FINAL REPORT

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Title: Diffusional Transport and Fluid Connectivity in Mineral Aggregates

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DESCRIPTIVE SUMMARY

The objectives of this study were to determine diffusional transport rates of oxygen and selected geologically and environmentally important cations in polycrystalline mineral aggregates. The samples included both natural and hot-pressed single and polyphase aggregates of common mineralogies. In addition to determining grain boundary diffusion rates in these samples, bulk diffusivity measurements were made to evaluate the connectivity of common geological fluids as a function of temperature, pressure, fluid composition and volume fraction, mineralogy (anisotropy of interfacial energies), and stress state in the solid. An integral part of these investigations was the detailed characterization of the sample microstructures using SEM and TEM in order to evaluate whether a correlation between microstructure observations and bulk diffusional transport distances can be established, thus providing a valuable tool for predicting diffusional transport and fluid connectivity in natural samples. Applications of these data include evaluating the retentiveness of different geological medium for the isolation and confinement of nuclear and chemical wastes, modeling the migration of formation fluids and hydrocarbons through different rock types to refine exploration and development strategies for more efficient oil and natural gas recovery, and determining fluid/rock interactions and thermal histories from isotope systematics which, among other things, provide models for modern-day geothermal/hydrothermal energy systems and ore-body deposition associated with fossil hydrothermal systems.
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DESCRIPTION OF INDIVIDUAL RESEARCH PROJECTS

All of the objectives outlined in the research proposal have been achieved. In addition, as part of a no-cost extension of the project, the research was expanded to include experimental determinations of silicon diffusion in mineral aggregates when it became apparent that this important contribution was possible using our experimental methods. Details of each part of the research follow. Seven manuscripts have been published in peer reviewed international scientific journals, ten abstracts were presented at meetings of the American Geophysical Union (three of which were invited), results of this research were presented as an invited talk at a Gordon Conference, and four additional papers are in review or will be submitted for publication by the end of 1999.

Magnesium Grain Boundary Diffusion in Forsterite Aggregates at 1000°-1300°C and 0.1 MPa to 10 GPa

Magnesium grain boundary diffusion rates in forsterite aggregates have been experimentally determined from 1000° to 1300°C and 0.1 MPa to 10 GPa. The samples are fine-grained (mean linear intercept of 4.3 μm) hot-pressed aggregates. The technique employs a 26Mg-enriched surface layer and depth profiling using an ion microprobe. Values of the product of the grain boundary diffusion coefficient (D') and the effective grain boundary width (δ) were calculated using appropriate analytical solutions to the grain boundary diffusion equation of Whipple (1954). The Arrhenius parameters for the 0.1 MPa data for samples annealed in H₂+CO₂ and CO+CO₂ gas mixtures are $D_0' = 2.1 \times 10^{-10}$ and $7.7 \times 10^{-10}$ m²/s and $Q = 343\pm27$ and $376\pm47$ kJ/mol, respectively. The reproducibility of D'δ measurements is a factor of 2. A determination of D' independent of δ yields a calculated effective grain boundary width of ~3 nm, similar to the physical grain boundary width of 1-3 nm estimated from high-resolution transmission electron microscopy observations. The data indicate a very low pressure dependence for magnesium grain boundary diffusion in forsterite with an apparent activation volume for grain boundary diffusion of $\leq-1$ cm³/mol at 1100°C. The results of this study provide information concerning diffusion creep in solid state deformation of forsterite aggregates over a broad range of pressures and temperatures.

Publications:


Grain Boundary Diffusion of Oxygen, Potassium and Calcium in Natural and Hot-Pressed Feldspar Aggregates

