RENDICONTI DELLA SOCIETÀ ITALIANA DI MINERALOGIA E PETROLOGIA, 1988, Vol. 43-2, pp. 343-354

The K-feldspar mineralogy of granites and rhyolites: a generalized case of pseudomorphism of the magmatic phase

ROBERT F. MARTIN
Department of Geological Sciences, McGill University, 3450 University Street, Montréal, Québec, Canada H3A 2A7

ABSTRACT. — Felsic igneous rocks that preserve truly magmatic feldspars probably do not exist on Earth; what is found is a pseudomorphic assemblage. Rhyolites generally consist of sanidine cryptoperthite phenocrysts in which exsolution-related lamellae formed by spinodal decomposition. Where devitrified, the matrix likely consists of strain-free, more ordered alkali feldspars. Ion-exchange reactions may disturb original bulk compositions. In pristine hypersolvus rocks, exsolution and ordering have evolved from the sanidine cryptoperthite stage, but recrystallization is very localized, possibly owing to «hydrogen-hopping» to pry open tetrahedra and induce Al-Si ordering. Later introduction of water completes the ordering, coarsens the assemblage, and removes structural strain, but tell-tale domains of the precursor may remain. Subsolvus rocks probably do not go through a stage of coherent perthitic intergrowth; success of the orthoclase - microcline inversion depends on the availability of water, but also is affected by many other factors. The effective grain-size in coarse-grained, inversion-twinned microcline, on the scale of ten micrometers, explains its propensity to open-system behavior, which generally leads to isotopic disturbances and geochemical anomalies.

Key words: K-feldspar, Al-Si order, exsolution, hydrogen hopping, role of water.

With rare exceptions, granitic rocks are igneous in the sense that they crystallized at high temperatures from a magma. But is the mineralogy of fresh-looking granitic rocks still igneous? The answer is no, again with minor exceptions. In other words, granitic rocks contain a suite of felsic and mafic minerals that have re-equilibrated (partly or completely) with an aqueous fluid that circulated through the granite body as it contracted and cooled. These *in situ* recrystallization-type reactions may well leave the overall textural relationships among the felsic and mafic minerals intact, leading to the widely held belief that the fresh-looking minerals also are intact. This brief review focuses on the nature of the potassium-rich feldspar in felsic rocks, volcanic as well as plutonic, and explores some of the consequences of the fact that the observed K-feldspar, sanidine, orthoclase or microcline, is a pseudomorph of the magmatic phase, which was disordered sanidine or anorthoclase (or an assemblage of both) in the presence of the silicate melt.

Magmatic alkali-rich feldspar(s) in near-surface magmas

The distribution of tetrahedrally co-ordinated Al and Si exhibits long-range disorder in a felsic magma, by definition. The same applies to quenched samples of such magmas (e.g., glass in obsidian). Should such magmas be allowed to begin to crystallize prior to eruption, one could expect a single disordered alkali-rich feldspar (sanidine solid solution) to form near the liquidus. Vitrophyric quartz-feldspar porphyries, which are commonly encountered in areas of recent felsic volcanism, provide good examples of such interrupted hypersolvus crystallization.

Yet, the subsolidus modifications that are the subject of this paper can begin to take place within hours or days of eruption; investigations of the feldspar mineralogy of such vitrophyric porphyries generally indicate that the matrix has begun to devitrify, and the feldspar has begun to unmix and to order.

Are there examples in nature of «brutally» quenched systems? The answer is yes, but they are very rare. Unexsolved and disordered (Na, K)-feldspar occurs in partially fused granite xenoliths transported to the surface in melilite nephelinite lava in the volcano Nyiragongo, in eastern Zaire (LEHTINEN & SAHAMA, 1981). MOROGAN & MARTIN (1985) characterized the feldspar mineralogy of a suite of partially melted fenitized granitic rocks similarly transported to the surface in the natrocarbonatite lava at Oldoinyo Lengai volcano, Tanzania. Electron-microprobe data and refined cell parameters indicate that single-phase disordered anorthoclase and disordered sanidine ($2t_1$ 0.52-0.54; for maximum disorder, a $2t_1$ value of 0.50 is expected) both occur in this suite. Such low-calcium (Na, K)-feldspars are easy to synthesize, but are so reactive that they can only be expected in crustal xenoliths brought to the surface and quenched in a pyroclastic eruption.

O'BRIENT (1986) has described «an extraordinary example of arrested plutonic development» in a volcanic and shallow subvolcanic complex of calc-alkaline affinity in Rabb Park, New Mexico. In addition to rhyolite porphyry, O'BRIENT described sanidine granite, sanidine aplite, and sanidine pegmatite. The sanidine, which has begun to unmix in all cases (as revealed by a schiller phenomenon), coexists with oligoclase; average compositions of pairs considered to have formed at equilibrium give temperature estimates of 650-750°C. The average bulk composition of the sanidine in the pegmatitic facies is $Or_{55}Ab_{43}An_2$. KEEFER & BROWN (1978) found a cryptoperthite of bulk composition $Or_{51}Ab_{48}An_1$ from the same unit to consist of a largely coherent intergrowth of untwinned, monoclinic sanidine ($Or_{65}Ab_{35}$, $2t_1$ 0.56) and exsolved anorthoclase lamellae ($Or_{22}Ab_{78}$) up to 50 nm across, in which the extreme strain in the lattice precludes a calculation of the degree of Al-Si order. The compositions inferred by KEEFER and BROWN (1978) are consistent with attempted equilibration at 465 ± 20°C. This example is thus more evolved than the two cases from East Africa discussed above, but the extent of the changes are not so great that the original assemblage cannot be inferred closely.

