of albite has not yet been established.

Mason's study, following earlier workers (Martin, 1969; Raase, 1971; Trembath, 1973;

Senderov, 1974), shows clearly the importance of the composition of the fluid on ordering rate in hydrothermal experiments. When NaOH and SiO₂ are present as well as H₂O and feldspar at the start of the experiment, ordering rates are much faster than with H₂O alone. Exactly why these, and other additional components, have their striking effects is not clear. The usually accepted mechanism for the interaction of water with the feldspar framework was put forward by Donnay, Wyart, and Sabatier (1959). They supposed that a proton, diffusing into the structure, would become attached to a framework oxygen, then the corner of an SiO₃OH tetrahedron, and that this would leave an adjacent tetrahedron incomplete giving space for escape of Si and Al ions. It is interesting that Mason's experiments show a strong dependence of ordering rate on pH of the solution (as measured at room *T* and *P*) and that alkaline solutions give the fastest rates. This perhaps suggests that OH⁻ incorporation during crystal growth is important, rather than diffusion of protons into the crystal during the ordering process. Quantitative interpretation of mechanisms is hindered, at the present time, by lack of knowledge of complexing in aqueous solutions at high *T-P*; the effect of different electrolytes on ordering rate disappears at *T* > 700 °C, as solutions become less ionic in character (e.g. Barnes and Ernst, 1963; Helgeson and Kirkham, 1976).

It is difficult to assess the relevance of effects due to solution composition and properties to the natural environment, particularly in view of the larger size of the natural crystals. It is easier to entertain the possibility of such interactions if one remembers that cleavages and the fluid inclusions that commonly accompany advancing exsolution in feldspars may make the effective grain size for diffusion very much smaller than the external crystal size. There is circumstantial evidence, in both igneous and metamorphic rocks, that fluid composition is important, discussed after the next section.

Two important questions remain virtually untouched by experimental studies. The relationship between Na:K ratio and equilibrium degree of order in alkali feldspars has not been properly explored, except in a simple study of ordering in potassian albites (Parsons, 1968). Unfortunately the data are even more difficult to interpret in the light of Mason's discoveries concerning the role of fluids. On the face of it, however, mixed Na-K feldspars probably have a lower equilibrium degree of order than the pure end-members at the same temperature, as suggested by Smith and MacKenzie (1961). A second unanswered question is whether crystals growing slowly in a plutonic environment may grow with an initial degree of order, or whether

they, like quickly grown synthetic crystals, always initially form as disordered phases. Perhaps the crystal-growing techniques pioneered by Lofgren (1974) may provide answers to this question.

Relationship between feldspar structural state and lithology

General studies of feldspar structural-state variation usually stress cooling rate, assessed from size and structural setting of the cooling rock mass, or annealing in a specific temperature range (e.g. Martin, 1974; Stewart and Wright, 1974). Parsons and Boyd (1971), and several others, have shown that in many igneous plutons there is a very close relationship between the development of microcline at the expense of orthoclase and the degree of fractionation of the host rock (as evidenced by its normative mineralogy and location in 'petrogeny's residua system'). This factor far outweighs any possible cooling-rate control, and the plutons considered (both hyper- and subsolvus) crystallized at a variety of temperatures. Fig. 9 brings up to date our 1971 repertoire of intrusions that show this regular behaviour, and extends it into the undersaturated portion of the residua system. For several of these complexes detailed microprobe studies of the mafic phases confirm most satisfactorily the progressive chemical evolution of each intrusion. In all these intrusions (and many others, see Parsons and Boyd, 1971), whether hyper- or subsolvus, over- or under-saturated, microcline evolves in place of orthoclase progressively as compositions corresponding to thermal minima are approached. In all the hyper-solvus intrusives perthitic intergrowths coarsen towards these minima. The writer is not aware of any intrusive that shows chemical variation consistent with progressive fractionation in which feldspars are *systematically* less coarsely exsolved and less well ordered in more fractionated members, although there are many examples of irregular relationships between rock chemistry and feldspar type.