Grain boundary diffusion rates of oxygen, potassium and calcium in fine-grained feldspar aggregates were determined experimentally. The starting materials were a natural albite rock from the Tanco pegmatite and aggregates hot-pressed from fragments of Amelia albite or Ab, Or and An composition glasses. The technique employed isotopic tracers (\(^{18}\)O, \(^{41}\)K, \(^{42}\)Ca) either evaporated onto the surface or in an aqueous solution surrounding the sample and depth profiling using an ion microprobe (SIMS). From the depth profiles, the product of the grain boundary diffusion coefficient (D') and effective boundary (δ) was calculated using numerical solutions to the appropriate diffusion equation. The experimental reproducibility of D'δ is a factor of 3. A separate determination of D independent of δ yields an effective grain boundary width of ~3 nm, consistent with high resolution TEM observations of a physical grain boundary width <5 nm. Oxygen (as molecular water) grain boundary diffusion rates were determined in the Ab and Or aggregates at 450° to 800°C and 100 MPa (hydrothermal), potassium rates in Or aggregates at 450° to 700°C both at 0.1 MPa (in air) and at 100 MPa (hydrothermal), and calcium rates in An aggregates at 700° to 1100°C and 0.1 MPa (in air). Oxygen grain boundary diffusion rates are similar in all three of the Ab aggregates and in the Or aggregate. Potassium and oxygen depth profiles measured in the same samples yield different D'δ values, confirming a diffusional transport mechanism. Potassium diffusion in the Or aggregate has a greater activation energy (216 vs 78 kJ/mol) than oxygen, and the Arrhenius relations cross at ~625°C. Potassium D'δ values in Or aggregates are about a factor of five greater in hydrothermal experiments at 100 MPa than experiments at 0.1 MPa in air. Calcium grain boundary diffusion rates in An aggregates are 4 to 5 orders of magnitude slower than potassium in Or and have greater (291 kJ/mol) activation energy. These results suggest that differences in formal charge and/or size of diffusing species may play an important role in their relative grain boundary diffusion rates.

Publications:


Interphase Boundary Diffusion of Oxygen and Potassium in K-Feldspar/Quartz Aggregates

Interphase boundary diffusion rates of oxygen and potassium in fine-grained K-feldspar/quartz aggregates were determined experimentally at 450° to 700°C and 100 MPa (hydrothermal). The starting materials were hot-pressed and crystallized using equal weights of natural quartz fragments and orthoclase (KAlSi3O8) composition glass. The technique employed isotopic tracers (18O, 41K) in an aqueous solution surrounding the sample, and depth profiling using an ion microprobe (SIMS). From the depth profiles, the product of the average boundary diffusion coefficient D'δ and average effective boundary width (δ) was calculated using numerical solutions to the appropriate diffusion equation. Potassium and oxygen profiles measured in the same samples are different, confirming a diffusional transport mechanism. Potassium diffusion in the K-feldspar/quartz aggregate has a greater activation energy than oxygen (218 vs. 75 kJ/mol), and the Arrhenius relations cross at 600°C. The D'δ values in the K-feldspar/quartz aggregates are about a factor of four greater than both oxygen and potassium D'δ values previously determined in monomineralic K-feldspar aggregates, and a factor of 20-40 greater than oxygen D'δ values in monomineralic quartz aggregates. The Arrhenius relations show the activation energies for both oxygen and potassium are similar for the K-feldspar/quartz and monomineralic K-feldspar aggregates, and significantly lower for oxygen in K-feldspar/quartz versus monomineralic quartz aggregates.

Publications:


Volume and Grain Boundary Diffusion of Calcium in Natural and Hot-Pressed Calcite Aggregates

Calcium self-diffusion rates in natural calcite single crystals were experimentally determined at 700° to 900°C and 0.1 MPa in a stream of CO2. Diffusion coefficients (D) were determined from 42Ca concentration profiles measured with an ion microprobe. The Arrhenius parameters yield an activation energy (Q) = 382 ±37 kJ/mol and pre-exponential factor (D0) = 0.13 m²/s, and there is no measurable anisotropy.

Calcium grain boundary diffusion rates were experimentally determined in natural (Solnhofen limestone) and hot-pressed calcite aggregates at 650° to 850°C and 0.1 to 100 MPa pressure. The Solnhofen limestone was first pre-annealed for 24 hours at 700°C and 100 MPa confining pressure.
under anhydrous conditions to produce an equilibrium microstructure for the diffusion experiments. Values for the product of the grain boundary diffusion coefficient \( (D') \) and the effective grain boundary diffusion width \( (\delta) \) were determined from \(^{42}\text{Ca} \) concentration profiles measured with an ion microprobe. The results show that there is no measurable difference between \( D'\delta \) values obtained for pre-annealed Solnhofen samples at 0.1 and 100 MPa or between hot-pressed calcite aggregates and pre-annealed Solnhofen samples. The temperature dependence for calcium grain boundary diffusion in Solnhofen samples annealed at 0.1 MPa is described by the Arrhenius parameters \( D'\delta = 1.5 \times 10^{-9} \text{ m}^2/\text{s} \) and \( Q = 267\pm 47 \text{ kJ/mol} \).