The early stages of ordering and exsolution are generally considered to be diffusion-controlled. Cryptoperthitic intergrowths of sanidine and disordered albite form by spinodal decomposition, as the magmatic sanidine solid-solution «bypasses» the strain-free solvus and crosses the coherent solvus (path H, Fig. 1). The extent of coarsening of the lamellae in the cryptoperthite and of adjustments in their composition varies as a function of cooling rate. In a study of sanidine phenocrysts in a section of the Bishop Tuff, SNOW & YUND (1985) found a bulk composition of $Or_{66.4}Ab_{32.3}An_{1.3}$; as result of the cooling of this blanket of ignimbritic material, the single-phase sanidine unmixed to largely coherent lamellae of approximate composition Or_7 and Or_{77} (inferred compositions corrected for the influence of elastic strain due to coherence) as it crossed the coherent solvus, at approximately 475°C. The lamellar spacing ranges from 78 (top and bottom of the 60-m section) to 155 nm 43 m below the top. The degree of Al-Si order increased from a value $2t_1$ of 0.50 (maximum disorder) to 0.62 as a result of annealing in the ignimbritic deposit. SNOW & YUND (1985) did not mention whether or not these samples of rhyolitic ignimbrite still possess a glassy matrix. On the assumption that they do not, one must question the hypothesis that what went on within the sanidine crystal is entirely due to a diffusion-related process. Devitrification of the groundmass was accompanied by a significant development in secondary porosity (~ 8%) and permeability, thus increasing the possibility that hydrogen or water (or both) became involved in Al-Si ordering and, perhaps, unmixing in some way (see below). The involvement of hydrogen could explain why lamellar coarsening in sanidine from the Bishop Tuff seems to be much faster than the extrapolated rate from experimental data. Whereas the presence of water does not seem to affect the rate of diffusion of Na and K (e.g., HOKANSON & YUND, 1986), it is conceivable that a film of water in the feldspar grain or, on an even smaller scale, «hydrolytic weakening», can enhance the mobility of atoms by inducing local mobilization of (TO_4) groups. The extent of mobility at this stage clearly was restricted, however, in view of the persistence of 1) strain in the two structures that make up sanidine cryptoperthite, and 2)

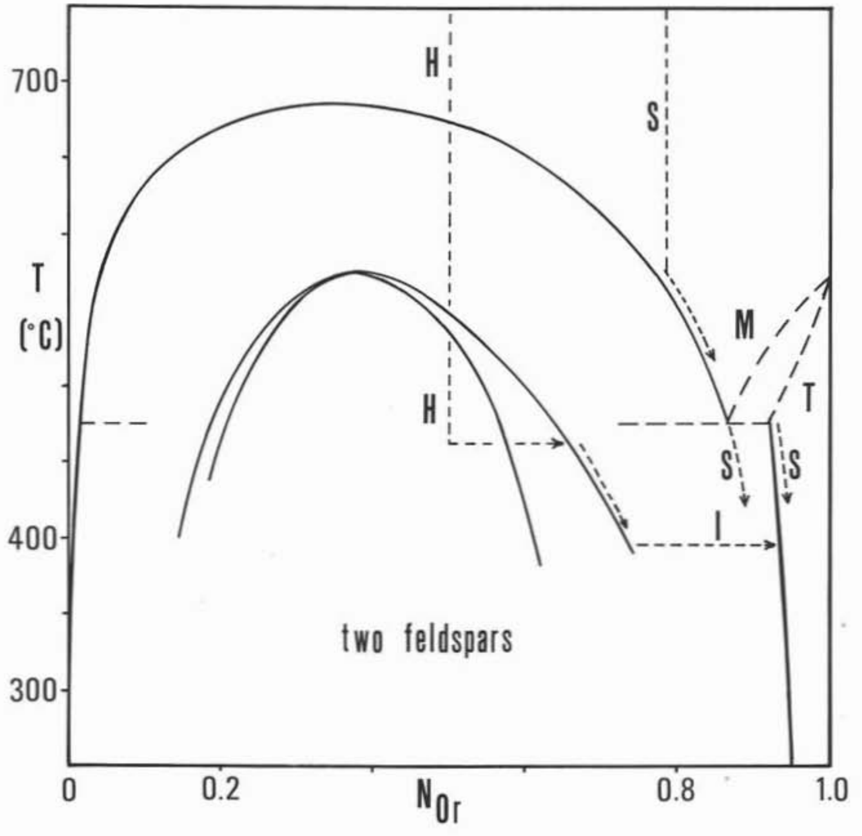

Fig. 1. — One interpretation of the subsolidus phase relationships in the system $NaAlSi_3O_8$ - $KAlSi_3O_8$ at low confining pressure. The strain-free solvus shows a discontinuity on the K-rich limb that reflects the first-order break expected between a relatively disordered monoclinic feldspar (M) and triclinic K-rich feldspar (T). A homogeneous (Na, K)-feldspar typical of a volcanic assemblage or a hypersolvus epizonal plutonic rock (i.e., bulk composition between $Ab_{70}Or_{30}$ and $Ab_{30}Or_{70}$; see text) may fail to nucleate exsolution lamellae upon crossing the strain-free solvus. As an example, $Ab_{50}Or_{50}$ will follow path H as it cools further as a metastable phase, and eventually will encounter the coherent solvus, with which is associated the coherent spinodal. Once across, such a homogeneous phase will undergo spinodal decomposition to a lamellar intergrowth of two strained, metastable feldspars whose final composition is defined by the two limbs of the coherent solvus at the closure temperature. A fluid phase, such as is expected to be released during the cooling of ignimbritic bodies (see text), will efficiently convert the metastable K-rich feldspar to a bulk composition on the strain-free solvus (path I). The more potassic bulk-composition of the primary K-feldspar expected to crystallize from a magma subject to subsolvus crystallization (subsolidus path S, $Ab_{22}Or_{78}$ chosen as an example) clearly precludes the same subsolidus path as in the first case. Here, two cases are possible: either the orthoclase will invert to coarsely albite- and pericline-twinned microcline, or it will be preserved metastably as «orthoclase», though M-twinned on a very fine scale (tweed texture) upon crossing the inversion. The strain-free solvus was determined experimentally by MARTIN (1974); the two-phase loop (dashed in) is consistent with the experimental data reported in that study. The coherent solvus and coherent spinodal are those of YUND (1984, Fig. 1), relevant to disordered structures at low confining pressures.

compositions consistent with attempted equilibration in the region 500-400°C (Fig. 1), rather than at a lower temperature.

