# Compositional changes of minerals associated with dynamic recrystallizatin

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**Abstract.** The rate of compositional and isotopic exchange between minerals may be enhanced significantly if the rock is deformed simultaneously. The enhanced exchange rate may result from a reduction in grain size (shorter distance for volume diffusion), dissolution and growth of grains by diffusion creep (pressure solution), or the movement of high-angle grain boundaries through strained grains during recrystallization in the dislocation creep regime. The migration of high-angle grain boundaries provides high diffusivity paths for the rapid exchange of components during recrystallization. The operation of the latter process has been demonstrated by deforming aggregates consisting of two plagioclases ($An_1$ and $An_{79}$) at 900° C, 1 GPa confining pressure, and a strain rate of $\sim 2 \times 10^{-6} s^{-1}$. The polygonal, recrystallized grains were analyzed using an analytical transmission electron microscope and have a variable but often intermediate composition. At the conditions of these experiments, the volume interdiffusion rate of NaSi/CaAl is too slow to produce any observable chemical change, and microstructural-chemical relations indicate that the contribution from diffusion creep was insignificant except for initially fine-grained (2-10 μm) aggregates. These results indicate that strain-induced recrystallization can be an effective mechanism for enhancing the kinetics of metamorphic reactions and for resetting the isotope systematics of minerals such as feldspars, pyroxenes, and amphiboles.

## Introduction

Ductile deformation and mineralogical changes often occur simultaneously during metamorphism and previous attention has focused on how the deformation mechanism and rock strength may be affected by mineralogical changes (e.g., White and Knipe 1978; Rubie 1983). The effect of deformation on the nature or kinetics of mineralogical changes has received some attention (e.g., Brodie and Rutter 1985; Snow and Yund 1987), but there

have been few attempts to evaluate these interactions experimentally. We will consider here whether compositional or isotopic exchange rates between minerals can be enhanced by simultaneous deformation in the dislocation-creep field when the deformation is accompanied by grain-boundary migration recrystallization.

The term recrystallization is often used to indicate different processes by mineralogists, petrologists, and geochemists on the one hand, and by structural geologists and material scientists on the other hand. The latter group uses this term to refer to the formation of new grains of the same composition. This process is driven by the elastic strain energy and may occur by grain-boundary migration or by progressive rotation of subgrains (see below). Other earth scientists use the term recrystallization in a less restrictive sense to refer to various processes including grain growth and the nucleation and growth of new phases (neomineralization). Grain growth is driven by a reduction in the interfacial energy of the aggregate, and a transformation or reaction is driven by a reduction in the Gibbs energy. Grain growth results in larger grains whereas a reaction involves a reduction in the size of some grains and the nucleation and growth of others.

Dislocation creep is generally the dominant deformation mechanism in the crust except at shallow levels or for very fine grain sizes (Poirier 1985). In order to achieve steady-state flow (high strain at a constant stress), this deformation mechanism involves two processes. Strain is accomplished by the generation and glide of dislocations along their slip planes. However, a recovery process is needed to prevent intersecting dislocations from becoming tangled and immobile, which would raise the stress for continued deformation (work-hardening).

Work-hardening can be limited in two ways, which we will refer to as climb-accommodated and recrystallization-accommodated dislocation creep (Tullis and Yund 1985; Urai et al. 1986; Hirth and Tullis, in press). These processes are shown schematically in Fig. 1. The left-hand side of this diagram represents the situation

CLIMB–ACCOMMODATED
DISLOCATION CREEP

RECRYSTALLIZATION–
ACCOMMODATED
DISLOCATION CREEP



INCREASING
STRAIN
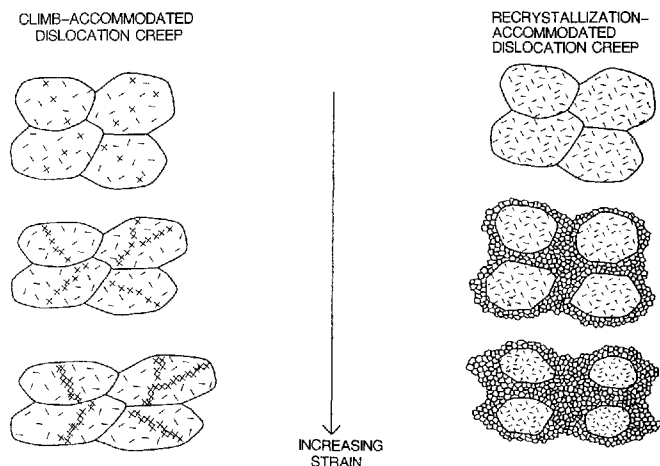
**Fig. 1.** Schematic illustration of the essential difference for a mineral deformed in the dislocation creep field, where work-hardening may be limited by dislocation climb (left-hand column) or by grain-boundary migration recrystallization (right-hand column). Dislocations are shown as *short lines* and dislocation arrays (subgrain boundaries) by *diagonal crosses;* amount of recrystallization in right-hand column is exaggerated for this amount of shortening. See text for discussion

where climb of dislocations is relatively easy because diffusion rates are rapid. This results in the formation of low-energy dislocation walls or networks, indicated schematically by X's, which outline subgrains. With continued deformation, more dislocations climb into these subgrain walls; the original grains are homogeneously deformed and the subgrains undergo progressive misorientation until they are separated by a high-angle grain boundary. [The rotation of subgrains is not shown in Fig. 1.] The new high-angle grain boundary may or may not migrate (Guillope and Poirier 1979) and it may be difficult to distinguish these from recrystallized grains formed by the process described below. This mechanism of climb-accommodated dislocation creep is probably the one by which qaurtz deforms over a wide range of temperatures and strain rates in nature (e.g., White 1976; Hirth and Tullis, in press).