Comparison of the results of this study with previously published data show that calcium is the slowest volume diffusing species in calcite. The calcium diffusivities measured in this study place constraints on several geological processes that involve diffusive mass transfer including diffusion-accommodated mechanisms in the deformation of calcite rocks.

Publications:


Deformation-enhanced fluid distribution in feldspar aggregates and implications for ductile shear zones

Experiments at 900°C and 1.4 GPa show that the distribution of aqueous fluid in fine-grained feldspar aggregates changes from isolated pores under hydrostatic conditions to mostly wetted grain boundaries during deformation; the isolated pore distribution is rapidly regained during annealing following deformation. The deformation-enhanced fluid distribution causes a switch from dislocation creep to diffusion creep accompanied by a significant decrease in strength; it also increases the bulk transport rate through the aggregate by more than an order of magnitude. A change in fluid distribution is not observed in fine-grained quartz aggregates deformed at similar conditions. If deformation-enhanced fluid distribution occurs in naturally deformed feldspathic rocks, it could help to explain the localization of strain and enhancement of bulk transport in ductile shear zones.

Publications:


Oxygen Grain Boundary Diffusion in Natural and Hot-Pressed Calcite Aggregates

Oxygen grain boundary diffusion rates were experimentally determined in natural (Solnhofen limestone) and hot-pressed calcite aggregates at 300° to 500°C and 100 MPa water pressure. The Solnhofen limestone was pre-annealed for 24 hours at 700°C and 100 MPa confining pressure under anhydrous conditions to produce an equilibrium microstructure for the diffusion experiments. The synthetic calcite aggregates were formed by hot isostatic pressing of an intimate mixture of 1-2 μm calcite grains plus 5 wt % 0.3 μm alumina grains at 700°C and 200 MPa for 3-10 days. Values for the product of the grain boundary diffusion coefficient ($D\delta$) and the effective grain boundary diffusion width ($\delta$) were determined from $^{18}$O concentration profiles measured with an ion microprobe. There is no measurable difference between $D\delta$ values obtained for pre-annealed Solnhofen samples and hot-pressed calcite aggregates; the temperature dependence for oxygen grain boundary diffusion at 100 MPa is described by the Arrhenius parameters $D_0\delta = 3.8 \times 10^{-14}$ m$^2$/s and $Q = 127 \pm 17$ kJ/mol.

Comparison of the results of this study with previously published data show that the rate of oxygen grain boundary diffusion in calcite aggregates is four to five orders of magnitude greater than that of volume diffusion in calcite single crystals, and the activation energy is less. Grain boundary diffusion of oxygen in calcite aggregates is five to six orders of magnitude greater than that of calcium, when the latter is extrapolated to the temperature range of this study. In addition, oxygen grain boundary diffusion rates in calcite aggregates are about a factor of 4-10 and ~100 times greater than that in feldspar and quartz aggregates, respectively, under similar experimental conditions.

Publications:


Oxygen Bulk Diffusion Measurements and TEM Characterization of a Natural Ultramylonite: Implications for Fluid Transport in Mica-Bearing Rocks

Oxygen bulk diffusion rates were experimentally determined in a natural ultramylonite sample (~5 μm grain size; 15-20% biotite, 20% quartz, 60-65% feldspars, and minor Fe-oxides) from the Gerrish Island shear zone, SE Maine, USA. The diffusion experiments were done at 250° to 550°C and 100 MPa water pressure. Oxygen bulk diffusion rates were determined both parallel and perpendicular to the strong foliation of the sample. The Arrhenius parameters for transport parallel to the foliation are: $D_{0_{bulk}} = 2.0 \times 10^{-11}$ m$^2$/s and $Q = 30 \pm 6$ kJ/mol. The bulk diffusivity perpendicular to the foliation is about a factor of 3.5 less than parallel to the foliation with the same activation energy.
The values of bulk diffusivity and activation energy obtained are consistent with ionic diffusion through a static aqueous fluid suggesting that an interconnected fluid exists in the ultramylonite even under hydrostatic conditions. The microstructure of the ultramylonite was characterized using transmission electron microscopy (TEM). The nature and distribution of the interconnected fluid cannot be completely resolved from the TEM analysis; however, the low percentage of three-grain channels and open grain/interphase boundaries suggests that the fluid resides as a thin film on the grain surfaces. The results of this study have direct applications in many important geological settings and provide valuable insights into the observed rapid diffusion rates, strong lithological control, and pervasive nature of fluid transport in mica-bearing rocks.

