Diffusion creep in feldspar aggregates: experimental evidence

JAN TULLIS and RICHARD A. YUND

Department of Geological Sciences, Brown University, Providence, RI 02912, U S A

Abstract—A combination of mechanical and microstructural results for experimentally deformed albite aggregates of 2-10 μm grain size indicates a regime of grain boundary diffusion creep that depends upon the presence of water, temperature and strain rate. At 900°C and 10^{-5} s^{-1}, deformation occurs dominantly by recrystallization accommodated dislocation creep when the aggregates contain < ~0.2 wt% water, but by grain boundary diffusion creep when the aggregates contain 0.9 wt% water. Experiments at other temperatures and strain rates indicate that fine grained aggregates with added water may go directly from cataclastic flow to grain boundary diffusion creep with increasing temperature or decreasing strain rate, bypassing the field of dislocation creep.

Microstructural evidence for grain boundary diffusion creep in the wet fine grained aggregates includes the development of rectangular grains rather than polygonal grains, grain growth, a very low average dislocation density, open grain boundaries including pores and channels, and the presence of overgrowths of a different composition on grains in a two plagioclase (An₁ and An₇₀) aggregate. Additional evidence for diffusion creep in the wet fine grained aggregates is indicated by their similar microstructures and strengths when deformed at 600 and 1500 MPa, in contrast, dry feldspar aggregates deforming by dislocation creep show an increase in strength and a transition to semi brittle behavior at lower confining pressures. Grain boundary diffusion creep of feldspars may be common in naturally deformed rocks, due to the ease of grain size reduction by both cataclasis and dynamic recrystallization

INTRODUCTION

ZONES of localized ductile deformation in the crust are almost always characterized by extreme grain size reduction, suggesting that fine grained rocks are weaker than their protoliths There are several possible mechanisms of ductile flow in fine grained aggregates, including dry or fluid assisted volume or grain boundary diffusion creep, grain boundary sliding and dislocation creep Diffusion creep and grain boundary sliding have been little studied experimentally until relatively recently, because fine grain sizes, high temperatures and low stresses are required to produce measurable laboratory strain rates However, a transition from dislocation creep to diffusion creep plus grain boundary sliding with decreasing grain size has been demonstrated for calcite aggregates by Schmid et al. (1977, 1980) and for olivine by Karato et al. (1986). For experiments on fine grained aggregates, a transition from dislocation creep to grain boundary diffusion creep was observed to accompany the addition of a small quantity of melt in albite (Ji & Mainprice 1986) and in granite (Dell'Angelo et al. 1987) Similarly, in fine grained olivine aggregates, Karato et al. (1986) found that addition of ~0.2 wt% water produced a change from volume to grain boundary diffusion creep, although Cooper & Kohlstedt (1984) found that addition of ~4.0% melt only caused an enhancement of the grain boundary diffusion creep rates.

Previous experimental deformation studies of relatively coarse grained (~180 μm) feldspar aggregates have documented a regime of brittle faulting at low pressures and/or temperatures (Tullis & Yund 1987); a regime of cataclastic flow, involving distributed cracking with no dislocation motion, at intermediate tempera-

tures and pressures (Tullis & Yund 1987), and a regime of recrystallization-accommodated dislocation creep at higher temperatures and moderate to high pressures (Tullis & Yund 1985). Addition of trace amounts of water (0.1–0.2 wt%) lowers the temperature of the transition from cataclastic flow to dislocation creep (Tullis & Yund 1980) Within the recrystallization accommodated dislocation creep regime, deformation produces an extremely fine grained (~1 μm) aggregate, but there is no microstructural evidence for a switch to diffusion creep in the recrystallized material (Tullis et al. 1990) Observations of naturally deformed feldspathic rocks indicate that there is a further transition to climb accommodated dislocation creep at upper amphibolite to granulite grade conditions (e g. White & Mawer 1986), but this is not observable at experimental strain rates due to the onset of melting

In this paper we present the results of an experimental study of fine grained (2-10 μm) albite, with microstructural and mechanical evidence that addition of a small (~1 wt%) amount of water causes a switch from dislocation creep to grain boundary diffusion creep These results have important implications for ductile shear zones in the crust

EXPERIMENTAL DETAILS

We used hot pressed plagioclase aggregates in this study. Most samples were composed of pure albite, obtained from a fine grained albite rock (Ab₉₈An₁Or₁) from the border zone of the Hale pegmatite, CT, which we have used in previous experimental deformation studies (e.g. Tullis & Yund 1980, 1985, 1987) We

crushed this material in an agate mortar and separated out a grain size fraction of 2-10 μm by settling in distilled water The powder was washed in alcohol and dried in an oven at 100°C Cylindrical samples were hot pressed *in situ* in a modified Griggs type apparatus prior to deformation Due to feldspar's two excellent cleavages, the compaction process causes all of our hot-pressed aggregates to have a strong crystallographic preferred orientation prior to deformation, therefore the presence of a preferred orientation in deformed samples cannot be used as diagnostic evidence for dislocation creep, as it can for cores of natural aggregates.

Experiments were done on samples with a range of different water treatments, ranging from added water, to no added water, to vacuum drying. Weight loss of the coarse grained starting material after vacuum heating to 800°C indicates a 'water' content of ~0.1 wt% Similar weight loss measurements indicate that the 2-10 μm powder contains an additional ~0.1 wt% of adsorbed water, for a total of 0.2 wt%. For some experiments we added ~0 7 wt% water to the powder and used either weld sealed or mechanically sealed Pt or Au capsules, for a total water content of ~0.9 wt%. Previous experience (e g Tullis & Yund 1980, Kronenberg & Tullis 1984) shows that our technique of mechanical sealing definitely retains the added water For other experiments we placed untreated powder in mechanically sealed capsules (total water content of ~0 2 wt%) For several experiments we vacuum dried the powder at 300°C and immediately weld sealed it in Pt capsules, this treatment should have removed most of the adsorbed water, but not changed the internal water-related species (Kronenberg *et al.* 1989). We estimate these samples to have approximately the same 'water' content as the coarse grained starting material, namely ·0.1 wt%. Obviously individual samples may have varied somewhat in their water content, due to differences in ambient humidity etc

Our NaCl sample assembly tends to buffer near Ni-NiO We infer this from an experiment in which pieces of Cu, Ni, Ta and Mo foils were placed between discs of quartzite in a sealed Pt tube, and taken to 900°C and 1500 MPa for 12 h; the Ta and Mo foils were oxidized but the Ni and Cu foils were not.