For minerals in which diffusion of one or more ions is very slow, such as Al/Si diffusion in feldspars, dislocation climb may be limited even on a geological time scale. In this case, shown schematically on the right-hand side of Fig. 1, deformation results in a high density of immobile (tangled) dislocations. New strain-free grains are formed by grain-boundary bulging or nucleation, due to local differences in dislocation density, and the migration of high-angle grain boundaries through a portion of the original, work-hardened grain. These strain-free grains undergo an increment of strain and are themselves replaced. Thus a high-angle grain boundary may sweep past a given point in a crystal many times, depending on the total strain. We have referred to this mechanism as recrystallization-accommodated dislocation creep (Tullis and Yund 1985; Hirth and Tullis, in press), and it is typical of how feldspars deform at ~900–1,100° C at laboratory strain rates (Tullis and Yund 1985), and from ~450 to ~650° C at natural strain rates

(e.g., Simpson 1985). At higher temperatures and natural strain rates the accommodation mechanism is dislocation climb and subgrain rotation (e.g., FitzGerald et al. 1983), although at the highest temperatures grainboundary mobility may increase and give rise to a third regime, which also involves recrystallization by grainboundary migration (Guillope and Poirier 1979; Hirth and Tullis, in press). This might explain the grain-boundary migration recrystallization reported in some natural plagioclases from amphibolite-granulite gneisses formed in the lower crust (Ji and Mainprice 1990).

The grain size produced by either mechanism of recrystallization will be a function of the differential stress, but in almost all deformed rocks, dynamically recrystallized feldspar grains are appreciably smaller than the original grains. Thus either of these recrystallization mechanisms will provide shorter diffusion distances for subsequent chemical or isotopic exchange by volume diffusion. Even if volume diffusion is too slow to be effective for the recrystallized grain size, exchange will be enhanced if it occurs simultaneously with deformation by recrystallization-accommodated dislocation creep. The migrating high-angle grain boundaries provide faster diffusion paths than volume diffusion, allowing chemical or isotopic components to reach the interiors of the recrystallized grains, and this results in faster exchange between neighboring grains or between grains and a grain-boundary fluid. We have previously suggested this process could be important for reactions involving plagioclase (Yund and Tullis 1989) and other minerals whose deformation behavior is similar.

In this paper we present experimental evidence for enhanced chemical exchange between phases in synthetic two-plagioclase aggregates (grain size 53–63 μm) deformed by recrystallization-accommodated dislocation creep. The compositions of recrystallized grains, determined by analytical TEM (transmission electron microscopy) techniques, are variable but often intermediate. The contribution from volume diffusion was evaluated in comparison experiments done at hydrostatic conditions at the same confining pressure and temperature, and was found to be negligible. The contribution from diffusion creep was evaluated in experiments on samples of different grain sizes, and found to be important only in very fine-grained (2–10 μm) aggregates.

## Experimental procedures

The starting materials were Hale albite ($An_1$) and Crystal Bay bytownite ($An_{79}$), which were crushed and sieved, or sized by settling in water. Two-plagioclase mixtures, consisting of equal weights of the two materials, were prepared for three different grain-size ranges: ~2–10, ~53–63, and ~150–180 μm. The powder was loaded into a Pt cylinder (6.4 mm diameter by 17 mm long), which was crimp sealed. The experiments were done in a modified Griggs type apparatus (Kronenberg and Tullis 1984), using NaCl as the confining medium, at 1 GPa and 900° C for 69–119 h. No water was added to the samples but they all contained about 0.1 wt% water dissolved in the crystals. The 2–10 μm aggregates contained an additional ~0.1 wt% adsorbed water. These estimates are based on weight loss after heating. The cylindrical samples were shortened ~40% at ~$2 \times 10^{-6}$ $s^{-1}$.
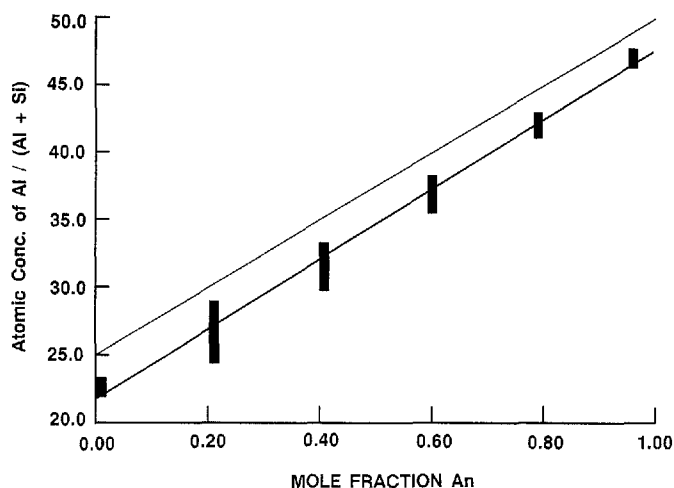
Fig. 2. The concentration of Al/(Al + Si) as determined by energy-dispersive analysis (EDX) using the electron microscope is shown as a function of plagioclase composition (mole fraction An) determined by electron-microprobe analysis. The *upper light line* is the expected relation if there is no error in the EDX analysis

After an experiment, two longitudinal thin sections were prepared from the cylinder, one for optical and one for TEM examination. For the latter a 3 mm diameter, 50 mesh Ni grid was epoxied on the desired area and a 3 mm brass ring epoxied on the grid. Rings were removed along with the 20 μm thick wafer of sample and ion thinned for examination with a Philips EM420 operating at 120 kV. This instrument is equipped with an energy dispersive x-ray analysis system (EDX). A beam diameter of 0.1 μm was used for the analyses and because of the low count rate for Na and its volatility under the beam, it was found that the best analyses were obtained by measuring the integrated peak areas for only Al and Si. Background was manually selected and peak areas were determined by the programmed curve-fitting routine after centering the Si peak at 1.739 eV. The peak areas were converted into an elemental ratio using K values provided by the EDX program. [K is defined by the relation $C_{Al}/C_{Si} = K (I_{Al}/I_{Si})$, where $C$ and $I$ are concentration and measured-integrated intensity, respectively.]