Using as points of comparison the interlamellar spacing and the inferred degree of Al-Si order, the cryptoperthitic sanidine phenocrysts in the Bishop Tuff seem to be further removed from their starting point, a homogeneous disordered sanidine, than the material from the Rabb Park subvolcanic complex. In both cases, and others that show straight, coherent lamellae in bright-field transmission electron microscopy (e.g., HOKANSON & YUND, 1986, Fig. 1a), the evolution is to be considered a result of an isochemical process; within the boundaries of the original single crystal, the definition of a closed system must have been closely satisfied.

How widespread and representative is coherent sanidine cryptoperthite in the 150 km^3 of Bishop Tuff, to focus on one example? The mineralogical and geochemical study of HILDRETH (1979) and the TEM investigation of SNOW & YUND (1985) are based on samples that are relatively pristine. Does such a metastable phase persist in areas where hydrothermal circulation has been more active, and where vapor-phase deposits are prominent (e.g., SHERIDAN, 1970; FISHER & SCHMINCKE, 1984; chapter 8)? Follow-up investigations to characterize the microtexture and degree of Al-Si order of the feldspars in such areas will be required to investigate the nature of the transition from a magmatic to a hydrothermal assemblage of feldspar minerals. Also, how common is such cryptoperthite in Paleozoic or Precambrian volcanic complexes? One would expect that the older the volcanic suite, the greater the likelihood that it has been reheated regionally. Such a metamorphic overprint would effectively promote the transformation of the cryptoperthitic assemblage of strained K-rich and Na-rich feldspars into a strain-free, noncoherent pair of feldspars that may or may not preserve the original bulk composition.

In view of the complications of open-system behavior possible during the cooling of ignimbritic rocks and during subsequent metamorphic overprints, careful TEM and X-ray-diffraction investigations of the early stages of destruction of coherent cryptoperthitic intergrowths would seem to be most welcome at this point.

Cryptoperthitic sanidine in the context of open-system behavior in ignimbritic complexes

Felsic magmas that attain water saturation near the earth's surface erupt explosively. The resulting ash-flow tuffs contain magmatic water in two forms: 1) dissolved in glass (which makes up the bulk of the ignimbritic deposit), on account of the sluggish response of the system to decompression as the magma rose, and 2) in vesicles in the vitrophyric pumice lapilli, which represent «clasts» of vesiculating magma. As welding occurs deep in the interior of an ignimbritic cooling unit, the water that was trapped in vesicles is forced to the rim of the flattened pumice fragment. This water can then rise through the cooling unit, migrating down the temperature gradient. It can induce devitrification of glass, and will become saturated in a host of phases, including the feldspars, which may appear in vapor-phase deposits that are characteristic of the more vesicular upper parts of the cooling unit (e.g., SMITH, 1960; FISHER & SCHMINCKE, 1984). As the ignimbritic deposit cools, joints (typically columnar) form and provide meteoric water an access to the deep interior of the sheet. The front of devitrification can be thought of as migrating efficiently away from any crack; because of the attendant decreases in volume of the rock as it cools (due to thermal contraction) and as it devitrifies (owing to the more efficient packing in crystalline matter than in glass), the process is self-propagating, unless of course the deposition of the assemblage of hydrothermal minerals reduces the secondary porosity and seals the channelways.

In terms of feldspar mineralogy, one must question the fate of sanidine cryptoperthite in this setting. In view of the widespread availability of water, be it magmatic or meteoric or, more likely, a mixture, it seems clear that an assemblage of strained feldspars that constitute the phenocrysts in the ignimbrite will quickly be converted to discrete domains of strain-free Na- and K-rich feldspars that have the composition and degree of Al-Si order dictated by the thermodynamically stable assemblage of phases (path I, Fig. 1). As the groundmass resulted from devitrification induced by an aqueous fluid (i.e., no aqueous fluid, no devitrification), the Na-rich and K-rich feldspars in the felsitic groundmass most likely are strain-free, and also have the composition and degree of Al-Si order dictated by the thermodynamically stable assemblage at the time of formation. Of course, further cooling will typically lead to compositionally well-equilibrated, but structurally metastable, assemblages. In addition, younger orogenies can reheat an area regionally, leading to superimposed effects that can further modify an assemblage of feldspars texturally, compositionally (including isotopically) and structurally. The older the volcanic rock, the more likely are these younger modifications. A general rule of thumb predicts that the finer the grain size, the more likely is the assemblage to approach a fully equilibrated one, compositionally as well as structurally. In these settings, isochemical behavior is not to be expected. Preferential removal of the alkalis and oxygen isotopic exchange can be expected to lead to discrepant K/Ar ages in devitrified rhyolite (CERLING et al., 1985).

Detailed X-ray-diffraction studies of the feldspar mineralogy of older ignimbritic deposits are rare, in spite of the fact that mobility of economically important elements (e.g., U, Th, Pb, Zn) commonly accompanies the hydrothermal events that modified the feldspars. PAYETTE & MARTIN (1986) found that in a uraniferous high-fluorine rhyolitic ignimbrite at Harvey, in New Brunswick (eastern Canada), which was not later reheated, most samples contain orthoclase ($2t_1 = 0.88$; nomenclature of RIBBE 1983) and albite. Some samples, which presumably have interacted with water at a lower temperature, contain intermediate microcline and albite. However, the proportion of K-rich feldspar to albite has been disturbed by Na-for-K exchange. In two samples in which the exchange is extreme, the phenocrysts now consist of an albite pseudomorph of the original assemblage, whereas the matrix contains orthoclase and a mere trace of albite. Single-crystal studies (X-ray or electron diffraction) have yet to be carried out to confirm that all traces of coherence have been removed during recrystallization. However, the absence of anomalies in the *a* parameter of the orthoclase and intermediate microcline are consistent with this proposal.