Some of the experiments on samples with added water were done in weld sealed capsules and buffered sample assemblies, using standard materials and configurations (e g Chou 1987), our assembly is shown in Fig 1 The dried albite powder was loaded into a 5 mm Pt tube whose bottom end was mechanically sealed by folding it over a Pt disc About 0 7 wt% water was added, and the top end was sealed in a similar manner. This was placed inside a 0 25" Au tube which had a cup of Au weld sealed to one end and small centering rings of Au placed in the bottom to hold the inner Pt tube About 300 mg of a metal-metal oxide buffer (Huebner 1971) was placed between the Pt and Au tubes together with 3-10 mg water The buffers used were Mn₃O₄-Mn₂O₃, Ni-NiO and Mo-MoO₂, which provide a range of nearly eight orders of magnitude in f_{H_2} and 15 orders of magnitude in
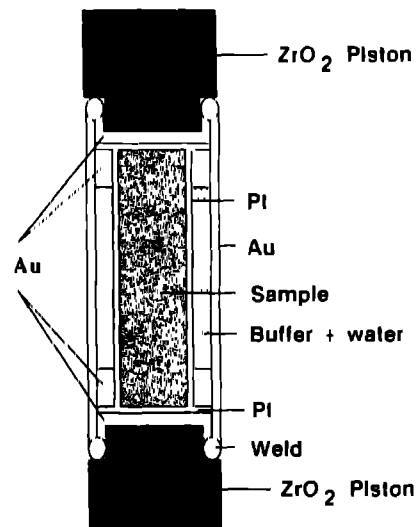
f_{O_2} at the conditions of these experiments About 95% of the buffer mixture was the phase which tended to be consumed during the experiment, except for the Mo-MoO₂ buffer where Mo foil was used because it oxidizes quickly A top centering ring of Au was slipped over the Pt tube, and another Au cup weld sealed at the top. The top and bottom ZrO₂ pistons fit snugly into the Au cups The presence of water was confirmed at the end of an experiment by weight loss after puncturing the tube and drying, and the solid buffer phases were identified by X-ray diffraction

Hydrostatic experiments showed that the high initial porosity (~35-40%) of the samples was reduced to about 1-2% after ~6 h at 900°C and 1500 MPa The hot pressed samples retained very close to a right circular cylindrical shape, with almost all of the volume reduction occurring by a decrease in length, presumably due to the axial geometry and presence of rigid end pistons All of the deformed samples were first hot pressed for 5-6 h at pressure and temperature

In all experiments we used a noble metal jacket, ZrO₂ end pistons, and a stepped graphite furnace to reduce temperature gradients. The confining medium was NaCl for experiments · 900°C, and soft fired pyrophyllite for experiments at 1000-1100°C. For experiments using NaCl, the nominal confining pressure may include a contribution of up to 100 MPa from friction (Green & Borch 1989) Stresses were measured with an external load cell, and are reproducible to within ± 50 MPa

Axial compression, constant displacement rate experiments were done at 800-1100°C, 2 × 10⁻⁵ and 2 × 10⁻⁶ s⁻¹, and 1500 and 600 MPa. Samples were shortened approximately 30-40%. We do not know the fluid pressure in the experiments, although it was less than total pressure because there was no axial cracking. Deformed samples were quenched to 300°C, unloaded, and impregnated with epoxy, two longitudinal thin sections were made, one for optical and one for trans
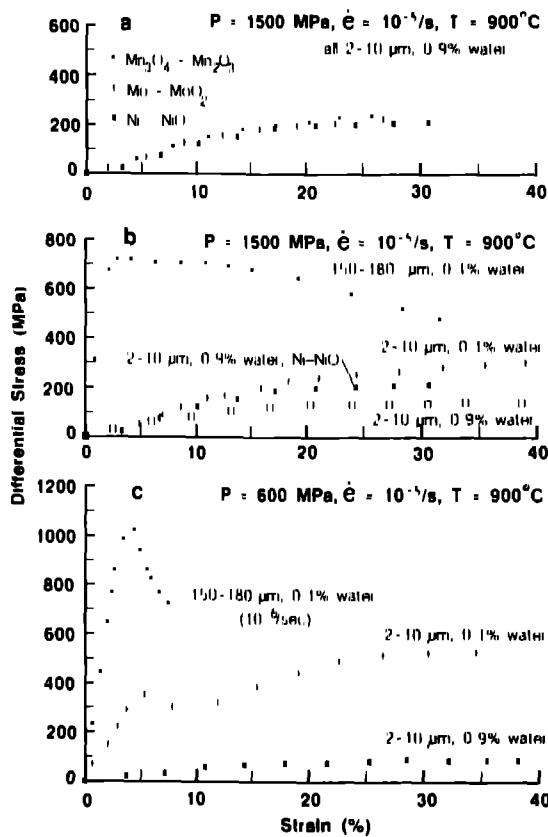
Fig. 2 Stress-strain curves for representative experiments on feld spar aggregates at 900°C and 2 × 10⁻⁵ s⁻¹ (a) Curves for buffered and weld sealed 2-10 μm samples containing ~0.9 wt% water, showing that f_H, and f_O, have no measureable effect on strength (b) Curves for samples deformed at 1500 MPa, drier samples (with ~0.1 wt% water) deform by dislocation creep, whereas wet samples (with ~0.9 wt% water) deform by diffusion creep The curve for the weld sealed sample buffered with Ni-NiO is repeated from (a). (c) Curves for samples deformed at 600 MPa, drier samples (with ~0.1 wt% water) undergo complex mixed mode deformation, whereas wet samples (with ~0.9 wt% water) deform by diffusion creep.

mission electron microscope (TEM) observations. TEM observations were made on a Philips EM420 instrument operating at 120 kV

A few comparison experiments were performed on samples consisting of intimate mixes of 50% albite and 50% bytownite (Ab₃₀An₇₀Or₁, from Crystal Bay, Min nesota). Three different grain size fractions were util ized 160-180, 53-63 and 2-10 μm Untreated powders were mechanically sealed and deformed (in unbuffered sample assemblies) at 900°C, 1000 MPa and 2 × 10⁻⁶ s⁻¹, to approximately 40% shortening.

RESULTS

Mechanical results

Stress-strain curves for representative experiments on the 2-10 μm aggregates deformed at 1500 MPa are shown in Fig 2. All of the water-added, weld-sealed, buffered samples deformed at 1500 MPa, 2 × 10⁻⁵ s⁻¹ and 900°C have a strength of ~200 MPa (Fig. 2a); there are no detectable differences which could be correlated

to f_H, or f_O, For deformation at the same conditions, a mechanically sealed sample with the same amount of water added, but no buffer, has a slightly lower strength (-150 MPa) (Fig 2b). We believe this indicates a small contribution to the measured strength from the layer of metal-metal oxide powder directly around the buffered samples (Fig 1).

A sample which was vacuum dried at 300°C and immediately weld sealed has a higher strength (~300 MPa) than any of the water added samples (Fig. 2b). For comparison, we include the stress-strain curve for a core of Hale albite rock (grain size 150-180 μm), which we believe to have the same water content (~0.1 wt%), deformed at the same conditions (Fig 2b). It has a high initial yield strength (~725 MPa), followed by strain weakening which accompanies the progressive dynamic recrystallization (Tullis & Yund 1985) It appears that the strength for this core is approaching that of the dry 2-10 μm sample as recrystallization pro duces a similar grain size

A few samples were deformed at 600 MPa for com parison (Fig 2c) A mechanically sealed sample contain ing ~0.9 wt% water (no buffer) deformed at 900°C and 2 × 10⁻⁵ s⁻¹ had a slightly lower strength (~100 MPa) than a similar sample deformed at 1500 MPa However, a sample which was vacuum dried at 300°C and weld sealed and deformed at 600 MPa has a much higher strength (~1000 MPa) than similar samples deformed at 1500 MPa Again we include, for comparison, the stress-strain curve for a core of Hale albite rock de formed at the same conditions. It is significantly stronger than an equivalent sample deformed at 1500 MPa, and developed a through going fault (although there was no sudden stress drop). A similar increase of strength with decreasing pressure is exhibited by quartz aggregates deformed by dislocation creep (Kronenberg & Tullis 1984), apparently due to a dependence of dislocation glide and/or climb on f_H₂O (Tullis & Yund 1989, Farver & Yund 1990b) However, there is no reason for grain boundary diffusion rates to depend strongly on pressure, so it seems reasonable that the strength of samples undergoing grain boundary diffusion creep should not be pressure sensitive (except insofar as solubility is increased by pressure)

