GRAIN BOUNDARY TRANSPORT AND RELATED PROCESSES
IN NATURAL FINE GRAINED AGGREGATES

Report of Progress

for Period August 15, 1991 to August 15, 1992

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Grain Boundary Transport and Related Processes in Natural Fine Grained Aggregates

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Abstract

We are pleased to report that all of the original research objectives will be realized by the end of the project period. In summary, we have developed a new technique for measuring grain boundary diffusion rates in polycrystalline aggregates and have successfully employed this technique to determine oxygen grain boundary diffusion rates in natural fine-grained quartz aggregates (novaculites) over a wide range of temperatures (Farver and Yund, 1990; Farver and Yund, 1991a). In addition, we have demonstrated the major role of fluid composition on the microstructure and oxygen bulk diffusivity in a novaculite sample (Yund and Farver, 1990; Farver and Yund, 1992). Most recently, we have successfully produced hot-pressed fine-grained monomineralic quartz and feldspar aggregates and have measured oxygen grain boundary diffusion rates in these aggregates for comparison to the natural novaculite samples (Farver and Yund, 1991b). Details of these results follow.

Oxygen Grain Boundary Diffusion in Fine-Grained Quartz Aggregates

Oxygen grain boundary diffusion rates have been measured in two fine-grained quartz aggregates (Arkansas novaculite) with 1.2 and 4.9 μm diameter grains. SEM and TEM observations show that both samples have equilibrium microstructures consisting of equant grains with triple grain junctions that meet at $\sim 120^\circ$. In addition, the grain boundaries are very tight with physical widths on the order of ≤ 10 nm. Samples were annealed hydrothermally at 450° to 800°C and 100 MPa confining pressure using 98% ^{18}O enriched water. Profiles of $^{18}\text{O}/(^{18}\text{O}+^{16}\text{O})$ with depth from the surface were measured using an ion microprobe. Data are collected from a 68 μm diameter circle centered on a rastered area 150-200 μm on a side. Hole depths are measured using an optical interferometer. By collecting data from an area much larger than the grain size of the

sample, diffusion along many individual boundaries is averaged to yield a representative value for grain boundary diffusion in the sample.

Using graphical solutions appropriate to the boundary conditions employed, and knowing the volume diffusion coefficient, the product of the grain boundary diffusion coefficient (D') and effective boundary width (δ) is calculated. The value of $D'\delta$ is independent of the grain size, geometry and grain boundary tortuosity. An Arrhenius plot (Fig. 1a) of the data yields straight lines for both the 1.2 and 4.9 μm grain size samples and the Arrhenius parameters are: $D'\delta = 2.6$ and $3.4 \times 10^{-17} \text{ m}^3/\text{s}$, and activation energy (Q) = 27 ± 1 and $26 \pm 3 \text{ kcal/mol}$, respectively. The activation energy of both samples, $\sim 27 \text{ kcal/mol}$ (113 kJ/mol), is significantly less than that for volume diffusion of oxygen in quartz, but greater than that for ionic diffusion in a static fluid. Measured $D'\delta$ values are within the range of values reported from theoretical considerations and field observations as well as experimentally determined lamellar boundary diffusion of oxygen in perthite. Assuming an effective grain boundary width of $\sim 10 \text{ nm}$, the measured oxygen grain boundary diffusion is 3 to 4 orders of magnitude greater than oxygen volume diffusion in quartz and ~ 5 orders of magnitude less than ionic diffusion in a static fluid over the temperature range of the experiments.

The Role of Fluid Composition on Microstructure and Oxygen Grain Boundary Transport in Fine-Grained Quartz Aggregates

Oxygen grain boundary and bulk diffusion rates have been measured in the 1.2 μm grain size quartz aggregate (Arkansas novaculite) described above, after anneals with wetting and non-wetting fluids, to determine the effect of microstructure on oxygen grain boundary diffusion rates. Samples were annealed at 800°C and 150 MPa confining pressure for 6 to 12 days with pure CO_2 , pure H_2O , or $\text{H}_2\text{O} + \text{NaCl}$ ($\sim 6\text{M}$) to produce new equilibrium microstructures. The pure CO_2 and pure water fluids produced non-wetted structures ($\theta > 60^\circ$); samples annealed in pure CO_2 showed no changes, and samples annealed in pure water showed minor changes, including the formation of small pores at many of the triple grain junctions. In contrast, the water + NaCl fluid produced a wetted microstructure ($\theta < 60^\circ$) with large pores at essentially all of the triple junctions. These microstructures are consistent with the wetting behavior of these fluids for quartz aggregates as reported by other workers.