We interpreted this relationship as a direct result of the acknowledged increase in magmatic water content with fractionation. The only proviso may be that, in hypersolvus rocks, An-content may modify exsolution rates, which will in turn inhibit ordering, so that two controls may be operating in parallel.

Not all feldspar workers have accepted this relationship. Martin (1974, p. 331) commenting on Parsons and Boyd (1971) says: 'The metastable persistence of orthoclase does not seem to be restricted to less fractionated members of igneous complexes. . . . We did not say that it was, and took care to point out that some intrusions do not show

regular patterns of feldspar variation. What we did say was that *when a regular variation* in feldspar type occurred, microcline rather than orthoclase was always found in the most fractionated members, never the reverse.

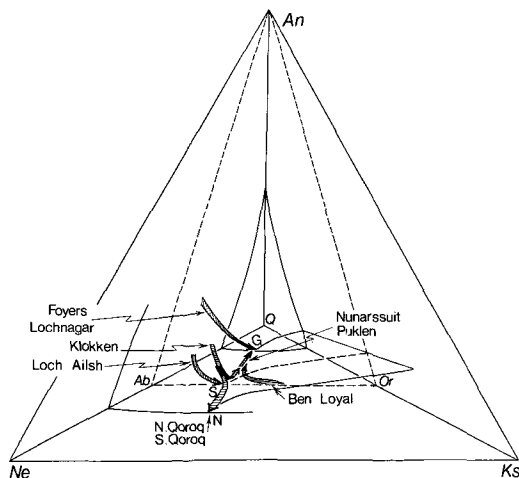


FIG. 9. Fractionation paths for a range of plutonic igneous complexes plotted in petrogeny's residua system $Ne-Ks-Q-An$. Foyers (Parsons and Boyd, 1971) and Lochnagar (McCormac, 1974) are Caledonian calc-alkaline granodiorite-granite plutons; Loch Ailsh (Parsons, 1965) is an unusually Na-rich Caledonian syenite plotting on the $Ab-Or-An$ plane, while Ben Loyal (Parsons and Boyd, 1971), of similar age, is more potassic and plots beneath the two-feldspar surface. Klokken is a small Gardar complex with minor oversaturated residua while Puklen (Parsons, 1972) and Nunarsuit (Anderson, 1974) are respectively small (4×2 km) and very large (45×20 km) syenite-alkali-granite complexes. N. and S. Qoroq (Chambers, 1976, and Stephenson, 1976) are each augite-syenite and nepheline syenite ring complexes. In each case maximum microcline becomes predominant over monoclinic K-feldspar in the direction of the arrows. G, S, and N are respectively the granite, syenite, and nepheline syenite minima.

It seems to the writer that the link between feldspar subsolidus evolution and magmatic evolution is so common as to be bordering on a truism. Hints of this relationship are found in much earlier petrographic work. We find, for example, in Johannsen, 1932, vol. 2, p. 145: 'In many cases, especially in two mica granites, *much less commonly* in granite or hornblende granite microcline accompanies orthoclase, or is intergrown with it, or is the only feldspar.'

Metastable preservation of orthoclase

Many workers have commented on the preservation of orthoclase in immense batholithic granites (e.g. the 160×100 km Wiborg rapakivi

complex, described by Vorm, 1971) and in regionally metamorphosed terrains (Guidotti, Herd, and Tuttle, 1973), where cooling rate has unquestionably been extremely slow. The Cornish granites (MacKenzie and Smith, 1962) and many Caledonian acid plutons (Parsons and Boyd, 1971; McCormac, 1974) contain orthoclase-bearing units. Stewart and Wright (1974, p. 369) interpret the common occurrence of orthoclase 'as a result of thermal buffering by crystal-melt equilibria, not because orthoclase has a more favourable Al/Si configuration'. Thus occurrence of orthoclase is explained by the thermal regime prevalent during termination of crystallization in subsolvus granitic rocks and inception of partial melting in regional metamorphism. Martin (1974) also favours prolonged annealing in the same thermal range, but explains the persistence of orthoclase as a result of his concept of 'ordered orthoclase'.