We cannot resolve the flow stresses sufficiently to determine flow laws for the 2-10 μm aggregates, and in particular to determine whether the stress exponent is close to 3 for the dry samples, consistent with dislocation creep, and close to 1 for the wet samples, as it should be for diffusion creep. However, in addition to the mechan ical evidence presented above, we believe there is com pelling microstructural evidence that the wet 2-10 μm aggregates have deformed dominantly by grain bound ary diffusion creep, this evidence is described in the next section

Microstructural results

In this section we will first briefly review the optical and TEM microstructures characteristic of recrystal

lization accommodated dislocation creep in initially dry, coarse grained feldspar aggregates. Then we will describe the microstructures of the fine grained aggregates containing approximately the same amount of water (~0 1 wt%), deformed at the same conditions (1500 MPa, 900°C and 2 × 10⁻⁵ s⁻¹). Then we will describe the striking differences in microstructure observed with increasing water content, which we believe to indicate grain boundary diffusion creep Finally we will briefly describe the changes in microstructure as a function of changing temperature, strain rate and confining pressure We will make some first level interpretations in this section, and justify them in more detail in the Discussion

Coarse grained albite samples Previous work (Tullis & Yund 1985) has documented that for coarse grained feldspar aggregates containing ~0 1-0 2 wt% water, deformed in the lower temperature portions of the dislocation creep regime, dislocation climb is extremely difficult and grain boundary migration recrystallization is the accommodation process that offsets work hardening and allows steady state flow Original grains develop high densities of tangled dislocations, and very small (~1 μm), polygonal, strain-free recrystallized grains develop by grain boundary migration (Fig 3a) Original grains remain little deformed but are progressively consumed by the recrystallized grains (Fig. 3b). The recrystallized grains can undergo an increment of unimpeded dislocation glide before they become work-hardened and are replaced by a new episode of grain boundary migration, thus the aggregate undergoes progressive strain weakening until recrystallization is complete At any time, some recrystallized grains have a very low dislocation density (~10⁸ cm⁻²) while others have an intermediate to very high density (~10¹⁰ cm⁻²) Although we cannot rule out a component of diffusion creep in the fine, recrystallized grains, the presence of a very strong crystallographic preferred orientation indicates that the dominant deformation mechanism is dislocation creep.

Fine grained albite samples

(i) 'Dry' samples: dislocation creep. To investigate the effect of grain size alone, we prepared a 2-10 μm sample which was vacuum dried at 300°C (to remove adsorbed water) and weld sealed, and thus had the same 'water' content as the coarse grained starting material (~0 1 wt%), and deformed it at 900°C, 1500 MPa and 2 × 10⁻⁵ s⁻¹ The microstructures of this sample are identical to those of the recrystallized portions of coarse grained samples deformed at the same conditions, which we have previously shown to result from recrystallization accommodated dislocation creep. There has been an overall grain size reduction; the grains are polygonal with irregular boundaries (Fig. 3c). Throughout the sample one observes very small (~0 5 μm diameter) polygonal recrystallized grains with a very low dislocation density growing into grains with a much higher density (Fig 3d) Thus it appears that for

albite deformed at these conditions, a reduction in grain size from 180 to 2-10 μm by itself does not induce a visible component of diffusion creep

(ii) 'Wet' hydrostatic sample A fine grained aggregate with ~0 9 wt% water was held hydrostatically at 900°C and 1500 MPa for 6 h, and then removed for observation The microstructures of this sample, which represents the 'starting material' for many of the deformed samples described in this paper, are illustrated in Figs 4(a) & (b) The grains are irregular in shape, and there is a range of grain sizes due to crushing during pressurization followed by sintering and some grain growth during the hydrostatic anneal (Fig 4a) TEM shows abundant small angular pores at grain triple junctions (Fib 4b), which we believe to have been filled with water during the experiment. Some of the grains contain mechanical twins, but there are few dislocations (Fig. 4b).

(iii) 'Wet' samples: diffusion creep. Fine grained samples deformed at the same conditions as the 'dry' samples, but with a water content of ~0.9 wt%, show dramatic differences in their microstructures. We see no differences in the microstructures of samples with ~0.7 wt% water added which were weld sealed and buffered and those which were mechanically sealed and unbuffered. The microstructures of a buffered (Ni NiO), water added, weld sealed sample shortened ~40% at 900°C, 1500 MPa and 2 × 10⁻⁵ s⁻¹ are illustrated in Figs. 4(c)-(f). There has been considerable grain growth during the deformation, as evidenced by the large size and rectangular shape of many of the grains (Fig 4c). TEM shows sharp, square corners which must have grown (or been preserved) during deformation, and almost all of the grains have a very low dislocation density (Figs. 4d & e). Most of the grain boundaries are open (Figs 4d-f). These open grain boundaries cannot just be due to ion thinning of the TEM foils, because we still see the impregnating epoxy along them (Fig 4f, small arrows) Incongruent dissolution of albite is indicated by the occasional presence of subspherical grains (~0.1 μm) of quartz (identified by analytical electron microscopy, EDX) at triple junctions (Fig 4f, large arrow). Although we have noted occasional trace amounts of melt in these samples, in most cases the pores and gaps are not melt filled. We believe that most of them were filled with water during the experiments.