After the textural equilibration anneals, the samples were annealed at 800° to 450°C and 100 MPa confining pressure with 98% ^{18}O -enriched water to determine the grain boundary diffusion rates. The short duration and lower temperature of the diffusion anneals produced no further changes in the microstructures. Profiles of $^{18}\text{O}/(^{18}\text{O} + ^{16}\text{O})$ with depth from the surface were measured using an ion microprobe, and the product of the grain boundary diffusion coefficient (D') and effective boundary width (δ) determined. Compared to the starting material, the $D'\delta$ values for samples texturally equilibrated with pure CO_2 and pure water are about the same and about four times greater, respectively. The $D'\delta$ values for samples texturally equilibrated with 6M

NaCl are three to four orders of magnitude greater than that for the starting material. In addition, the $D'\delta$ value for a sample texturally equilibrated first with 6M NaCl and then with pure CO_2 is about a factor of three greater than the value for the starting material, demonstrating that textural equilibration is reversible.

The results of this study indicate that grain boundary transport rates in quartz aggregates are strongly influenced by the microstructure which, in turn, depends on fluid composition. In non-wetted samples, changes in grain boundary structure or the formation of small isolated pores at triple junctions can change $D'\delta$ values by changing δ . However, this effect is minor compared to the change in $D'\delta$ values for samples with non-wetted versus wetted microstructures. The much faster rates for wetted samples are believed due to oxygen transport (probably in the form of molecular water) along the interconnected channels by ionic diffusion in a static fluid. The connected porosity in the wetted sample is <1% of the total porosity, a result which is consistent with estimates from natural contact zones.

Oxygen Grain Boundary Diffusion in Hot-Pressed, Fine-Grained Monomineralic Quartz and Feldspar Aggregates

The above technique that we have used for measuring grain boundary diffusion rates in polycrystalline aggregates requires fine grain size (<10 μm) material to eliminate grain boundary cracking. This constraint greatly limits the availability of natural samples, prompting us to hot-press fine-grained aggregates. We have begun with quartz which can be directly compared to the natural novaculites, and with alkali feldspars which afford the possibility of determining grain boundary diffusion rates for cations as well as oxygen in a geologically important mineral. The quartz aggregates were prepared using sized 1-3 μm diameter fragments of a natural quartz from US Silica (supplied by B. Evans). The albite aggregates were prepared using 2-4 μm sized fragments of a natural albite ($\text{NaAlSi}_3\text{O}_8$) and the orthoclase aggregates were prepared using 2-4 μm sized particles of 'orthoclase' (KAlSi_3O_8) glass from Corning (supplied by R. Cooper). All of the samples were vacuum dried at 250°C before hot-pressing at 900° (Qtz), 1060° (Ab) or 1100°C (Or) and 1.5 GPa, for 5 hours (Qtz) or 20-24 hours (Ab and Or). Grain-scale cracking was essentially eliminated by packing the sealed samples in NaCl and cooling at 3°C/minute along with slow decompression. TEM examination of the quartz aggregate indicates a microstructure similar to the novaculites with some porosity (<1%) located at three-grain junctions. The albite aggregate has some porosity (<1%) because the lath-shaped fragments do not pack well, but most grain boundaries are 'tight' (<10 nm). The orthoclase glass crystallizes to form an equilibrium texture with a very low porosity (near zero) and tight grain boundaries. Use of a fine particle size for devitrification of the Or glass is critical to produce an equilibrium rather than a spherulitic texture (R. Cooper, pers. comm.).

The product of the oxygen grain boundary diffusion coefficient (D') and the effective grain boundary width (δ) has been determined for these aggregates. The $D'\delta$ values for the Or and the Ab

aggregates are similar, and at 600°C are approximately a factor of four greater than that for a 4.9 μm novaculite and nearly equal to oxygen diffusion along macroperthite lamellae. The similarity between the D^{δ} values obtained for the two different feldspar aggregates indicates that the small amount of porosity remaining in the albite aggregate has no measurable influence on the oxygen grain boundary diffusion rates. This is consistent with our previous observations for quartz aggregates which indicated that it is not simply the presence, but rather the interconnectedness, of the porosity that influences the grain boundary transport rates in fine-grained aggregates. The activation energies for the feldspar aggregates, ~ 18 kcal/mole, are less than that for the 4.9 μm novaculite (26 kcal/mole), and much less than that for macroperthite lamellar boundaries (43 kcal/mole). The results of this study indicate that these hot-pressed aggregates can provide suitable material for grain boundary diffusion determinations of oxygen, and that the feldspar aggregates should be suitable for cation determinations as well.

Publications Resulting from DOE Sponsored Research

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