The fact that comparatively tiny, high-level hypersolvus plutons (e.g. Klokken, 4 km diameter; Puklen, 2 km diameter), which certainly crystallized at relatively high temperatures, contain microcline microperthites in the more fractionated, cross-cutting members, while less-fractionated members contain orthoclase, is surely convincing evidence that 'thermal buffering' is not an important control. Maximum microcline microperthite is not the rarity in small, non-orogenic complexes that Bonin and Martin (1974) imply: in the more-fractionated members it is the norm. Despite the high crystallization temperature and simultaneous cooling of rock units in such small intrusives into the stability field of microcline, the favoured forms of K-feldspar are none the less orthoclase or highly oblique microcline.

An alternative view is that orthoclase persists in plutonic rocks because, *in the cooling interval in which microcline becomes a stable phase*, fluids were not present to facilitate the process of domain coarsening. The persistence of orthoclase is a purely kinetic effect and when it persists (except, of course, in *very* small intrusives when cooling rate may be important) we have evidence that feldspars have not interacted with solutions in this particular and critical temperature interval, probably in the region of 400°C . Wright (1967) has estimated $375^\circ\text{C} \pm 50^\circ\text{C}$ as the upper temperature limit of maximum microcline, on the basis of its conversion to orthoclase in a contact metamorphic aureole. Feldspar-fluid interactions might take place at much lower temperatures, allowing oxygen exchange without disturbing Al-Si distributions (as demonstrated for microcline by Yund and Anderson, 1974), but it seems highly unlikely that under natural cooling rates, continuous feldspar-

fluid interactions could occur throughout this cooling interval without conditions being suitable for the development of microcline. The orthoclase configuration can be reached in the absence of fluids because it involves only localized diffusion of framework cations; the major reconstructions involved in subsequent domain enlargement require the presence of water.

It is possible that the composition of fluids, not merely their presence, is important. The role of fluid composition was stressed by Guidotti, Herd, and Tuttle (1973) who invoked the experimentally demonstrated inhibiting effect on ordering rate of high alumina in the fluid (Martin, 1969) to explain orthoclase persistence in high-grade migmatitic rocks. It is tempting to suggest that fluid composition is one reason for systematic feldspar diversity because increasing peralkalinity (molecular $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3$) is an essential accompaniment to fractionation in the syenite-alkali-granite and syenite-nepheline-syenite association, and peralkaline conditions are known experimentally to increase ordering rates.

Localization of fluids

A remarkable feature discussed by Parsons and Boyd (1971) and by several workers quoted therein is how sharply feldspar type is restricted to individual lithologies in composite plutons even when intrusive units are in contact. A most extreme example of this intimate association of contrasting feldspars is found in the Klokken syenite intrusion (Parsons, in preparation). In the layered series, forming the 2-km diameter core to this stock, there are two interleaved rock types (fig. 10). Sharply



FIG. 10. Upper section of the Klokken layered series. The pale bands are coarse, drusy, laminated syenite with turbid, coarsely exsolved feldspars. The dark horizons, with load-cast structures at the margins, and sometimes broken into pillows, are layers of less-fractionated granular syenite, with clear transparent cryptoperthitic or braid microperthitic feldspars. Figure for scale, centre, right.

bounded layers of a *granular syenite*, 0.1–30.0 m in thickness, alternate with coarser-grained *laminated syenite*. The granular layers are compact, sugary-textured rocks near the top of the intrusion, but coarsen downwards, while the laminated syenites are of essentially constant crystal size except where they exhibit pronounced mineral layering. The laminated syenites are conspicuously drusy rocks, the druses deforming the otherwise regular feldspar lamination. Where they are in contact with granular layers spectacular lobate load-cast structures form on the surfaces of the latter, and feldspathic material may extend upwards as veins or flame structures into the granular layers. Feldspars in these structures may be abnormally large, suggesting the accumulation of late magmatic fluids in them. These accumulations, and especially the druses, provide direct evidence for the development of a fluid phase at the end of crystallization in the laminated series.