(iv) Effect of temperature To investigate the effect of temperature on the fine grained aggregates, we deformed a mechanically sealed sample containing ~0 2 wt% water at the same pressure and strain rate but a higher temperature (1100°C) This sample showed the same microstructures observed in the samples containing ~0 9 wt% water deformed at 900°C: square corners, very low dislocation density, and open pores along grain boundaries and at grain boundary triple junctions (Figs 5a & b). It shows even more evidence of grain growth; a number of the grains are larger than any in the starting material (Fig 5a). There are no polygonal grains with variable dislocation density, indicative of dislocation
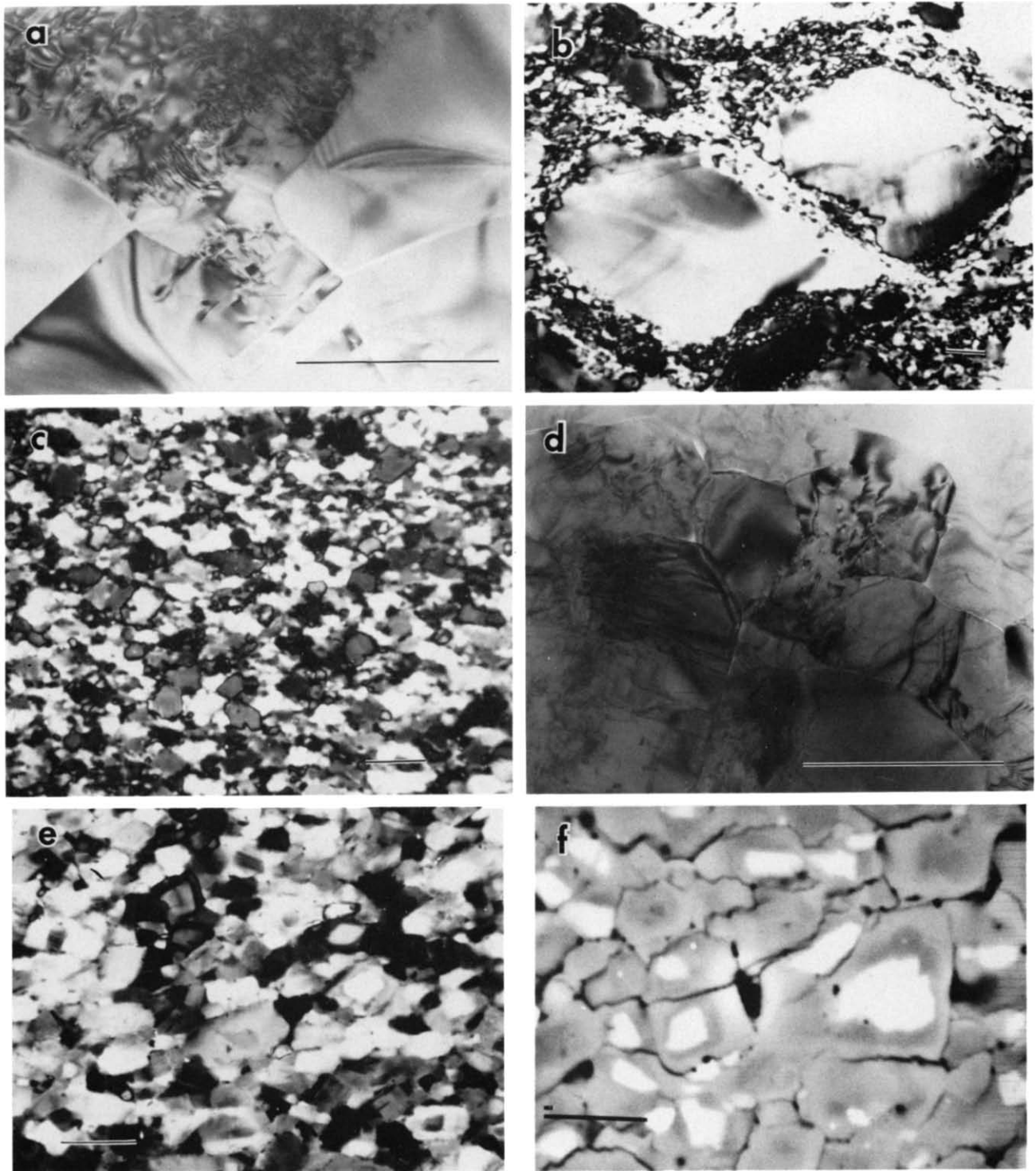
Fig. 3. (a)–(d) Dislocation creep microstructures developed in dry (~0.1 wt% water) feldspar aggregates. Scale bars for micrographs: optical, 1.0 mm; TEM, 1.0 μm. (a) TEM micrograph of coarse-grained aggregate shortened ~60% at 900°C, 2 × 10⁻⁶ s⁻¹ and 1500 MPa, showing dislocation-free recrystallized grains growing into original grain with high dislocation density. (b) Optical micrograph from same sample showing relatively undeformed remnants of original grains surrounded by recrystallized grains. (c) Optical micrograph of vacuum-dried 2–10 μm aggregate shortened ~50% at 900°C, 2 × 10⁻⁵ s⁻¹, and 1500 MPa. (d) TEM micrograph of same sample showing polygonal recrystallized grains with variable dislocation density. (e) & (f) Microstructures of 2–10 μm two plagioclase aggregate containing ~0.2 wt% water deformed at 900°C, 2 × 10⁻⁶ s⁻¹ and 1000 MPa. (e) Optical micrograph showing core and rim relations indicating extensive dissolution and reprecipitation. Scale bar 1.0 mm. (f) Back scattered electron microprobe image showing cores of composition ~An₇₀, an albitic zone, and rims of composition ~An₄₀. Scale bar 1.0 μm.