A similar chemical and powder-diffraction investigation has been carried out on the feldspar mineralogy of ignimbritic rocks from the Early Proterozoic Upper Aillik Group, in eastern Labrador. The ignimbritic rhyolitic sequence, which locally is uranium-mineralized and metasomatized (WHITE & MARTIN, 1980), was folded and reheated during the Elsonian orogeny, then again, perhaps, by the Grenville orogeny, in view of the area's proximity to the Grenville Front. During the hydrothermal stage of evolution of the ignimbrites, there is evidence for the development of convection cells. This circulation led to rocks that contain albite + quartz in the high-temperature parts of the cell, others that contain low microcline + quartz in the low-temperature portions. There is still material in which the proportion of K and Na has remained more or less intact. Although slight departures from complete Al-Si order in the microcline (t_1O 0.91-0.93) are encountered in some samples, very well-ordered microcline is the norm. Cases of arrested (incomplete) conversion show that the matrix may be monomineralic (albite or microcline), whereas the phenocrysts may still contain a second feldspar of the original perthitic assemblage; this is a result of the rule of thumb stated earlier concerning the greater reactivity of the fine-grained assemblages. As a result of these metasomatic modifications in the alkali feldspar, the bulk composition of the metaignimbrites can vary widely in K/Na value. These modifications have relevance in mineral exploration, because the mobility of the alkalis is linked with that of uranium (WHITE & MARTIN, 1980).

Compared to the relatively pristine cases discussed earlier, the ignimbrites of Harvey show the effects of limited open-system behavior in the mineralogy of the alkali feldspar(s), whereas the Aillik suite generally illustrates a complete equilibration of the feldspar assemblage to relatively pure, well-ordered microcline that coexists with pure ordered albite. In the latter instance, the profound metasomatic changes associated with mineralization likely are imposed during the original cooling and devitrification of the ignimbritic sequence, the conversion of orthoclase + slightly disordered albite (like at Harvey) to microcline + albite may have occurred as a result of the Hudsonian and Grenvillian orogenies.

Magmatic assemblages in plutonic bodies?

Are chances of preserving the magmatic alkali feldspar better in plutonic bodies? Intuitively, one should expect the answer to this question to be no, in view of the much slower rate of cooling in a truly plutonic body. In fact, the true answer depends almost entirely on the importance of fluxes of hydrogen and water (be it magmatic or externally derived) during the cooling of the pluton. Some plutons, especially those resulting from the intrusion of relatively unevolved magmas, seem to have crystallized from relatively dry magmas, at least compared to those that reached saturation and that were emplaced as ignimbrites in a volcanic setting. The most detailed case-study, which focuses on the Precambrian Klokken syenite, in Greenland, is that of PARSONS (1978), BROWN et al., (1983), BROWN & PARSONS (1984a) and PARSONS & BROWN (1984). Many horizons of the layered body of hypersolvus syenite contain cryptoperthite featuring coherent lamellae of K- and Na-rich feldspars exsolved from a ternary solid-solution (bulk compositions generally close to $Or_{38}Ab_{59}An_3$: PARSONS, 1978). On the other hand, some horizons are pegmatitic, and presumably formed from a «wetter» batch of magma. The cryptoperthite grains in these horizons are traversed by whitened cracks along which there has been «catastrophic» loss of coherency and very striking coarsening of the perthitic intergrowth. PARSONS (1978) made the point that locally derived water played an essential role in the conversion of the relatively strained, coherently intergrown assemblage in the cryptoperthite to a coarser, noncoherent integrowth of turbid microcline + albite.

In intrusive complexes like the Klokken, the relative dryness of the magma dictates that at the subsolidus stage of the pluton's history, hydrothermal recrystallization will be localized, and will approach the isochemical case. Studies by transmission electron microscopy (BROWN et al., 1983; BROWN & PARSONS, 1984a, b; see also PARSONS & BROWN, 1984) illustrate clearly the sequence of steps followed in the perthitic assemblages of the Klokken syenite. The authors related these steps to the relatively simple microtextures of the orthoclase cryptoperthites from the pristine ignimbrites and felsic dyke-rocks mentioned earlier. Such strictly planar lamellae as in the orthoclase cryptoperthite were clearly a precursor stage, but are not preserved at Klokken. They have given way to «wavy» lamellae of low albite and diagonally associated microcline in a braid microperthite that can still be found preserved in domains in even the most turbid grains (the turbid parts contain the «catastrophically coarsened», patchy assemblage of low microcline and low albite, and were not investigated by the TEM approach). Surprisingly, the lamellar spacings measured perpendicular to b^* in the Klokken case are similar to those found in the more quickly quenched systems. Many factors may influence the kinetics of coarsening of the lamellae, as evaluated by the authors, not the least of which is the influence of the anorthite component (which is more important in the Klokken samples, and which may counteract the effects of longer time and presence of structurally sited water).

A review of available TEM data on the development of microtextures in cryptoperthitic alkali feldspar (BROWN & PARSONS, 1984b) clearly shows that the coverage of the Klokken pluton was unique then; not much has happened in the intervening years to change the situation. Much more TEM work will be required on geologically well-understood felsic complexes to test the sequence of development of microtextures proposed (BROWN & PARSONS, 1984a, Fig. 8). Even in ancient igneous complexes containing coarsely perthitic alkali feldspar, vestiges of the early stages of the feldspar's history may well be preserved locally. However, the very fine scale and apparently high degree of structural coherency of cryptoperthitic intergrowths make a TEM approach mandatory.

A possible role for H^+ in the ordering reaction in cryptoperthite

In a summary of their findings concerning the nature of the K-feldspar to be expected in cryptoperthite, BROWN & PARSONS (1984b) pointed out the general lack of dislocations and other signs of structural strain at the interfaces. They appealed to the minimization of coherent elastic energy and to interface orientation as the factors that determine whether the K-rich member of the association will be orthoclase, so-called «high microcline», or low microcline. They viewed the ordering reaction of the K-rich phase as due to the diffusion of Al and Si. Most authors have viewed this phase transformation, which occurs at a temperature below 500°C, to be truly reconstructive, and *therefore* to involve the hydrogen ion, clearly required to «pry open» the *T* - O - *T* linkages (e.g., DONNAY et al., 1959). Al and Si simply do not diffuse through crystal structures like Na, K and O do; they are mobilized as tetrahedral complexes [$T(OH)_4$, perhaps]. Furthermore, at temperatures in the stability field of low microcline, perhaps closer to 400°C than 500°C, can true intracrystalline diffusion be sufficiently effective that some domains a hundred or more nanometers across grow at the expense of others, especially in the context of a cooling epizonal pluton?