Six plagioclases were used as standards to determine the relation between the atomic percent Al/(Al + Si) as determined by the above procedure and the known compositions of the plagioclases which were determined with a Cameca Camebax electron probe using wave-length dispersive analysis. Amelia albite and Lake County labradorite were used as primary standards for the electron-probe analyses. The resulting relation between the EDX analyses obtained with the TEM and the mole fraction of An determined with the electron probe is shown in Fig. 2. The vertical bar represents one standard deviation of from 10 to 20 EDX measurements.

There is a nearly constant displacement of the straight line through the data (heavy line) from the theoretical curve which is shown by the upper, lighter line in Fig. 2. The cause of this systematic error is not known. The empirical relation was used to correct the apparent compositions determined by EDX for recrystallized grains in the experimental samples. The reproducibility of the compositions determined in this way was often somewhat better than the error shown in Fig. 2 because these analyses were made under more nearly uniform conditions (tilt, sample thickness, background and peak positions, etc.) than for the data in Fig. 2.

## Experimental results

Compaction of the aggregate occurred during pressurization and this resulted in some crushing which pro-

duced finer fragments, especially in the two coarser size fractions. In order to evaluate the amount of crushing and subsequent grain growth during annealing, we hydrostatically annealed all three size fractions at 900° C, 1 GPa for 69–120 h. Optical micrographs of the 53–63 μm hydrostatic sample and one deformed at the same conditions for the same time are shown in Figs. 3a and b, respectively. A representative TEM micrograph of a fine-grained region in the hydrostatic sample is shown in Fig. 4a. Pressurization and annealing of this sample resulted in a reduction of ∼5% of the original fragments to < 10 μm; these have a variable size and shape and the dislocation density is low but twinning is common (Fig. 4a). The compositions of these grains are unchanged except for an occasional submicron fragment which is inhomogeneous, presumably due to some grain growth. (See discussion of 2–10 μm aggregate below.)

The 53–63 μm deformed sample shown in Figs. 3b and 4b–d was axially shortened by ∼40%. The original grains are not flattened and subgrains are absent (Fig. 4b). New small grains replace parts of the original grains, which have a high dislocation density (Fig. 4c). These new grains are mostly polygonal, they have low dislocation densities, their grain boundaries are relatively tight and straight, and they are mostly ∼1.0 μm in diameter (Fig. 4d). The microstructures in this sample are typical of grain-boundary migration recrystallization (Tullis and Yund 1985; Hirth and Tullis, in press). Crushed grains due to pressurization cannot be identified in the deformed sample, presumably because the fragments recrystallized during deformation.

A composite TEM micrograph of an area of recrystallized grains in a 53–63 μm deformed sample is shown in Fig. 5 along with a line drawing of the grains which indicates their compositions as determined by EDX. (The uncertainty in the compositions is about ±6 mol% An.) There are also remnants of original $An_1$ grains (A, C, D, E) and $An_{79}$ grains (F). Most of the recrystallized grains are not chemically homogeneous; some have compositions intermediate between those of the original grains while others have about the same composition as the original grains. Presumably the latter formed near original grains of one composition and there was little exchange of components with other grains. Another noteworthy feature is the absence of compositional gradients in the margins of adjacent $An_1$ and $An_{79}$ original grains. The deformed samples prepared using the 150–180 μm fraction are similar to the 53–63 μm fraction, but have fewer recrystallized grains and more of the recrystallized grains are either $An_1$ or $An_{79}$ rather than having an intermediate composition. The 150–180 μm sample will not be considered further.