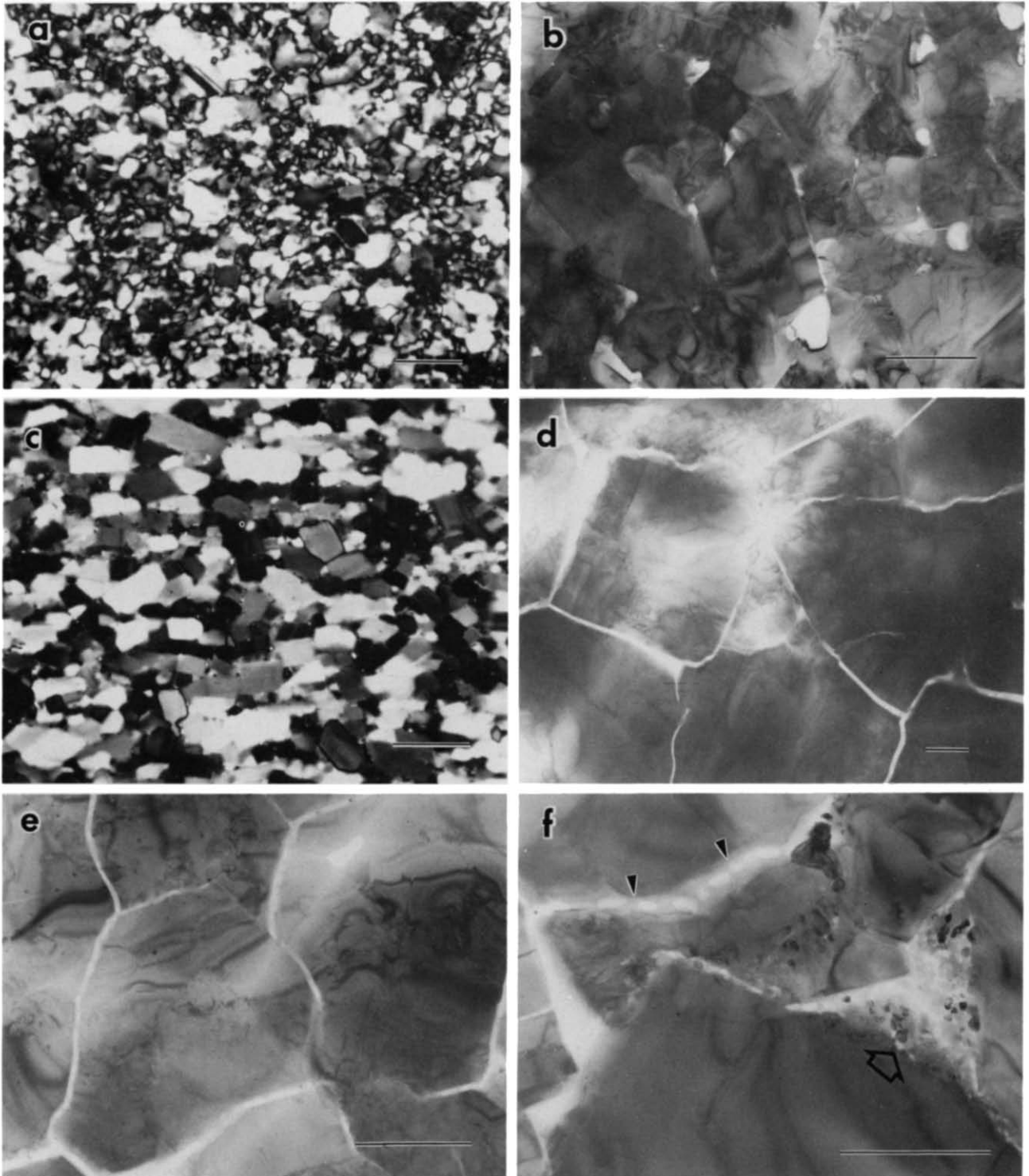
Fig 4 Diffusion creep microstructures developed in 2–10 μm aggregates containing ~0.9 wt% water at 900°C and 1500 MPa. Scale bars for micrographs optical, 1.0 mm, TEM, 1.0 μm (a) Optical micrograph of sample held hydrostatically 6 h (b) TEM micrograph of same sample (c) Optical micrograph of sample shortened ~50% at 2 × 10⁻⁵ s⁻¹. Note grain growth (d)–(f) TEM micrographs of same sample (d) Note open pores and grain boundaries and square corners on some grains (e) Note low dislocation density (f) Note fine grained SiO₂ rich material at triple junction (large arrow) Epoxy along grain boundary (small arrows) shows it was open during deformation
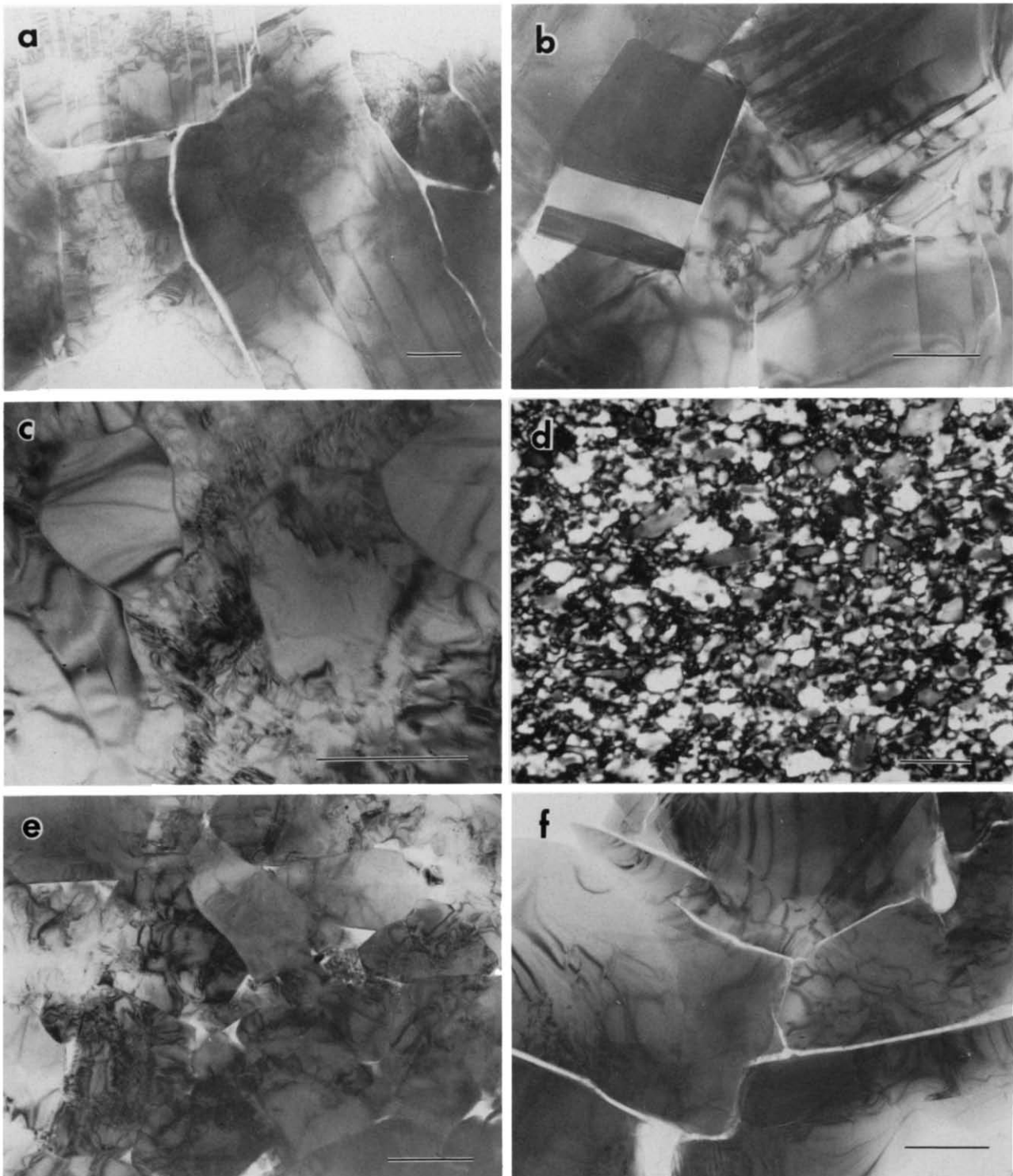
Fig. 5. Diffusion creep microstructures developed in 2–10 μm aggregates at other conditions. Scale bars for micrographs optical, 1.0 mm, TEM 1.0 μm. (a) & (b) TEM micrographs of sample with ~0.2 wt% water shortened ~50% at 1100°C, 2 × 10⁻⁴ s⁻¹ and 1500 MPa. Note large grains with square corners, low dislocation densities, and some twins, and open grain boundaries. (c) TEM micrograph of dry aggregate (~0.1 wt% water) deformed at same conditions, showing dislocation creep microstructures. (d) Optical micrograph of sample with ~0.9 wt% water shortened ~50% at 800°C, 2 × 10⁻⁵ s⁻¹ and 1500 MPa. (e) TEM micrograph of same sample, note open pores and low dislocation density. (f) TEM micrograph of sample with ~0.2 wt% water shortened ~50% at 900°C, 2 × 10⁻⁶ s⁻¹ and 1500 MPa. Note open pores and grain boundaries, square corners and low dislocation densities.