GOLDSMITH (1986, 1987, 1988) demonstrated in high-P (15-20 kbars), «essentially dry» experiments that changes in degree of Al-Si order take place orders of magnitude faster than at low pressures in the presence of water. He deduced that hydrogen, a very mobile species formed by dissociation of water in the solid pressure-transmitting medium surrounding the encapsulated sample, diffused into the sample holder in the piston-cylinder assembly (molecules of water could not have diffused through the noble-metal capsule). The dissociation constant of water is known to increase with increasing confining pressure, such that the phenomenon of «hydrogen hopping» can lead to measurable mobilization of TO_4 groups in the relatively short duration of Goldsmith's experiments (maximum 44 days). Dissociation of magmatic water in the Klokken complex, although inherently not as efficient as at high pressures, could have catalyzed the *in situ* conversion of a disordered monoclinic (Na, K)-feldspar to microcline in an as-yet poorly understood way distinct from solution and redeposition, the steps that occur in the presence of molecular water. The proposed role of hydrogen, which would permeate the feldspar structure with ease, may account for the scarcity of dislocations in the strained assemblages, as noted by BROWN & PARSONS (1984b), and for enhanced changes in degree of Al-Si order while a feldspar is being deformed (YUND & TULLIS, 1980). Although alkali feldspar is nominally anhydrous, detailed spectroscopic investigations (e.g., HOFMEISTER & ROSSMAN, 1985) do prove the presence of structurally sited OH and H_2O at ppm-type levels. As the H^+ would be repeatedly consumed and released, the absolute concentrations of hydrogen required in this closed-system ordering would be comparably small.

The influx of water in hypersolvus rocks

As the strained, very finely perthitic magmatic feldspar cools, it will contract. Cleavages become prominent at this stage, because thermal contraction is highly anisotropic. On a larger scale, the network of cooling joints in the igneous body allows the entry of water (recirculated magmatic water, meteoric water, or a mixture), which contributes to a more rapid cooling than by mere conduction. The water propagates to the interior of the crystals *via* the cleavage planes, and reacts with the strained assemblage, producing what PARSONS (1978) called «catastrophic coarsening» of the perthitic texture. At this stage, the K-rich feldspar becomes turbid, as a result of a dusting of finely crystalline pigments deposited on the walls of fluid inclusions (FOLK, 1955) and microfissures. A very common pigment in the vacuoles is hematite; its presence can be confirmed by electron-microprobe analysis (e.g., LALONDE & MARTIN, 1983). In a near-surface body, hematite pigmentation may well reflect the overall loss of hydrogen or influx of oxygen (or both) from outside the pluton. The pink coloration and «catastrophic coarsening» of the perthitic texture are commonly accompanied by an increase in the degree of Al-Si order and the removal of strain in the intergrowth. The new perthitic assemblage consists of strain-free K-rich feldspar (orthoclase, intermediate microcline, low microcline, or a mixture), usually in a highly modified exsolution texture. TAYLOR & FORESTER (1971) and FORESTER & TAYLOR (1977) have demonstrated that in the dominantly hypersolvus granites of the Scottish Tertiary complexes, the inception of turbidity is accompanied by exchange of oxygen in the feldspar structure with that in the fluid phase. Where the fluid is of meteoric origin, the $\delta^{18}O$ value of the recrystallized K-rich feldspar may be significantly reduced from its magmatic value, but where the fluid phase is of magmatic derivation, the $\delta^{18}O$ will be affected only in a very subtle way. It should be clear to the reader, however, that if solution and redeposition have occurred, not only the eight oxygen atoms (out of thirteen in a formula unit) have exchanged with the fluid, but all thirteen must have. In other words, Na and K, and, by implication, Rb, Sr, Ar, Ca, Ba, Sr and Pb, may well have been involved in the exchange. Part of the iron that forms the hematite pigment in the ubiquitous pink granites may have been rejected from the structure of the high-temperature feldspar upon its recrystallization, but it is clear that some of the iron is contributed from adjacent mafic phases, which generally are oxidized and altered in such isotopically disturbed granites (TAYLOR & FORESTER, 1971; FERRY, 1985).

The K-feldspar in subsolvus granitic rocks

Unlike hypersolvus rocks, in which the bulk composition of the magmatic feldspar generally falls between $Or_{30}Ab_{70}$ and $Or_{70}Ab_{30}$, and whose evolution was discussed in the previous section, subsolvus granitic rocks contain two primary feldspars, sodic plagioclase and a K-rich feldspar. The latter probably first formed as a disordered, monoclinic phase in the case of most magmas, but the reader should be aware of the existence of fluorine-rich leucogranitic melts whose solidus is so low that crystallization of primary microcline becomes a possibility. For example, WEBSTER et al. (1987) reported a solidus of 500°C for the felsic magma that was emplaced at Spor Mountain, Utah (1.2 wt.% F). Leucogranitic magmas with more than twice the amount of fluorine do exist, such that an even lower solidus could perhaps be expected in those rare instances. A detailed investigation of the feldspar mineralogy of such complexes has yet to be undertaken.