Details of the compositional variability of one of the larger recrystallized grains from the deformed 53–63 μm sample are shown in Fig. 6. The precision of these analyses is about ±3 mol% An. The grain is not homogeneous and the composition varies in a regular way as shown on the micrograph. The TEM plates from which Figs. 5 and 6 were prepared were taken after some, but not all, of the EDX analyses had been made. The circular
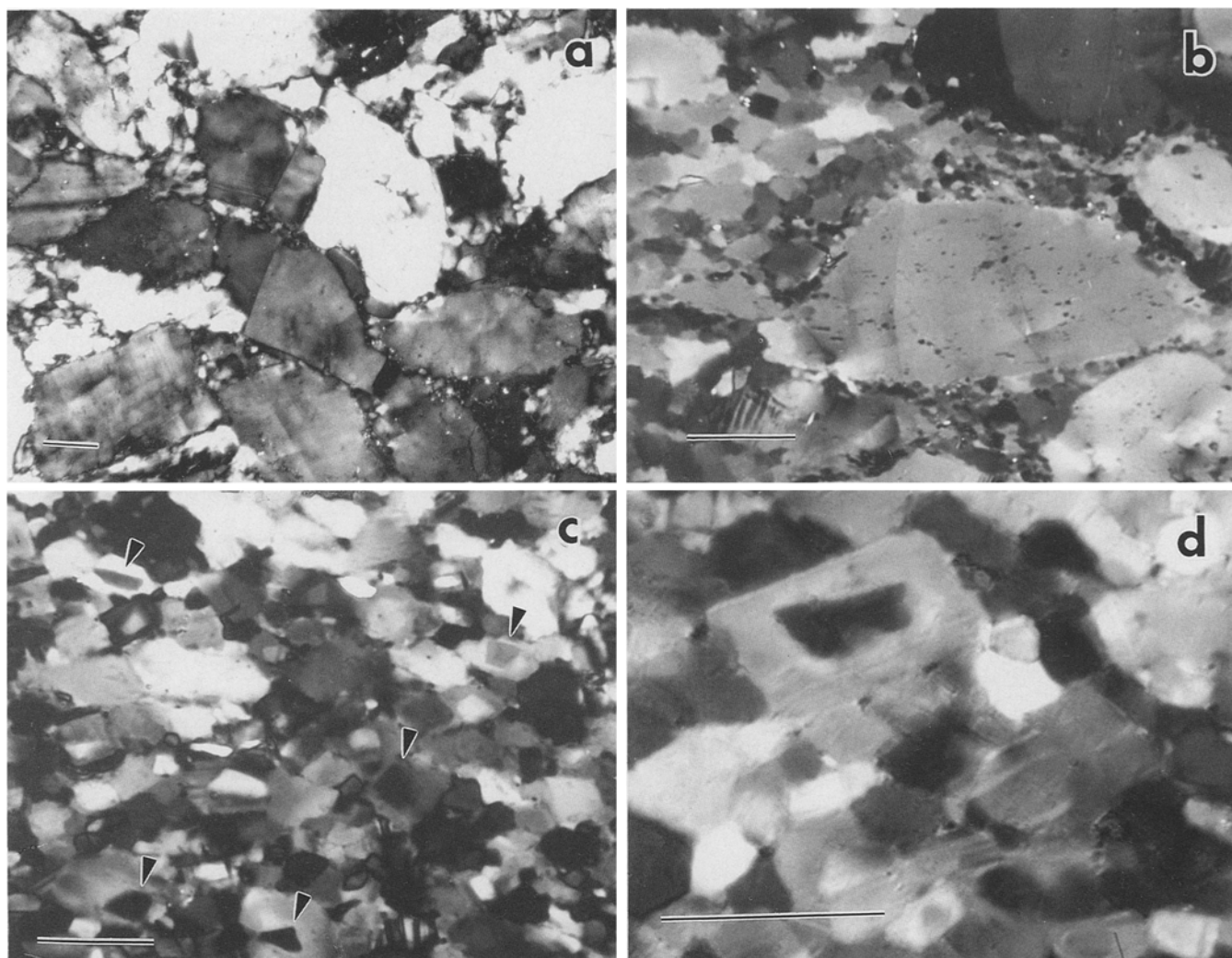
**Fig. 3a–d.** Optical micrographs, crossed polars, scale bars are 10.0 µm: **a** 53–63 µm sample, hydrostatically annealed, 900° C, 1000 MPa, for 70 h; **b** 53–63 µm sample deformed at 900° C, 1000 MPa, $2 \times 10^{-6}$ s$^{-1}$ to $\sim 40\%$ strain (119 h) showing recrystallized grains around larger original grains; **c** 2–10 µm aggregate deformed at 900° C, 1000 MPa, $2 \times 10^{-6}$ s$^{-1}$ to 40% strain (120 h), many grains (some indicated by *arrows*) have an original grain as a core and an overgrowth of a different composition; **d** details of a compositionally zoned grain. See also Fig. 4f

dark areas ($\sim 0.1$ µm diameter) on these micrographs are due to beam damage where the analyses were made.

These results together with numerous other analyses demonstrate that many of the new grains have the composition of one of the original plagioclase grains when they are surrounded by original grains of the same composition, but they often have an intermediate and variable composition if they formed near the boundary between original plagioclase grains of different compositions.

The microstructures and compositional relations of the 2–10 µm deformed samples are very different from those of the 53–63 µm samples, and we believe that the deformation of the fine-grained samples occurs primarily by diffusion creep. The new grains have a variable shape but the larger ones are often roughly rectangular in cross section (Fig. 3c, d), with the long axes of the laths roughly normal to compression. In addition, the porosity is larger (estimated to be $\sim 5\%$) than in the 53–63 µm sam-

ples, and more of the grain boundaries are open (Fig. 4e) than in the coarser-grained samples. Although ion thinning may increase the apparent width of a grain boundary, the greater widths of these boundaries are clearly indicated by the presence of epoxy, which was used to impregnate the samples and which remains along many boundaries after thinning. The grains also have a low dislocation density (Fig. 4e). (Nearly all of the contrast in Fig. 4e is due to twins and bend contours.)