Although feldspars in the two syenite types have similar bulk compositions (fig. 2), mafic mineralogy varies systematically showing continuous Fe-enrichment, pyroxenes in particular being sensitive indicators of fractionation (Parsons, in preparation). They show that the upper granular syenites are the least-fractionated rocks in the pile (ferroaugitic pyroxene), but they become more Fe-rich downwards (approaching hedenbergite). The enclosing laminated syenites are always more fractionated (hedenbergite-sodian-hedenbergite). Amphibole first appears in a downward progression through the granular series, which therefore show inverted cryptic and phase layering. Olivine (which also shows Fe-enrichment) is fresh in the granular syenites, but usually altered to iddingsite in the laminated series. A reasonable explanation for the structure of the intrusion seems to be that the granular layers represent roof chills of a body of fractionating syenitic magma, which fractionated by accumulation of crystals (largely feldspar), which formed the layered series. In the final stages of consolidation the chilled material sloughed off the roof of the magma chamber and settled on to the advancing cumulate syenite pile.

Whatever the correct interpretation of the structural relationships, the intimate association from magmatic temperatures of these two rock types, one more fractionated and richer in volatiles than the other, is not in question. Application of several mineral geothermometers and geobarometers (Parsons, in preparation) suggests crystallization of the whole series at $T > c. 850^\circ\text{C}$ and $P_{\text{H}_2\text{O}} < c. 1.1 \text{ kb}$. A suite of cross-cutting quartz-syenite aplites (hypersolvus, like all rocks in the intrusion) could have crystallized at lower temperatures $T \geq 690^\circ\text{C}$.

Feldspar variation shows the effects of post-magmatic fluids very clearly, and certainly indicates that these fluids were not able to circulate, willy-nilly, through the intrusion during cooling. The laminated layers are white in the field (fig. 10) and the feldspar has a silvery iridescence. The granular layers are darker in the field and on unweathered surfaces the feldspar is a clear grey-green, with a blue iridescence. In section the granular syenite feldspars are strikingly clear and free from inclusions or turbidity while the adjacent laminated syenite is, in patches, turbid. Feldspar crystal boundaries in the upper granular layers are beautifully simple (fig. 8A), but in lower layers they may become 'pleated' (fig. 8B). Crystal margins in laminated rocks are extremely intricate (fig. 8C). Feldspars in the upper granular layers are cryptoperthites (fig. 8A), at lower levels they are braid micropertthites (fig. 5A) and in laminated syenites they are often coarse patch perthites (fig. 5B) with only occasional relics of braided textures (fig. 7). Microcline twinning is visible, with care, in appropriately orientated thin sections. The cross-cutting quartz-syenite aplites contain coarse, lamellar perthites with obvious microcline-twinning. X-ray diffraction patterns (fig. 4) show progressive loss of coherency, and the progressive resolution of diffraction maxima for microcline. In all respects feldspar variation reflects the distribution of water in this pluton as it was imparted at the magmatic stage, and faithfully reflects progressive fractionation and concomitant build-up of magmatic water. Ilmenite-titanomagnetite intergrowths also change character in a similar way (Parsons, in preparation).

Fluids seem to have been very sharply localized in these contrasting rock units, and individual thin sections across granular-syenite-laminated-syenite contacts show a remarkable contrast in turbidity and exsolution textures. Apparently the compact texture of the granular layers made them unfavourable channels for hydrothermal fluids compared to the open-textured drusy laminated syenites, but the textural contrast between the lower and coarser granular syenites and the enclosing laminated syenite is relatively slight, and the failure of fluids to affect the feldspars in the former, even close to contacts, seems most remarkable.