Publications:


Silicon Diffusion in a Natural Quartz Aggregate: Constraints on Solution-Transfer Diffusion Creep

Silicon bulk diffusion rates were determined in a fine-grained (1.2 μm diameter) natural quartz aggregate (novaculite) from Hot Springs, AR. The diffusion experiments were done at 600° to 800°C and 150 MPa confining pressure (hydrothermal), and at 800° to 1100°C and 1 atm (in a stream of dry N₂). The technique employed an isotopic tracer (³⁰Si) and standard step-scan analysis using an ion microprobe (SIMS).

The temperature dependence of silicon bulk diffusion in the novaculite is described by the Arrhenius parameters: $D_{0,\text{bulk}} = 3.7 \times 10^{-10}$ m²/sec and $Q = 137\pm18$ kJ/mol, and $D_{0,\text{bulk}} = 6.2 \times 10^{-10}$ m²/sec and $Q = 178\pm38$ kJ/mol for the hydrothermal and dry experiments, respectively. At 800°C the silicon bulk diffusion rate at 150 MPa, hydrothermal is about a factor of ten greater than at 1 atm, dry. For an assumed effective grain boundary width of 2 nm, silicon grain boundary diffusion rates in novaculite are a factor of two to three less than oxygen diffusion rates for similar hydrothermal conditions, and more than twelve orders of magnitude greater than anhydrous silicon volume diffusion rates extrapolated to the temperature of these experiments. The results of this study provide valuable constraints on the role of diffusion-accommodated deformation in quartz-rich rocks.
Grain Boundary Diffusion of Selected Cations in a Natural Quartz (SiO$_2$) Aggregate

Bulk diffusion rates have been experimentally determined for Si, Ge, Ca, Sr, and Ba in a fine-grained (1.2 μm diameter) natural quartz aggregate (novaculite) from Hot Springs, AK. This material has been used previously for determining oxygen grain boundary diffusion rates. Bulk diffusivities for Si have been determined under hydrothermal conditions from 600°C to 800°C and 150 MPa, and under anhydrous conditions (1 atm in stream of dry N$_2$ gas) from 800°C to 1100°C. Bulk diffusivities have been determined under hydrothermal conditions at 150 MPa pressure and from 600°C to 800°C for Ge, and at 700°C for Ca, Sr, and Ba.

Charges for the hydrothermal experiments consist of a polished piece of novaculite weld-sealed in a thick-walled Au tube along with either $^{18}$O-enriched water and $^{30}$SiO$_2$ powder, or a 1000 ppm aqueous solution of Ge, Ca, Sr, or Ba. Charges for the anhydrous experiments were produced by quenching a thin layer of $^{30}$SiO$_2$ onto the surface of polished pieces of novaculite. After the experiments, isotope [$^{30}$Si/(30Si + $^{28}$Si)] or chemical [Ge, Ca, Sr, or Ba/Si] concentration profiles were determined using an ion microprobe (SIMS) and standard step-scan or depth-profile analysis techniques. At the time-temperature conditions of the experiments, volume diffusional exchange is negligible in the quartz grains (type-C kinetics regime), and the bulk diffusivity is obtained from standard inverse error function fits to the concentration profiles. Consistent with a diffusional exchange mechanism, no time dependence has been observed and the diffusion rates of different species in the same experiment are different.

The results indicate that Si bulk diffusivities are about a factor of 5-10 faster in hydrothermal experiments compared to anhydrous, with a slightly greater activation energy for the anhydrous experiments (~170 versus ~140 kJ/mol, respectively). Under hydrothermal conditions, Si bulk diffusion is about an order of magnitude slower than Ge, over the temperature range of the experiments. In addition, at 700°C, the bulk diffusivity of Ca is ~10x Sr, ~20x Ge, ~30x Ba, and ~200x Si, respectively, and about two orders of magnitude slower than oxygen.