Unlike the 53–63 µm samples, nearly all of the smaller diameter grains ($< \sim 4$ µm) in the 2–10 µm sample are $\sim An_{40}$, whereas the larger grains have irregular cores of original grains with overgrowths of a different composition. This zoning can be seen optically (Fig. 3c, d) and identified in back-scattered electron images (Fig. 4f). The cores of the larger grains are mostly $An_{79}$, while fewer are $An_1$. In most of these large grains there is a diffuse zone of $\sim Ab_{20-30}$ around the $An_{79}$ core, and then a thicker rim which is $\sim An_{40}$. The explanation
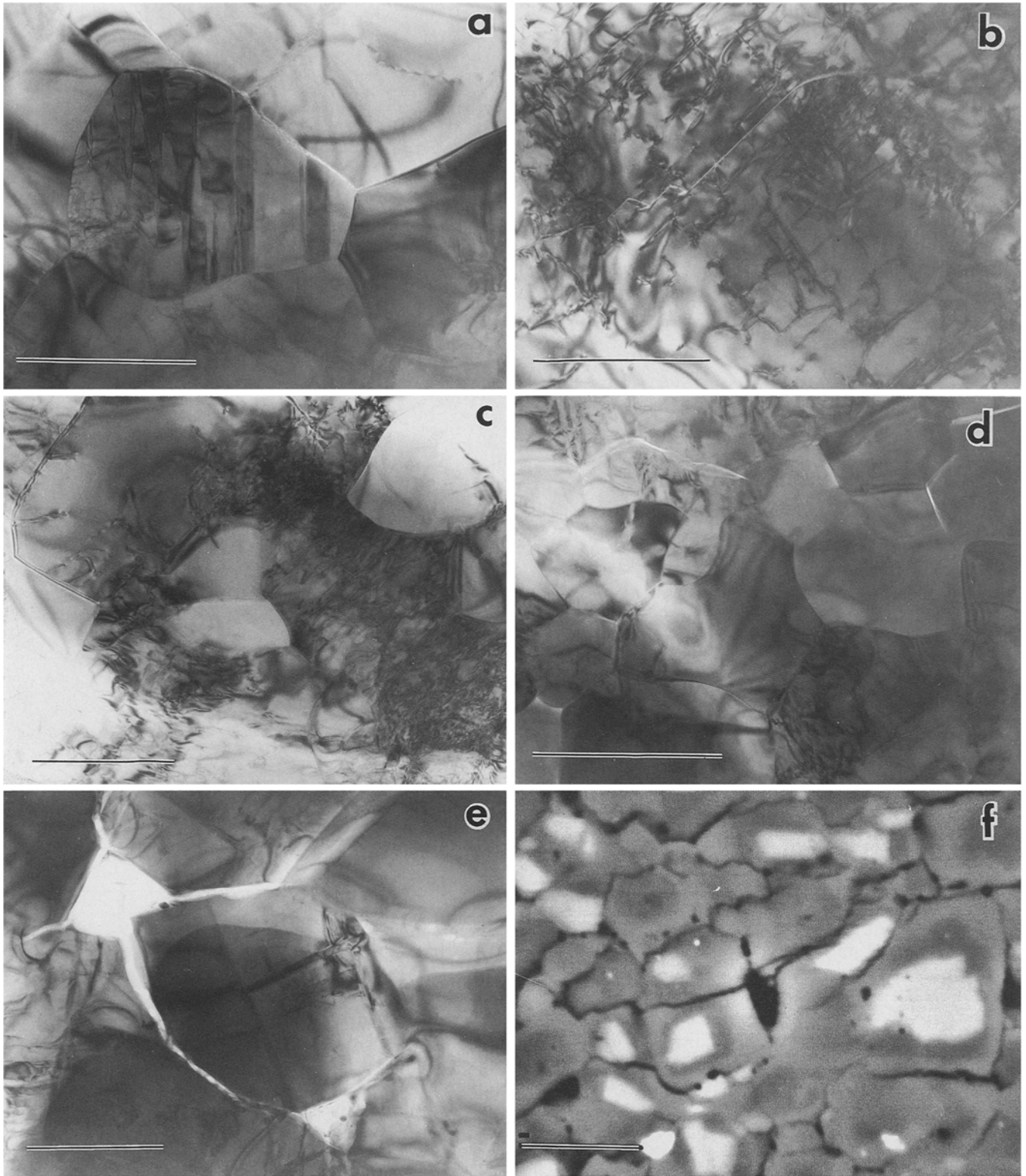
**Fig. 4a–f.** TEM bright-field micrographs. **a** through **e**, scale bars are 1.0 μm: **a** fine-grained area in 53–63 μm sample, hydrostatically annealed, 900° C, 1000 MPa, for 70 h, note Albite twins and low dislocation densities. **b** through **d** are 53–63 μm sample deformed at 900° C, 1000 MPa, $2 \times 10^{-6}$ s$^{-1}$ to ~40% strain (68–119 h): **b** high dislocation density in original grain of An$_1$; **c** recrystallized grains (*clear*) replacing original An$_{79}$ grain with high dislocation density; **d** typical polygonal, recrystallized grains with low disloca-tion densities. **e** and **f** are 2–10 μm aggregate deformed at 900° C, 1000 MPa, $2 \times 10^{-6}$ s$^{-1}$ to ~40% strain: **e** grains are mostly ~An$_{40}$ and have low dislocation densities, some twinning, grain boundaries are open, and pores common; **f** back-scattered electron image showing grains with An$_{79}$ cores (*white*), intermediate Ab-rich zone (*darker gray*), and outer rim of ~An$_{40}$ (*lighter gray*). Scale bar is 10.0 μm
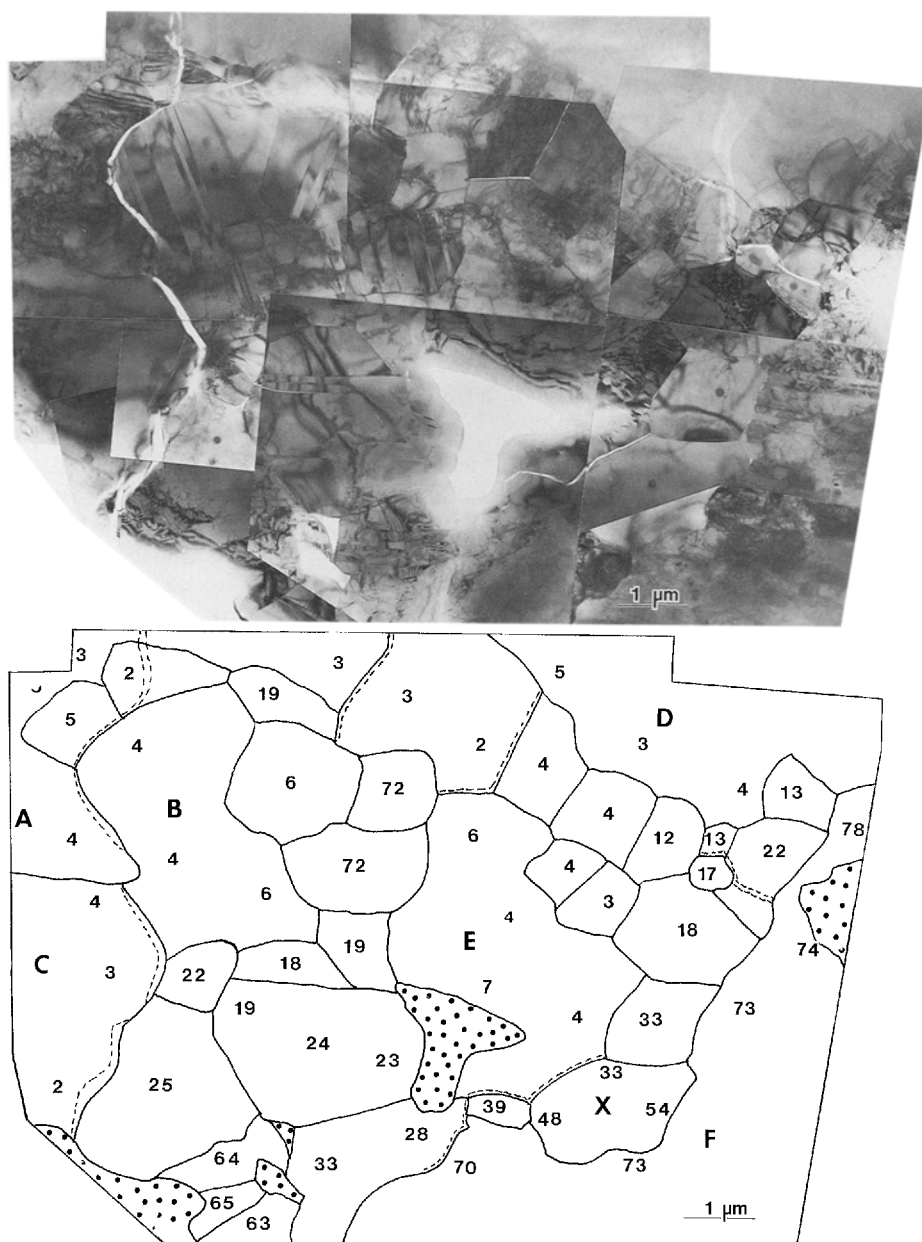
Fig. 5. Composite TEM micrograph showing an area with recrystallized grains between original grains of $An_1$ (*A* through *E*) and $An_{79}$ (*F*). Grains are identified on lower drawing and their approximate compositions from EDX analyses are shown in mol% An. Note the variable composition of the recrystallized grains. Grain *X* is shown in detail in Fig. 6. *Stippled areas,* holes; the 0.1 μm dark circles are beam-damage spots from EDX analyses