We discussed several similar, although less extreme, examples of restriction of feldspar types up to contacts between intrusive units in an earlier paper (Parsons and Boyd, 1971). Being unwilling to visualize intergranular steam restricted in this way we suggested, vaguely (p. 310), that 'the metastable preservation of orthoclase in the early feldspars [enclosed as xenolithic bodies in microcline-bearing rocks] is due to structural features impressed upon them at the time of initial crystal

growth at magmatic temperatures' and that 'it is the amount of water or the peralkaline or peraluminous character of the magma that dictates the final product of slow cooling'. This idea may, with hindsight, have introduced an unnecessary complexity; apparently fluid activity can be extremely localized, as at Klokken. But it is worth while considering the possibility that crystals growing in a hydrous peralkaline melt may inherit structural imperfections (either as regular defects, incorporated OH^- , or gross liquid inclusions) different from those in dry, more basic liquids. Such inherent differences could go some way in accounting for the curious differences in behaviour of chemically similar feldspar crystals, subject to identical thermal histories. The demonstration of the prevalence of OH^- as a trace constituent of certain feldspars (Wilkins and Sabine, 1973) and the recent direct demonstration of significant amounts of hydrogen in quartz (Tsong, McLaren, and Hobbs, 1976), are food for thought in this respect.

Concluding statements

Exsolution in alkali feldspars may terminate when the phases are coherent intergrowths; the rate of coherent exsolution is probably not dependent on the presence of intergranular water. Loss of coherency, which may occur catastrophically, at any stage of coherent exsolution, or more gradually, as part of a general coarsening process, is strongly dependent on the presence of intergranular fluids and provides a simple petrographic tool for recognizing water-rock interactions at subsolvus temperatures. It is difficult to envisage how extensive oxygen exchange could occur below the strain-free solvus without loss of coherency, except perhaps at very low temperatures. Where incoherent perthitic intergrowths can be proved to have developed from regular coherent intergrowths, relatively low-temperature water-rock interactions are implied. The intricacy of feldspar-feldspar grain boundaries may also be a sensitive guide to the passage of water through rocks. In many hypersolvus intrusive complexes, exsolution textures coarsen with increasing fractionation of the host rock; falling bulk feldspar An-content and increasing magmatic water content are parallel controls of this relationship.

In many intrusive complexes, both hyper- and sub-solvus in type, there is a straightforward correlation between degree of fractionation of the host rock and the development of microcline at the expense of a monoclinic K-feldspar. This tendency is quite independent of the size of the intrusion (apart from the smallest, high-level intrusives) or the relative size of the units, and is not a function of

cooling rate or any specific thermal regime. It is best explained if water, or perhaps solutions of favourable composition, are necessary for the orthoclase-microcline transformation, which essentially requires the coarsening of a triclinic domain texture. Orthoclase persists in rocks that had 'dry' histories as they entered the thermal stability range of microcline.

Evolution of microcline in parallel with bulk chemical fractionation implies that post-magmatic fluids in many plutonic complexes follow a magmatic pattern of water build-up with increasing magmatic evolution, and that the fluids are retained within the lithological units in which they formed. The restriction of fluids to individual lithologies can sometimes be extraordinarily sharp; it is at least possible that structural details inherited at the time of crystal growth from the melt are involved. Plutons showing these regular 'magmatic' patterns of fluid distribution contrast strongly with those showing evidence of all-pervasive fluid circulation, suggested by stable-isotope studies. If rocks from every lithological unit in the former type of pluton have isotopic compositions suggesting interactions between the intrusion and meteoric waters, then the water must either have entered at the magmatic stage, or oxygen exchange must have occurred at very low temperatures ($< 300\text{ }^{\circ}\text{C}$?) and caused no rearrangement of cations. It is possible that intrusives showing ostensibly irregular patterns of feldspar variation, not related to bulk chemistry, are those that have interacted with external sources of water in the critical temperature range of unmixing and ordering. In this case it should be possible to correlate feldspar crystallographic features with scale of isotopic exchange.

Alkali feldspar exsolution textures and framework structural-state variation in plutonic rocks are not primarily controlled by specific thermal events or cooling rate. They record water-rock interactions; with better understanding of mechanisms and clearer definition of the thermal range in which changes occur, there seems every hope that quantitative interpretation of textures will be possible.

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