BROWN & PARSONS (1984b) proposed that for an Or-rich primary feldspar typical of a subsolvus granite, orthoclase is expected. TEM investigations show the M-type array of finely twinned domains, characteristically arranged in a «tweed texture» (EGGLETON & BUSECK, 1980; FITZ GERALD & MCLAREN, 1982). Exsolved albite is usually present, but is invariably less prominent than in the hypersolvus case because of the richness of the original bulk composition in potassium. Also, and for the same reason, exsolution is expected to occur at a lower temperature than in the hypersolvus case. The tweed texture forms as the orthoclase crosses into the field of stability of microcline, below 500°C. The very sluggish kinetics of the ripening of this texture prevent its efficient recrystallization to coarsely twinned low microcline in many plutonic rocks, even of Archean age. In fact, the persistence of orthoclase in a plutonic body can be taken as an indication that the area in question escaped deformation, regional reheating and circulation of an aqueous fluid since the pluton cooled. These factors would have induced the conversion of orthoclase to low microcline. The persistence of orthoclase or intermediate microcline provides an indication that the rocks probably have behaved as a closed system since the original cooling; as a result, geochronological work based on Rb-Sr and K-Ar systems probably will be closely concordant with results of U-Pb dating using zircon.

In the micro- to macroperthitic texture typical of more coarsely twinned low microcline from subsolvus granites and pegmatites, the width of the albite lamellae may exceed 1 mm, and the presence of the polysynthetic twins in these lamellae may even be visible in a hand specimen, as in perthite from the type locality, Perth, Ontario. The boundary zones between albite and microcline domains generally are considered noncoherent in such coarse intergrowths; the cell parameters of the two feldspars show no evidence of strain. Did such coarse perthite go through a coherent cryptoperthitic stage? Or was cooling so slow that nucleation did occur upon crossing of the K-limb of the strain-free solvus (path S, Fig. 1)? If so, what was the role of water in this nucleation step and in the coarsening, so as to enhance (and, apparently, overtake) the diffusional process? These challenging questions, stated by YUND (1984), may not have unique answers; furthermore, an experimental approach cannot be used to provide answers. As an illustration, the interlamellar spacing expected by intracrystalline diffusion after 10,000 years, as extrapolated from laboratory results on cryptoperthite initially held at 570°C, is «only» 4600 Å at 300°C (cooling rate 0.0001°C/day, initial spacing 349 Å)!

It seems clear that to get an interlamellar spacing orders of magnitude greater, water must be involved. If this reasoning is sound, then petrologists and geochemists must address the next level of obvious questions: what of the original chemistry of the feldspar has survived intact? An isochemical case-history in the context of a process involving solution and redeposition, probably repeated, would seem to involve special pleading. Was the water in isotopic equilibrium with the feldspar? In view of the relative reactivity of the alkali feldspar among the rock-forming minerals, its oxygen isotope geochemistry cannot be expected to have survived unmodified, as mentioned earlier.

What about the argon content of orthoclase or microcline? Why are the conventional K-Ar ages they define commonly aberrant? HARRISON & MCDOUGALL (1982) showed that three microcline separates from a Cretaceous granitic batholith in New Zealand (age of emplacement: 114 Ma) yield plateau ages of 103, 99 and 93 Ma for the last 35% of ^{39}Ar released, which are consistent with a closure temperature of approximately 130°C. The first 65% of the ^{39}Ar released define a linear increase in age from 80 Ma to the above values, and represent a temperature interval over which an accumulation of radiogenic ^{40}Ar took place, below 100°C. The inferred diffusion gradients show that the microcline grains continued to respond to their environment at these low subsolidus temperatures. ZEITLER & FITZ GERALD (1986) and ZEITLER (1987) showed that K-rich feldspar concentrates than have a saddle-shaped age spectrum have incorporated excess ^{40}Ar near the grain margins at low temperatures. A TEM examination of two samples shows that noncoherent and semicoherent interfaces and dislocations serve to greatly reduce the effective size of grains, to create a large range in grain sizes, and to allow fast «diffusion» to occur along these pathways. Their analysis assumes that diffusion in fact is the dominant process to explain the mobility of argon isotopes; an alternative is that a fluid medium is a contributing factor, just as it seems to be in the coarsening of the exsolution texture (i.e., the mobility of Na and K). The movement of the excess ^{40}Ar component is efficient under water pressure, but negligible when the samples are heated dry (ZEITLER, 1987). This may indicate that water is (and was) directly involved in the migration, rather than hint at the structural siting of the excess argon, in anionic positions. The sanidine sample examined by Zeitler, from an ignimbrite, presumably is much more retentive of its argon because of the presence of continuous, coherent, and tightly spaced lamellae of K-rich and Na-rich feldspar. It seems clear that a thorough characterization of feldspar populations selected for investigation by stepwise $^{40}Ar/^{39}Ar$ analysis (X-ray or electron diffraction, transmission electron microscopy) will be required to fully model the behavior of argon entrapment and later release.

FITZGERALD & MCLAREN (1982) and MCLAREN (1984) described a bewildering array of microtextures in microcline from granites and pegmatites, and related these to observations made by optical microscopy. They showed that the cross-hatched pattern of twin-related domains is indeed due to sets of albite and pericline twin lamellae that were formed at the time of inversion from monoclinic to triclinic symmetry, close to 400°C. Lower-temperature recrystallization, presumably promoted by a fluid medium, preferentially replaces the pericline twin lamellae by a much finer set of serrated albite twins. This step greatly increases the interface boundaries and discontinuities and provides possible channelways for «fast diffusion» of water and various solutes like argon. The eventual disappearance of pericline twin lamellae in microcline would seem to provide a means to «rank» different samples of low microcline in an evolutionary sequence.

Much has been written concerning scatter in Rb-Sr isochrons. Although a thorough review is beyond the scope of this essay and may be very difficult for want of pertinent data, there probably is a close relationship between degree of Al-Si order in the K-rich feldspar (the main Rb-bearing phase in a granite), the microtexture defined by twinned domains, and the spacing of its exsolution lamellae on the one hand, and open-system behavior leading to scatter about an isochron or to an anomalously young age on the other. The clearest evidence of the great mobility of ^{87}Sr in K-feldspar comes from studies of rubidium-enriched, geologically evolved granitic pegmatites (e.g., CLARK & ČERNÝ, 1987). Attempts to correct the total Sr content of Rb-rich microcline for radiogenic ^{87}Sr commonly result in negative concentrations of Sr! Even in plutonic rocks that are not so extremely enriched in Rb, open-system behavior involving Rb and ^{87}Sr is widespread and subtle. It is very common to find a 200-Ma (or more) discrepancy between an Archean Rb-Sr age and a well-constrained U-Pb age determination using abraded zircon grains. The problem of resetting of the Rb-Sr system is particularly severe in orogenic belts subjected to episodic regional reheating (e.g., EASTON, 1986). The susceptibility of a plutonic suite to this type of resetting likely is a function of the «porosity» of the K-feldspar, which results from the density of noncoherent internal boundaries associated with twinned domains, and lamellae and patches of albite.