for the fewer $An_1$ cores and this zoning pattern may be related to the dissolution behavior or kinetics of plagioclase. At 800° C and 200 MPa, Adams (1968) reports that the albite component of plagioclase goes into solution leaving the anorthite component behind. Assuming there is sufficient water in these grain boundaries that dissolution of plagioclase occurs, and that this behavior is similar to the behavior in bulk water, the $An_1$ grains may 'dissolve' faster than the $An_{79}$ grains and reprecipitate in a narrow zone of $An_{20-30}$ on the orignal $An_{79}$ grains. With increasing time the grains become more homogenized and the outer rims and most of the smaller grains have a composition of $\sim An_{40}$.

The microstructural features and compositional relations observed in the 2–10 μm samples are clearly very different from those in the 53–63 μm samples and indicate that the deformation occurred by a different mechanism. We believe that the observed microstructural features and compositional relations in these fine-grained aggregates indicate that diffusion creep was the dominant deformation mechanism; this will be discussed in more detail below.

## Discussion

There are several mechanisms which could produce the intermediate compositions of the small grains in the 53–63 μm deformed samples: (1) volume interdiffusion of NaSi and CaAl between grains; (2) modification of grains by diffusion along existing grain boundaries (diffusion creep or pressure solution); (3) compositional ex-
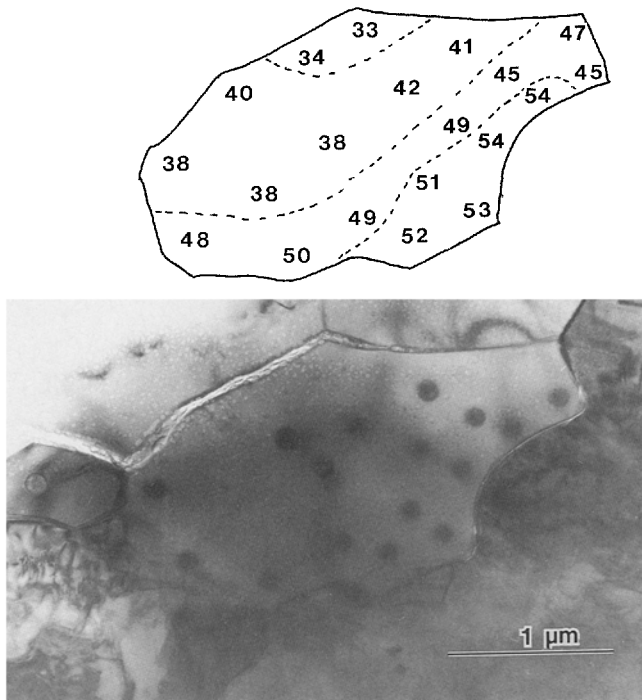
**Fig. 6.** TEM micrograph of a recrystallized grain ($X$ in Fig. 5) which is compositionally inhomogeneous. The 0.1 μm dark circles are beam-damage spots as a result of the analysis; the photo was taken before the analyses were completed

change by rapid diffusion along high-angle grain boundaries which sweep through the original grains during dynamic recrystallization in the dislocation-creep regime. These alternatives are considered below.