creep. Thus it appears that even for a decrease in the amount of water present (~0.2 instead of ~0.9 wt%), an increase of 200°C strongly enhances diffusion creep compared to dislocation creep.

There is a significant difference between the microstructures just described in the 2-10 μm sample with ~0.2 wt% water at 1100°C, and those of a coarse-grained, dry sample (containing ~0.1 wt% water), which was deformed at the same conditions. The latter sample shows polygonal grains of ~1 μm diameter with variable dislocation density and tight grain boundaries, which are characteristic of dislocation creep (Fig. 5c). Thus it appears to be the presence of the additional ~0.1 wt% adsorbed water in the 2-10 μm sample which has allowed diffusion creep to be competitive, even though the average grain size (~5-10 μm) is *larger* than that of the sample showing dislocation creep (1-2 μm).

In order to determine whether fine-grained samples with water added exhibited evidence of diffusion creep at lower temperature, we deformed a mechanically sealed sample containing ~0.9 wt% water at 800°C, 1500 MPa and 2×10^{-5} s^{-1}. At these conditions, dry coarse-grained samples (with ~0.1 wt% water) show deformational behavior that is transitional between cataclastic flow and dislocation creep, original grains develop high densities of tangled dislocations, mechanical twins and microcrush zones, together with some strain-free, polygonal, dynamically recrystallized grains (Tullis & Yund 1987). However, the wet 2-10 μm sample shows clear evidence of dominantly diffusion creep. The average grain size (Fig. 5d) is about the same as the 'starting material' (Fig. 4a), and much smaller than that in the sample deformed at 900°C (Fig. 4c). The average dislocation density is low, and there are abundant open pores and channels along grain boundaries (Fig. 5e). Thus with increasing temperature, wet, fine-grained aggregates appear to undergo a transition directly from cataclastic flow to diffusion creep, bypassing dislocation creep, at least at experimental strain rates.

(v) Effect of strain rate We have deformed a 2-10 μm sample with ~0.2 wt% water at 900°C and 2×10^{-6} s^{-1}. This sample showed the same microstructures observed in the samples containing ~0.9 wt% water which were deformed at the same temperature and 2×10^{-5} s^{-1}: square corners, very low dislocation densities, and open grain boundaries and pores at grain triple junctions (Fig 5f). Thus, even for a reduced water content (~0.2 wt% compared to ~0.9 wt%), a decrease in strain rate of one order of magnitude strongly increases the contribution of grain boundary diffusion creep compared to recrystallization accommodated dislocation creep.

Additional evidence for a strong effect of strain rate, and an additional type of evidence for the dominance of diffusion creep, comes from experiments on mixtures of two plagioclase compositions. We have deformed samples consisting of equal amounts of two plagioclases (An_1 and An_{79}), of three different grain sizes (160-180, 53-63 and 2-10 μm), at 900°C, 1000 MPa and 2×10^{-6}

s^{-1}. The compositional relations of these samples provide strong evidence for a change in deformation mechanism with decreasing grain size and increased water content. The 160-180 and 53-63 μm samples, which we believe to have negligible adsorbed water, show progressive dynamic recrystallization, essentially identical to that described previously from pure albite aggregates of the same grain size deformed at the same conditions (Tullis & Yund 1985). The relatively rapid and repeated motion of high angle grain boundaries during dynamic recrystallization has allowed a much more rapid homogenization of the plagioclase composition than could be achieved by volume and grain boundary diffusion alone (Yund & Tullis in press).

In contrast, the 2-10 μm samples, which contained ~0.1 wt% adsorbed water (for a total of ~0.2 wt%), show microstructures similar to those of the 2-10 μm pure albite aggregates deformed at the same temperature and strain rate (and 1500 MPa): rectangular grains with square corners, very low average dislocation densities, and open grain boundaries and triple junction pores. In addition, most of the larger grains show distinct cores and rims which have different compositions (Fig 3e). Analytical transmission electron microscopy techniques have shown that the cores are portions of original grains, most often An_{79}, which are overgrown with a narrow albitic zone (~Ab_{20-30}) and a wider ~An_{40} rim (Yund & Tullis in press). This zonation is observable in a back scattered electron image (Fig 3f). There are fewer grains with Ab-rich cores, and the smaller grains are mostly ~An_{40}. The explanation for this zoning and the fewer number of Ab-rich cores appears to be related to the dissolution behavior of plagioclase; at 800°C and 200 MPa the albite component of plagioclase goes into solution leaving the anorthite component behind (Adams 1968). Thus the An_1 grains tend to dissolve before the An_{79} grains and to precipitate as a narrow zone of An_{20-30} on the original An_{79} grains. With increasing time the grains become more homogenized and the outer rims and most of the smaller grains develop a composition of ~An_{40}. This evidence of solution and reprecipitation contrasts strongly with the compositional relations in the drier 53-63 μm samples, where the small (~1-2 μm), polygonal grains have a variable but intermediate composition, consistent with compositional exchange during dynamic recrystallization by diffusion along migrating high angle grain boundaries. The latter process is documented and discussed in a separate paper (Yund & Tullis in press).

(vi) Effect of confining pressure For comparison with the 1500 MPa samples, we have deformed two 2-10 μm aggregates of albite at 900°C and 2×10^{-5} s^{-1}, but at 600 instead of 1500 MPa; one was vacuum dried at 300°C and weld sealed, and the other had 0.7 wt% water added. The microstructures of the ~0.9 wt% water sample (Figs 6a-c) are indistinguishable from those of the equivalent sample deformed at 1500 MPa (Figs 4c-f), consistent with their nearly identical strengths (Figs. 2b & c). Both samples contain the same large rectangular

grains, square corners, very low dislocation density and open grain boundaries Thus we infer that diffusion creep was dominant in both

In contrast, the microstructures of the sample with -0 1 wt% water deformed at 600 MPa (Figs 6d-f) are very different from the dislocation creep microstructures of the equivalent sample deformed at 1500 MPa (Figs 3c & d) The average grain size is much smaller than the starting grain size (Fig 6d) This presumably is due to crushing (e.g Tullis & Yund 1987), since there are no polygonal dynamically recrystallized grains The grains have a variable but locally extremely high dislocation density (Figs. 6e & f) Most of the grain boundaries are tight, although there are open pores in some areas (Fig. 6f). Thus the deformation appears to have been accommodated by cataclastic flow with limited dislocation glide. This change in deformation behavior with decreasing confining pressure is consistent with what we have found previously for dry, coarse grained aggregates deformed at 900°C, they show a switch from dislocation creep to ductile faulting with a decrease in pressure from 1500 to 500 MPa (Tullis et al. 1979), apparently related to the decreased f_{H_2O} (Tullis & Yund 1989, Farver & Yund 1990a).

DISCUSSION

Evidence for grain boundary diffusion creep

The combination of our mechanical and microstructural results indicates that the fine-grained aggregates containing ~0 1 wt% water deformed at 900°C, 1500 MPa and 2×10^{-5} s^{-1} underwent dominantly recrystallization accommodated dislocation creep whereas those with ~0 9 wt% water underwent dominantly fluid assisted, grain boundary diffusion creep. This evidence is briefly summarized and evaluated below

The strengths and the microstructures in the *vacuum dried*, fine grained aggregates (with ~0.1 wt% water) are identical to those observed previously in coarser grained dry aggregates with the same water content deformed at the same conditions (Tullis & Yund 1985), where the flow law was determined to be power law creep (Shelton & Tullis 1981). This previous work showed that for starting grain sizes ranging from 50 to 200 μm, the size of the dynamically recrystallized grains is about 0 5-1.0 μm (at 900°C, 2×10^{-5} s^{-1} and 1500 MPa) Despite the extremely small size of the recrystallized grains, there is no microstructural evidence for a switch in dominant deformation mechanism to diffusion creep: the grains have a variable dislocation density, ranging up to ~ 10^{11} cm^{-2}, and a strong crystallographic preferred orientation (as indicated by extinction and gypsum plate effects). Also, despite the fact that progressive dynamic recrystallization causes strain weakening, the flow law remains a power law with stress exponent close to 3. An additional piece of evidence indicating that the dry, fine grained aggregates undergo

dominantly recrystallization accommodated dislocation creep is the fact that their strength at a confining pressure of 600 MPa is substantially higher than that at 1500 MPa, just as observed for coarse grained aggregates of feldspar and of quartz deformed in the dislocation creep regime (Tullis et al 1979, Tullis & Yund 1980, 1989, Kronenberg & Tullis 1984)