Concluding remarks

In a benchmark contribution on the mineralogical distinctions between volcanic and plutonic felsic rocks, TUTTLE (1952) concluded that the feldspars found in plutonic rocks «show much evidence of change from an initial character identical with the corresponding minerals of the extrusive equivalents». The intervening years have seen major advances in the characterization of these changes, firstly by X-ray-diffraction and electron-microprobe analyses, and more recently by transmission electron microscopy.

STEWART & WRIGHT (1974) reviewed the occurrence of sanidine, orthoclase and microcline in common igneous and metamorphic rocks. They stressed that there is not a unique path of Al-Si ordering in K-rich feldspars, and that natural assemblages seem most consistent with a continuous transformation between sanidine and orthoclase, then a discontinuous transformation between orthoclase and microcline. The occurrence of domains of tweed-textured orthoclase within microcline (FITZ GERALD & MCLAREN, 1982; ZEITLER & FITZ GERALD, 1986) is consistent with the discontinuity between orthoclase and microcline. If the transformation did not involve major recrystallization needed to coarsen the twin-related domains and to increase the degree of long-range order involving Al and Si, such metastable remnants would not be expected to occur. The easy diffusion of the hydrogen ion through crystalline matter may explain the very local, *in situ* early Al-Si ordering that occurs in cryptoperthite. An Archean pluton that crystallized from a relatively dry magma and that has not been subjected to later deformation and (hydro)thermal disturbances should still contain such cryptoperthitic alkali feldspar. The recrystallization of such fine intergrowths to micro- and macroperthite involves the influx of water. Even with an available source of water, the transformation is difficult, and in many cases, a cooling epizonal granite ends up with orthoclase microperthite or intermediate microcline microperthite (or a mixture of orthoclase + intermediate microcline + albite). The appearance of low microcline in such epizonal complexes may have to await an episode of local or regional reheating. Of course, the transformation is much more likely to go to completion in mesozonal and catazonal complexes. Broad generalizations are difficult, as bulk composition of the parent feldspar, that of the host rock, overall grain-size, effective grain-size, thermal history, deformation-related external stresses, fugacity of hydrogen, and pore-fluid composition will all exert an influence of the magmatic product to yield the observed pseudomorphic assemblage in a rhyolitic or granitic rock. Open-system behavior in K-rich feldspar introduces a serious «can of worms» that has to be properly evaluated in investigations of igneous petrogenesis and radiometric dating.

Acknowledgements. — I am very grateful for the invitation to participate in the SIMP conference on Granites and their Surroundings. Research costs are defrayed by an operating grant (A7721) from the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

BROWN W.L., BECKER S.M., PARSONS I. (1983) - *Cryptoperthites and cooling rate in a layered syenite pluton: a chemical and TEM study*. Contr. Mineral. Petrology, 82, 13-25.

BROWN W.L., PARSONS I. (1984a) - *Exsolution and coarsening mechanisms and kinetics in an ordered cryptoperthite series*. Contr. Mineral. Petrology, 86, 3-18.

BROWN W.L., PARSONS I. (1984b) - *The nature of potassium feldspar, exsolution microtextures and development of dislocations as a function of composition in perthitic alkali feldspars*. Contr. Mineral. Petrology, 86, 335-341.

CERLING T.E., BROWN F.H., BOWMAN J.R. (1985) - *Low-temperature alteration of volcanic glass: hydration, Na, K, ^{18}O and Ar mobility*. Chem. Geol. (Isotope Geosci. Sect.), 52, 281-293.

CLARK G.S., ČERNÝ P. (1987) - *Radiogenic ^{87}Sr, its mobility, and the interpretation of Rb-Sr fractionation trends in rare-element granitic pegmatites*. Geochim. Cosmochim. Acta, 51, 1011-1018.

DONNAY G., WYART J., SABATIER G. (1959) - *Structural mechanism of thermal and compositional transformations in silicates*. Z. Krist., 112, 161-169.

EASTON R.M. (1986) - *Geochronology of the Grenville Province*. In: The Grenville Province (J.M. Moore, A. Davidson & A.J. Baer, eds.). Geol. Assoc. Can., Spec. Pap., 31, 127-173.

EGGLETON R.A., BUSECK P.R. (1980) - *The orthoclase - microcline inversion: a high resolution transmission electron microscope study and strain analysis*. Contr. Mineral. Petrology, 74, 123-133.

FERRY J.M. (1985) - *Hydrothermal alteration of Tertiary igneous rocks from the Isle of Skye, northwest Scotland. II. Granites*. Contr. Mineral. Petrology, 91, 283-304.

FISHER R.V., SCHMINCKE H.U. (1984) - *Pyroclastic Rocks*. Springer-Verlag, Berlin.

FITZ GERALD J.D., MCLAREN A.C. (1982) - *The microstructures of microcline from some granitic rocks and pegmatites*. Contr. Mineral. Petrology, 80, 219-229.

FOLK R.L. (1955) - *Note on the significance of «turbid» feldspars*. Amer. Mineral., 40, 356-357.

FORESTER R.W., TAYLOR H.P. JR. (1977) - *$^{18}O/^{16}O$, D/H, $^{13}C/^{12}C$ studies of the Tertiary igneous complex of Skye, Scotland*. Amer. J. Sci., 277, 136-177.