*Compositional changes due to volume interdiffusion*

Volume interdiffusion rates are much too slow to produce significant compositional changes on the scale of 1 μm (the approximate recrystallized grain size) in the duration of our experiments. Using the interdiffusion data for NaSi/CaAl in peristerite (Yund 1986; Yund and Snow 1989), a diffusion coefficient $D$ of $10^{-21}$ m² s⁻¹ is a maximum value for the conditions of these experiments. The characteristic penetration distance [$x = 2(Dt)^{1/2}$] after $t = 120$ h would be 0.04 μm, which is much smaller than the average radius of the recrystallized grains. This calculation is based on interdiffusion rates when water is present at a high confining pressure; for a drier sample the diffusion rate would be even slower (Grove et al. 1984; Yund and Snow 1989). The absence of compositional gradients in the margins of original grains of $An_1$ and $An_{79}$ which are in contact confirms that volume diffusion is not significant. Thus the available evidence indicates that volume diffusion is too slow at the conditions of these experiments to produce significant compositional exchange of Na/Si for Ca/Al on the scale of these recrystallized grains.

The presence of dislocations in the deformed plagioclase would slightly enhance the exchange rate by vol-

ume diffusion because of faster diffusion along static or moving dislocation cores. We have previously shown and argued (Yund et al. 1989), however, that any enhancement in the exchange rate due to dislocations is minor even at laboratory strain rates. Furthermore, the original grains with a high dislocation density in our experiments do not exhibit intermediate compositions even at their margins; it is the recrystallized grains with a low dislocation density which have intermediate compositions.

*Compositional changes due to diffusion creep*

Grain boundaries provide high diffusivity paths but the components along the grain boundaries still must exchange with the interiors of grains. If the grain boundaries are static there is little enhancement of the exchange rate. On the other hand, if the grains undergo dissolution and reprecipitation (diffusion creep) or if high-angle grain boundaries sweep through the grains (recrystallization-accommodated dislocation creep) the components have access to the interiors of grains.

Diffusion creep involves either diffusion along grain boundaries (Coble creep) or within grains (Nabarro-Herring creep) (Poirier 1985). We are interested only in Coble creep because Nabarro-Herring creep depends on volume diffusion rates which are too slow to be significant in these experiments. (Some grain-boundary sliding may accompany either type of diffusion creep.) Diffusion creep is most important in fine-grained aggregates where the diffusion distances are short and this mechanism has been shown to be important in fine-grained calcite (Schmid et al. 1977) and olivine (Karato et al. 1986) aggregates. We are evaluating the role of diffusion creep in fine-grained (< 10 μm) feldspar aggregates under experimental conditions (Tullis and Yund, in press) and will only briefly summarize the results here.

At 900° C, 1 GPa confining pressure, and a strain rate of $\sim 10^{-6}$ s⁻¹ there is microstructural and compositional evidence for grain-boundary diffusion creep in the 2–10 μm fraction aggregates as noted in the previous section. In addition there is a difference in the yield strengths of the 53–63 and 2–10 μm fractions. The yield strength of the 53–63 μm fraction is about 250–300 MPa whereas for the 2–10 μm fraction it is < 100 MPa. A correlation of strength with grain size is expected for diffusion creep but not for dislocation creep (Poirier 1985), and the difference in strengths is consistent with a change from dominantly dislocation creep to dominantly diffusion creep for the 53–63 to 2–10 μm aggregates. The presence of the small but unknown amount of adsorbed water on the 2–10 μm grains is essential for diffusion creep, presumably because it increases grain-boundary diffusion rates. When these aggregates are first vacuum dried at or above 300° C the deformation mechanism is dominantly dislocation creep (Tullis and Yund, in press); the microstructures and compositional relations are like those in the initially coarser aggregates.

We conclude that diffusion along existing grain boundaries together with local dissolution and reprecipitation (pressure solution) played a major role in the development of the microstructural and compositional relations observed in the 2–10 μm aggregates. In contrast, the microstructures, compositional relations, and strength of the 53–63 μm aggregates indicate recrystallization-accommodation dislocation creep, and the intermediate but variable composition of some of the new grains must be related to this deformation mechanism. Similar microstructures were observed in the 150–180 μm aggregates but there is less recrystallization because of the smaller total surface area.

*Compositional changes due to recrystallization in the dislocation creep regime*

Diffusion along high-angle grain boundaries as they sweep through an original grain provides a mechanism for generating recrystallized grains of intermediate composition. In order to lower the elastic strain energy due to a high dislocation density in original $An_1$ or $An_{79}$ grains, strain-free grains form by grain-boundary bulging of an area with a lower dislocation density, or nucleation of a strain-free grain (Poirier 1985). As the high-angle grain boundary sweeps through part of an original work-hardened grain, Na/Si and Ca/Al can exchange with the surface of neighboring grains by diffusion along the high-angle grain boundary, and the new recrystallized grain will have an intermediate composition. The effectiveness of this exchange mechanism will depend on the grain-boundary diffusion rate, the effective grain-boundary width, the recrystallized grain size, and the proximity of grains of a different composition. The composition of a recrystallized grain may not be homogeneous because the supply of material along the grain boundary would be expected to vary with time as the high-angle grain boundary continues to migrate through an original grain.

Grain-boundary diffusion coefficients ($D_{gb}$) are greater than volume diffusion coefficients ($D_v$) and the diffusion rate will be a function of the nature of the grain boundary and especially whether a fluid, such as water, is present along the boundary (i.e., Rubie 1986). Joesten and Fisher (1988) have suggested on the basis of the limited data available that grain-boundary diffusion rates for most cations in silicates may be similar at a given temperature. Using their data and assuming a grain-boundary width of 10 nm, a representative value for $D_{gb}$ at the conditions of our experiments might be $10^{-14}$ m$^2$ s$^{-1}$ (dry) to $10^{-10}$ m$^2$ s$^{-1}$ (wet), compared with ($D_v$) for NaSi/CaAl interdiffusion of about $10^{-21}$ m$^2$ s$^{-1}$. These values for $D_{gb}$ would result in a characteristic penetration distance of 130 μm (dry) or 1.3 cm (wet). Of course the flux of material to the recrystallizing grain would depend on the effective grain-boundary width. Although our knowledge of grain-boundary diffusion rates and grain-boundary widths in silicates is very limited, and more quantitative data are needed, the available evidence indicates that grain-boundary diffusion is sufficiently rapid to account for a compositional exchange on the scale of these 1 μm diameter recrystallized plagioclase grains.