Evidence for the dominance of grain boundary diffusion creep in the *water added* fine-grained feldspar aggregates (with ~0.9 wt% water at 900°C and 2×10^{-5} s^{-1}, and with ~0 2 wt% water at 1100°C and 2×10^{-5} s^{-1}, and at 900°C and 2×10^{-6} s^{-1}) is primarily microstructural The microstructures of these samples are very different from those of the dry aggregates deformed at the same conditions. First, these samples show progressive grain growth, rather than maintenance of an equilibrium dynamically recrystallized grain size Second, the average free dislocation density is substantially lower. Third, there are abundant open pores and gaps along the grain boundaries, most of which appear to have been filled with fluid (not melt) Fourth, in the samples composed of two plagioclase compositions, the compositional differences between cores and rims indicate that solution and reprecipitation resulted in the growth of some grains. Finally, although these water added fine-grained aggregates do exhibit a strong crystallographic preferred orientation (as indicated by extinction and gypsum plate effects), this does not argue against diffusion creep because (1) the samples started out with a strong preferred orientation due to hot pressing, and (2) it appears that grain growth is anisotropic and so may actually enhance the starting preferred orientation (e g. Fig. 6a) (Shelley 1989)

Although we realize the potential danger of inferring the portion of total sample strain contributed by different mechanisms solely from microstructures (e.g Brodie & Rutter 1986), the differences in the suites of microstructures are so striking that we feel confident in concluding they reflect a switch in the *dominant* deformation mechanism. We are beginning a study to determine the flow laws of fine grained aggregates with different water contents, utilizing a molten salt sample assembly in order to achieve greater stress sensitivity (Green & Borch 1989).

What is the possibility that the difference in behavior of the wet and dry fine grained aggregates is simply due to hydrolytic weakening? Previous studies of coarse grained albite aggregates (Tullis & Yund 1980) showed that addition of ~0.2 wt% water caused definite weakening for deformation within the dislocation creep regime, consistent with our observations of reduced strength of the wet fine grained aggregates However, hydrolytic weakening of the coarse grained aggregates was not associated with significant changes in the deformation microstructures; the most obvious effect was a slight increase in the size of the recrystallized grains The microstructures of the fine grained aggregates with approximately the same amount of water (~0.2 wt%) deformed at the same conditions (900°C, 2×10^{-6} s^{-1}, 1500 MPa) are very different (Fig 5f), they are not

consistent with dislocation creep and therefore cannot be due to hydrolytic weakening. We conclude that although some of the reduced strength of the wet fine grained aggregates could be due to hydrolytic weakening, the microstructures reflect a substantial component of diffusion creep. It remains to be determined whether coarse grained aggregates with greater amounts of added water might show evidence of diffusion creep in their fine grained recrystallized portions.

A final piece of evidence for the dominance of diffusion creep in the wet, fine grained aggregates is the similarity of the flow stress for samples deformed at 600 and 1500 MPa. As mentioned above, this behavior is in strong contrast to the increasing strength with decreasing pressure shown by feldspar (and quartz) aggregates undergoing dislocation creep, but it is what one would expect for fluid assisted grain boundary diffusion creep. Dislocation creep depends on volume diffusion, which depends on pressure through its strong dependence on f_{H_2O} (Farver & Yund 1990a). Grain boundary diffusion creep depends on two factors. There are few data for grain boundary diffusion, but this process should be much less dependent on pressure, since the openness of the grain boundary cannot change very much between 600 and 1500 MPa. There are also few data for the solubility of feldspar as a function of pressure, but J Farver (personal communication 1990) observes no apparent increase in solubility of feldspar up to 1500 MPa, in strong contrast to the behavior of quartz.

Our evidence indicates that the transition from dislocation to diffusion creep depends on grain size, water content, temperature and strain rate. At 900°C, 1500 MPa and 2×10^{-5} s^{-1}, and for a grain size of 2-10 μm, there appears to be a transition from dominantly dislocation to diffusion creep as the water content is increased from ~0.1 to 0.9 wt%. For a grain size of 2-10 μm and a water content of ~0.2 wt%, there is a similar transition accompanying an increase of temperature from 900 to 1100°C or a decrease in strain rate from 2×10^{-5} to 2×10^{-6} s^{-1}.

It is not surprising that the transition from dislocation to diffusion creep at a given grain size is quite sensitive to fluid content. Diffusion rates in a grain boundary fluid, even if it is thin and therefore 'structured', should be significantly faster than those in a dry grain boundary (e.g. Rutter 1983, Rubie 1986). The degree of enhancement of grain boundary diffusion creep rates by fluids will depend on the degree of wetting of the grain boundaries. If the wetting angle for aqueous fluids in feldspar aggregates is < 60°, as it is for quartz (Watson & Brenan 1987), then even a very small amount of fluid (~1%) will form an interconnected network of channels along grain boundary triple junctions. We have observed evidence for these channels as well as for isolated pores (e.g Fig 4f) These microstructural features, plus the compositional zoning in the two plagioclase samples, indicate that the difference in deformation mechanism between the water added and vacuum dried fine grained aggregates results from faster diffusion due to the presence of interconnected fluid channels and pores in the former.

The compositional zoning also indicates that the deformation occurs by grain boundary rather than volume diffusion creep, verification would require careful evaluation of the grain size dependence of the flow stress

Significance of results for buffered samples

There has been much speculation recently about the effect of chemical environment on flow stress or deformation mechanism or both, Hobbs (1985) suggested that there might be a measurable strength dependence on hydrogen fugacity for deformation of silicates in the dislocation creep regime. Ord & Hobbs (1984) reported that for quartz single crystals deformed in buffered assemblies, there was a factor of 5 decrease in strength with a decrease in log f_{H_2} from 4.5 to -4.5. However, Kronenberg et al (1986) were unable to duplicate these results, and Rovetta et al. (1986) found that quartz crystals annealed in buffered assemblies showed an increase in broad band IR absorbance (correlated with water weakening) with increasing f_{H_2}. We have deformed fine grained quartz aggregates in the climb accommodated dislocation creep regime (Hirth & Tullis in press), using buffered sample assemblies identical to that shown in Fig 1, and found no detectable difference in strength or microstructure over a range of eight orders of magnitude of f_{H_2} (Tullis & Yund 1988) This is consistent with the recent results of Farver & Yund (1990b), showing that the oxygen diffusion rate in quartz (and feldspar) does not depend on f_{H_2} or f_{O_2}, although it depends strongly on f_{H_2O}

The fact that we find no differences in strengths or microstructures in the wet, fine grained feldspar aggregates deformed over a wide range of f_{H_2} and f_{O_2}, probably does not add much to the original debate concerning the possible effect of chemical environment on deformation, because the original hypotheses were formulated for deformation by dislocation creep controlled by volume diffusion, whereas our buffered samples all appear to have deformed dominantly by grain boundary diffusion creep. A far more important factor affecting deformation by this mechanism is whether the fluid is wetting or not (Watson & Brenan 1987, Yund & Farver 1990)