GOLDSMITH J. (1986) - *The role of hydrogen in promoting Al-Si interdiffusion in albite ($NaAlSi_3O_8$) at high pressures*. Earth Planet. Sci. Lett., 80, 135-138.

GOLDSMITH J. (1987) - *Al/Si interdiffusion in albite: effect of pressure and the role of hydrogen*. Contr. Mineral. Petrology, 95, 311-321.

GOLDSMITH J. (1988) - *Enhanced Al/Si diffusion in $KAlSi_3O_8$ at high pressures: the effect of hydrogen*. J. Geol., 96, 109-124.

HARRISON T.M., MCDOUGALL I. (1982) - *The thermal significance of potassium feldspar K-Ar ages inferred from $^{40}Ar/^{39}Ar$ age spectrum results*. Geochim. Cosmochim. Acta, 46, 1811-1820.

HILDRETH W. (1979) - *The Bishop Tuff: evidence for the origin of compositional zonation in silicic magma chambers*. In: Ash-Flow Tuffs (C.E. Chapin & W.E. Elston, eds.). Geol. Soc. Amer., Spec. Pap., 180, 43-75.

HOFMEISTER A.M., ROSSMAN G.R. (1985) - *A spectroscopic study of irradiation coloring of amazonite: structurally hydrous, Pb-bearing feldspar*. Amer. Mineral., 70, 794-804.

HOKANSON S.A., YUND R.A. (1986) - *Comparison of alkali interdiffusion rates for cryptoperthites*. Amer. Mineral., 71, 1409-1414.

KEEFER K.D., BROWN G.E. (1978) - *Crystal structures and compositions of sanidine and high albite in cryptoperthitic intergrowth*. Amer. Mineral., 63, 1264-1273.

LALONDE A.E., MARTIN R.F. (1983) - *The Baie-des-Moutons syenite complex, La Tabatière, Québec. I. Petrography and feldspar mineralogy*. Can. Mineral., 21, 65-79.

LEHTINEN M., SAHAMA T.G. (1981) - *A note on the feldspars in the granite xenoliths of the Nyiragongo magma*. Bull. Volcanologique, 44, 451-454.

MARTIN R.F. (1974) - *The alkali feldspar solvus: the case for a first-order break on the K-limb*. Soc. Franç. Minéral. Crist. Bull., 97, 346-355.

MCLAREN A.C. (1984) - *Transmission electron microscope investigations of the microstructures of microclines*. In Feldspars and Feldspathoids (W.L. Brown, ed.). D. Reidel, Dordrecht, Holland (p. 373-409).

MOROGAN V., MARTIN R.F. (1985) - *Mineralogy and partial melting of fenitized crustal xenoliths in the Oldoinyo Lengai carbonatitic volcano, Tanzania*. Amer. Mineral., 70, 1114-1126.

O'BRIENT J.D. (1986) - *Preservation of primary magmatic features in subvolcanic pegmatites, aplites, and granite from Rabb Park, New Mexico*. Amer. Mineral., 71, 608-624.

PARSONS I. (1978) - *Feldspars and fluids in cooling plutons*. Mineral. Mag., 42, 1-17.

PARSONS I., BROWN W.L. (1984) - *Feldspars and the thermal history of igneous rocks*. In: Feldspars and Feldspathoids (W.L. Brown, ed.). D. Reidel, Dordrecht, Holland (p. 317-371).

PAYETTE C., MARTIN R.F. (1986) - *The Harvey volcanic suite, New Brunswick. II. Postmagmatic adjustments in the mineralogy and bulk composition of a high-fluorine rhyolite*. Can. Mineral., 24, 571-584.

RIBBE P.H. (1983) - *Chemistry, structure and nomenclature of feldspars*. In: Feldspar Mineralogy (2nd edition, P.H. Ribbe, ed.). Mineral. Soc. Amer., Rev. Mineral., 2, 1-19.

SHERIDAN M.F. (1970) - *Fumarolic mounds and ridges of the Bishop Tuff, California*. Geol. Soc. Amer. Bull., 81, 851-868.

SMITH R.L. (1960) - *Ash flows*. Geol. Soc. Amer. Bull., 71, 795-842.

SNOW E., YUND R.A. (1985) - *Thermal history of a Bishop Tuff section as determined from the width of cryptoperthite lamellae*. Geology, 13, 50-53.

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

TAYLOR H.P. JR., FORESTER R.W. (1971) - *Low-^{18}O igneous rocks from the intrusive complexes of Skye, Mull, and Ardnamurchan, western Scotland*. J. Petrology, 12, 465-497.

TUTTLE O.F. (1952) - *Origin of the contrasting mineralogy of extrusive and plutonic salic rocks*. J. Geol., 60, 107-124.

WEBSTER J.D, HOLLOWAY J.R., HERVIG R.L. (1987) - *Phase equilibria of a Be, U and F-enriched vitrophyre from Spor Mountain, Utah*. Geochim. Cosmochim. Acta, 51, 389-402.

WHITE M.V.W., MARTIN R.F. (1980) - *The metasomatic changes that accompany uranium mineralization in the nonorogenic rhyolites of the Upper Aillik Group, Labrador*. Can. Mineral., 18, 459-479.

YUND R.A. (1984) - *Alkali feldspar exsolution; kinetics and dependence on alkali interdiffusion*. In Feldspars and Feldspathoids (W.L. Brown, ed.). D. Reidel, Dordrecht, Holland (p. 281-315).

YUND R.A., TULLIS J. (1980) - *The effect of water, pressure, and strain on Al/Si order-disorder kinetics in feldspar*. Contr. Mineral. Petrology, 72, 297-302.

ZEITLER P.K. (1987) - *Argon diffusion in partially outgassed alkali feldspars: insights from $^{40}Ar/^{39}Ar$ analysis*. Chem. Geol (Isotope Geosci. Sect.), 65, 167-181.

ZEITLER P.K., FITZ GERALD J.D. (1986) - *Saddle-shaped $^{40}Ar/^{39}Ar$ age spectra from young, microstructurally complex potassium feldspars*. Geochim. Cosmochim. Acta, 50, 1185-1199.