The question needs to be asked whether some of the driving energy for the microstructural changes observed in these samples could be due to a lack of chemical equilibrium. At 1 GPa and 900° C a homogeneous plagioclase of intermediate composition has a lower Gibbs energy than a two-plagioclase mixture. It has been suggested that the energy barrier for recrystallization may be overcome by a decrease in the Gibbs energy associated with a compositional change of the mineral which is recrystallizing (Etheridge and Hobbs 1974). Several authors have noted that recrystallized plagioclase grains may have a different composition than the original plagioclase in the rock (e.g., Olsen and Kohlstedt 1985).

In our experiments, however, it seems unlikely that recrystallization is driven or even significantly aided by a compositional change for the following reasons:
1. We see very little recrystallization in samples which were sintered hydrostatically at the same pressure and temperature and for the same time as the deformed samples, although some of the broken grains in the sintered samples do have moderately high dislocation densities due to local nonhydrostatic stresses during pressurization.
2. The extent of recrystallization is the same for aggregates made from a single plagioclase composition as for the two-plagioclase aggregates, all deformed at the same conditions.

Thus the available evidence indicates that grain-boundary mobility was sufficiently easy that grain boundaries could move due to the difference in the elastic strain energy, and the compositional changes are associated with this recrystallization but not the cause of it.

There is another interaction between grain-boundary diffusion and grain-boundary migration which can produce a compositional change when volume diffusion is slow. This process is referred to as diffusion-induced grain-boundary migration (DIGM) (Balluffi and Cahn 1981). This mechanism was first reported for metals, but Hay and Evans (1987) have shown that this process is also operative in synthetic calcite bicrystals and Yule marble. For example, when pieces of Yule marble were surrounded with a powdered mixture of 250 ppm $Li_2CO_3$ flux in $SrCO_3$ and annealed at 680° C for 48 h in air, a small percentage of the boundaries within 10 to 300 μm of the marble surface migrated horizontal distances of up to 100 μm. Concentrations of Sr of up to 1–3 wt% were observed in portions of a crystal swept by a grain boundary. No motion or compositional change was observed unless $Li_2CO_3$ was present.

The detailed mechanism of DIGM remains unclear, but as Hay and Evans (1987) point out, it involves the formation of a compositionally distinct phase which grows by material transport along the advancing grain or interphase boundary. The process is driven, at least in part, by a reduction in the chemical free energy associated with the chemical change.

There is no evidence that DIGM contributed in a significant way to the compositional changes we ob-

served in our plagioclase aggregates. If DIGM had occurred, we would expect to see compositional changes along *non*-recrystallized interfaces between original plagioclase grains in either the deformed or hydrostatically annealed samples. However, we observed no compositional changes in these regions.

## Significance of this mechanism in nature

We believe that these experiments demonstrate the potential importance of recrystallization-accommodated dislocation creep for the exchange of elements or isotopes between mineral grains (or fluid) in a rock. For plagioclase this deformational regime is likely to be most important between ~450 and ~650° C (e.g., Simpson 1985). Volume diffusion rates in pyroxenes and amphiboles are also very slow (e.g., Freer 1981), implying that dislocation climb is limited even at geologic strain rates. Textural evidence suggests that recrystallization-accommodated dislocation creep is also the dominant deformation mechanism in these minerals at middle metamorphic grades (Etheridge 1975; Cumbest et al. 1989). Thus it is likely that the exchange mechanism we have demonstrated for plagioclase is also effective for other minerals.

The distinction between recrystallized grains which have formed by recrystallization-accommodated or climb-accommodated dislocation creep is important. Although recrystallized grains produced by subgrain rotation during climb-accommodated dislocation creep are bounded by a high-angle grain boundary, they are not swept by high-angle grain boundaries. Thus we would predict that the enhancement of the exchange rate would be less in the climb-accommodated dislocation creep regime. Unfortunately we cannot test this idea with feldspars because at experimental conditions the dominant mechanism is always recrystallization-accommodated dislocation creep. Quartz can be deformed experimentally in both accommodation fields (Hirth and Tullis, in press), but its fixed composition makes it difficult to monitor compositional changes.

Recrystallization by either mechanism will produce smaller grains which will provide shorter *volume* diffusion distances. If the grain-size reduction is followed by a long anneal at a sufficiently high temperature, volume diffusion could result in compositional or isotopic changes. In fine-grained aggregates diffusion creep may be important and this could also produce compositional or isotopic changes. The critical size for the transition from diffusion to dislocation creep will be considerably larger at natural strain rates than at experimental rates. The transition appears to occur at about 0.5 mm for calcite at 600° C and a strain rate of $\sim 10^{-14}$ s$^{-1}$ (Schmid et al. 1977), but may be different for feldspars depending on the grain-boundary diffusion rate and temperature. Either volume diffusion or diffusion creep could be important in fine-grained materials such as mylonites or cataclasites, especially if water is present.

Although we have demonstrated the effectiveness of recrystallization-accommodated dislocation creep for the exchange of major chemical components in plagio-

clase, it is likely that this process will be even more important in the exchange of Sr isotopes, and will reset mineral ages when volume diffusion is too slow to be effective even for very small grains. Gromet and Getty (1989) have recognized the importance of this process and used it to help explain isotopic relations they determined for minerals in high-grade deformed rocks from eastern Connecticut. Any time radiometric dating techniques are being used on a rock in which there is microstructural evidence for grain-boundary migration recrystallization, the possibility of compositional or isotopic adjustment during the deformation must be considered. This can be especially important when different minerals in a rock do not deform by the same mechanism during the metamorphism, resulting in a preferential resetting of some radiometric ages and not others.

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