Publications:


Full length paper to be submitted to Journal of the American Ceramic Society by December 1999.
Grain boundary diffusion rates of $^{30}$Si in aggregates of albite, orthoclase and anorthite compositions have been experimentally determined. The aggregates were first crystallized and hot pressed from 2-5 micron glass particles of the appropriate compositions and then hydrothermally coated with $^{30}$Si$^{18}$O$_2$. Diffusion anneals were done at either 0.1 MPa in dry nitrogen gas (<1 ppm H$_2$O) and from 800-1100°C or hydrothermally at 100 to 150 MPa and from 600-800°C. $^{30}$Si and $^{18}$O profiles were determined using SIMS and depth profiling or step scanning with an O$^+$ beam. The oxygen profiles were longer than the silicon profiles and consistent with published oxygen grain boundary diffusion rates (Farver and Yund, 1995). The anneals were in the type-C kinetic regime for silicon and yielded bulk diffusion coefficients, $D_{\text{bulk}}$. These were converted to $D_{gb\delta}$ using a grain diameter of 5 µm, a tortuosity of 1.5, and a grain boundary thickness (δ) of 2 nm.

For silicon diffusion the activation energies in the 0.1 MPa series are 210±71 (σ) kJ/mole for Ab, 194±71 kJ/mole for Or, and 176±61 kJ/mole for An. Log $D_{gb\delta}$ (m$^2$/s) at 900°C for Ab and Or is -23.3 and for An -24.3. Although the values for all three compositions at the dry conditions of the 0.1 MPa anneals are similar, diffusion in the An aggregate is measurably slower. For the hydrothermal Or anneals at 150 MPa the activation energy is 147±27 kJ/mole and at 900°C (extrapolated), log $D_{gb\delta}$ is -21.5 (m$^2$/s). Thus at 150 MPa water pressure the diffusion rate is faster than in the dry anneals at 0.1 MPa but only by about a factor of 100. For Ab aggregates, the Si diffusion rate at 900°C and 0.1 MPa is about 100 times slower than that for oxygen at 900°C and 100 MPa hydrothermal. The silicon D value for Ab at 1000°C and 0.1 MPa is very similar to the value determined from Ab rim growth rate (Liu et al., 1997) at 1000°C and 700 MPa in which the rate limiting diffusing species was unknown. Dry oxygen diffusion in the 0.1 MPa series is faster than Si diffusion as indicated by longer $^{18}$O profiles. Thus Si is the rate limiting grain boundary diffusion species in feldspars at the experimental conditions studied. The difference in grain boundary diffusion rates between silicon (dry or wet) and oxygen (wet) increases at lower temperatures due to the lower activation energy for oxygen when water is present.

Publications:


Full length paper to be submitted to American Mineralogist by 31 December 1999.
Silicon Diffusion in Forsterite Aggregates: Implications for Diffusion Accommodated Creep

Silicon bulk diffusion rates have been experimentally determined in fine-grained (~4 \( \mu m \) diameter) hot isostatically pressed forsterite aggregates (with slight excess in MgO or SiO_2) at 900° to 1200°C and 1 atm (in a stream of dry N_2 or H_2/CO_2 gas mixture).

Experimental charges were produced by quenching a thin layer of \(^{30}\text{Si}^{18}\text{O}_2 \) onto the surface of polished pieces of forsterite. After the experiments, isotope \([^{30}\text{Si}/(^{30}\text{Si} + ^{28}\text{Si})]\) concentration profiles were determined using an ion microprobe (SIMS) and standard step-scan or depth-profile analysis techniques. At the time-temperature conditions of the experiments, silicon volume diffusional exchange is negligible in the forsterite grains (type-C kinetics regime), and the bulk diffusivity is obtained from standard inverse error function fits to the concentration profiles. Consistent with a diffusional exchange mechanism, no time dependence has been observed and the different isotope tracers (\(^{30}\text{Si} \) and \(^{18}\text{O} \)) yield profiles of different lengths (oxygen is longer).

The results indicate that Si bulk diffusivities are not measurably influenced by buffering the SiO_2 activity with MgO or MgSiO_3, nor by changes in the oxygen and water fugacities from atmospheric to log \( f(\text{O}_2) = -13 \) and log \( f(\text{H}_2\text{O}) = -0.54 \) atm. At 1200°C, silicon grain boundary diffusion is about ten orders of magnitude greater than volume diffusion with a significantly lower activation energy (203 vs 320 kJ/mol). The Si grain boundary diffusion rates are similar to previously reported values for Mg in the same material. In addition, the Si grain boundary diffusion rate measured at 1000°C matches the value obtained by Yund (1997, CMP, 126:224-236) from Fo reaction rim growth studies, and the rate measured at 1250°C is within a factor of three of the value calculated by Hirth and Kohlstedt (1998, JGR, 100:1981-2000) from experimental Coble creep data.

Publications:


Full length paper to be submitted to Geophysical Research Letters by 31 December 1999.