Comparisons with other materials

Our inference of a switch from dislocation to diffusion creep in the water added, fine grained aggregates is based primarily on microstructural evidence, but is consistent with microstructural observations made on other materials where there is additional support from rheological studies. For dry aggregates of calcite, Schmid et al (1977, 1980) observed that decreasing grain size caused a change from dislocation to diffusion creep. At 400°C and 10^{-5} s^{-1}, decreasing the grain size from 200 to 4.2 μm was accompanied by microstructural changes from flattened, internally deformed grains with a moderately high dislocation density and well formed subgrains to equant, strain free grains with a low dislocation density
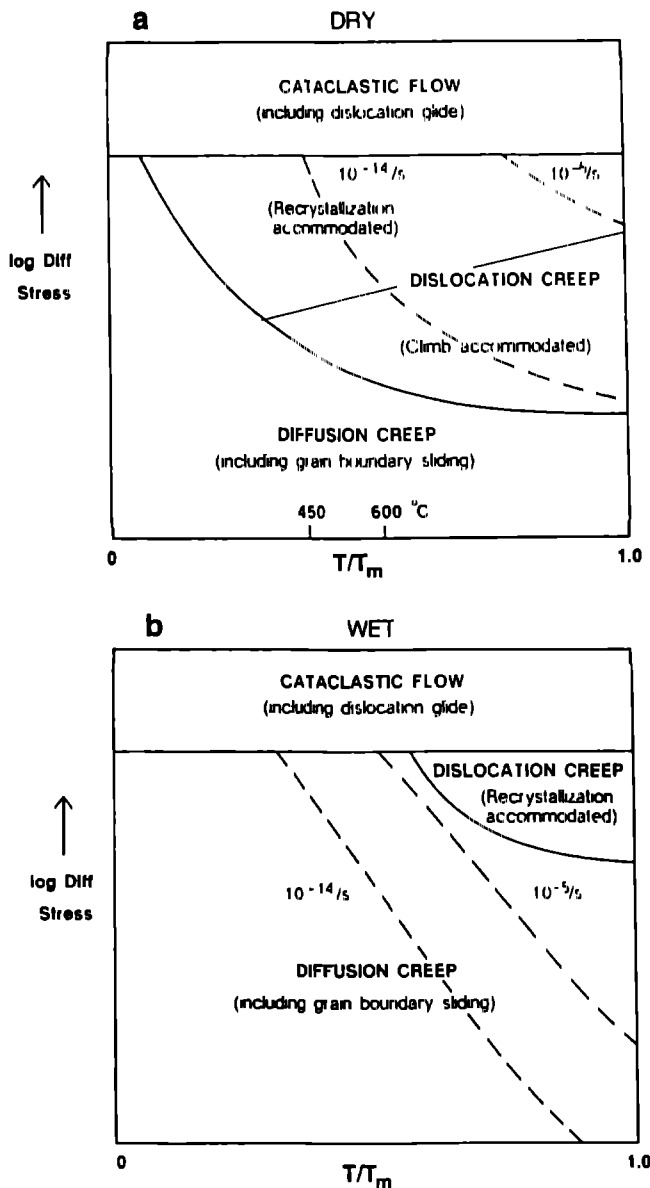
a   DRY

b   WET

Fig. 7 Schematic deformation mechanism maps for fine grained (~2-10 μm) feldspar aggregates (a) Map for 'dry' aggregates (b) Map for 'wet' aggregates Dotted lines show strain rate contours for 10^{-5} and for 10^{-14} s^{-1}

aggregates (Fig 7a) shows that at an experimental strain rate of 10^{-5} s^{-1} there is a transition with increasing temperature from cataclastic flow to recrystallization accommodated dislocation creep (Tullis & Yund 1987). Although dislocation climb becomes easier with increasing temperature, melting precludes any experimental investigation of climb-accommodated dislocation creep. The natural strain rate contour (10^{-14} s^{-1}) shows a transition from cataclastic flow to recrystallization accommodated dislocation creep at low to moderate metamorphic grades (e.g Evans 1988), and a transition to climb accommodated dislocation creep at high grades (e.g. Simpson 1985, White & Mawer 1986). The latter transition is the least-well constrained at present: the slow natural strain rates should allow diffusion creep to occur in drier and coarser aggregates than is the case at experimental strain rates, but we have no way of know

ing whether the equilibrium recrystallized grain size is larger or smaller than the critical size for diffusion creep

The schematic deformation mechanism map for wet, fine grained feldspar aggregates (Fig. 7b) shows a different configuration Because of the faster diffusion rate through fluid pores, channels and films, the diffusion creep field is expanded at the expense of the dislocation creep field. At experimental strain rates there is a transition directly from cataclastic flow to fluid assisted grain boundary diffusion creep At natural strain rates, we infer that this same transition will occur at lower temperatures Confirmation of this is provided by Shelley's (1989) observation that albite in lower greenschist grade schists shows textures and preferred orientations indicative of anisotropic selective growth, rather than cataclastic or plastic deformation. (It is important to note that wet, coarse-grained feldspar aggregates would be able to deform at high metamorphic grades at natural strain rates by climb accommodated dislocation creep without significant grain size reduction, and so on a deformation mechanism map for this situation the dislocation creep field would be larger than that shown here.)

There are several implications of the experimental results for naturally deformed feldspathic rocks Recrystallization accommodated dislocation creep itself produces strain weakening that can lead to ductile shear zones (Tullis et al 1990) However, at natural strain rates, and especially in the presence of a grain boundary fluid phase, dynamically recrystallized grains would almost certainly be small enough to allow a switch in the dominant deformation mechanism to grain boundary diffusion creep, and this would allow even more strain localization, perhaps leading to the 'superplastic' mylonites described by Boullier & Gueguen (1975) Similarly, the extreme grain size reduction produced during frictional sliding or cataclastic flow of feldspars (Tullis & Yund 1987, Yund et al 1990), coupled with the fluid influx likely in such dilatant rocks, could promote a switch to diffusion creep even at relatively low temperatures Of course it is also likely that fine grain size and fluid influx would promote reaction to weaker, hydrous phases (e.g Mitra 1978, Evans 1988)

CONCLUSIONS

A regime in which grain boundary diffusion creep is dominant has been identified in experimentally deformed fine grained (2-10 μm) feldspar aggregates, on the basis of mechanical and microstructural evidence This deformation mechanism is enhanced by increasing amounts of water, increasing temperature, and decreasing strain rate. For example, at 800-900°C and 2×10^{-5} s^{-1}, deformation occurs dominantly by recrystallization accommodated dislocation creep when the aggregates contain ~0 2 wt% water, but by grain boundary diffusion creep when the aggregates contain ~0.9 wt% water Conversely, for samples containing ~0.2 wt% water, deformation occurs dominantly by dislocation creep at 900°C and 2×10^{-5} s^{-1}, but dominantly by

diffusion creep at 1100°C and 2 × 10⁻⁵s⁻¹, and at 900°C and 2 × 10⁻⁶ s⁻¹. At natural strain rates the transition should occur at lower temperatures and larger grain sizes, and may be important in ductile shear zone formation

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