The interaction of migrating grain boundaries and fluid inclusions in rock analogues: the effect of wetting angle and fluid inclusion velocity

Joyce Schmatz¹, Oliver Schenk¹,² and Janos L. Urai¹

Accepted for publication in Contributions to Mineralogy and Petrology

(1) Structural Geology, Tectonics and Geomechanics, Geological Institute, RWTH Aachen University, Lochnerstrasse 4-20, 52056 Aachen, Germany
(2) Schlumberger Center of Excellence for Petroleum Systems Modeling, Ritterstrasse 23, 52072 Aachen, Germany

Corresponding author: j.schmatz@ged.rwth-aachen.de
Phone: +49 241 80 95723
Fax: +49 241 80 92358
Abstract

The distribution of fluids in grain boundaries, fluid inclusion morphology and kinetics have important effects on the evolution of microstructure and transport properties and should be understood for correct interpretations for studies of thermobarometry and paleorheology. We compare results of in-situ annealing experiments on rock analogues in the presence of different pore fluids in transmitted light: bischofite with saturated brine, camphor with ethanol, and camphor with ethylene glycol. The solid–liquid systems vary in terms of wettability and solubility, while homologous temperatures, strain rates, annealing times and the initial textures are similar. In agreement with earlier work and theory, we observe different types of grain boundary–fluid inclusion interaction at sufficiently low grain boundary velocity such as drag and drop, necking, and the break up into arrays of smaller inclusions. In all three systems the maximum possible velocity of a fluid inclusion being dragged by a moving grain boundary is dependent on the fluid inclusion size. We interpret this to reflect the fluid inclusion mobility, and compare the trend with theoretical models which suggest that for all three systems the rate limiting process is bulk diffusion and not surface diffusion or solution-precipitation.

Keywords

Fluid inclusions; grain boundary migration; wetting angle; in situ experiments; fluid inclusion velocity
Introduction

Fluid-bearing grain boundaries serve as fast intergranular diffusion pathways and allow for stress-driven mass transfer such as pressure solution (dissolution-precipitation creep: e.g., Rutter 1976; Spiers and Schutjens 1990) or fluid-assisted grain boundary migration (e.g., Urai et al. 1987). Fluid distribution, its connectivity and the wetting properties of the solid-liquid interface have important consequences on rheology and mass transfer processes in rocks. Primary and secondary recrystallization as well as microfractures modify the grain-scale fluid distribution and complicate the interpretation of fluid inclusions with respect to varying p-T conditions in metamorphic rocks (Boullier 1999). In addition the second phase affects the recrystallized texture (e.g., Bons and Urai 1992; Herwegh and Kunze 2002; Becker et al. 2008) and therefore limits paleostress predictions by grain size piezometry (Fitz Gerald et al. 2006; Schléder and Urai 2007; Austin and Evans 2007).

Studying fluid inclusions in model systems contributes to an understanding of fluid-rock interactions in the deep crust (Renner et al. 2002; Schenk and Urai 2005; Walte et al. 2005; Schmatz and Urai 2010). For monomineralic rocks many studies have shown that the recrystallized grain size is controlled by the flow stress (e.g., Twiss 1977; Post and Tullis 1998), however the effect of fluids and solid second phases on the texture is still poorly understood. Immobile particles may pin the grain boundary (e.g., Smith 1948, Olgaard and Evans 1986) while a mobile second phase may be deformed and dragged along by a migrating grain boundary (Olgaard and Evans 1988; Schmatz and Urai 2010).

Schmatz and Urai (2010) show that above a critical grain boundary velocity, fluid inclusions do not affect passing grain boundaries in rock-analogue system camphor–ethanol, in agreement with models (Gottstein and Shvindlerman 1993). Below this limit they observed a range of interactions of fluid inclusions and grain boundaries, such as drag and drop of fluid inclusions and pinning of grain boundaries by immobile fluid inclusions. Basic theory predicts that if the ratio of fluid inclusion mobility \( M_{fi} \) and grain boundary mobility \( M_{gb} \) is \( M_{fi} / (N \cdot M_{gb}) \geq 1 \) (Fig. 1a, with the number of fluid inclusions per unit volume \( N \) ) fluid inclusions have a minor effect on grain boundary migration recrystallization and the recrystallized grain size, whereas a mobility ratio of \( M_{fi} / (N \cdot M_{gb}) < 1 \) (Fig. 1b) implies effects by drag and drop of second phase, and for \( M_{fi} / (N \cdot M_{gb}) \ll 1 \) Zener drag is dominant (e.g., Brook 1969; Herwegh and Berger 2004).
The mobility of fluid inclusions is controlled by transport of material, either by bulk diffusion (b), surface diffusion (s), or a solution-precipitation (sp) process (Fig. 1c, Chuang et al. 1979; Gratier and Jenatton 1984). As described in a number of models (e.g., Hsueh et al. 1982; Svoboda and Riedel 1992; Petrishcheva and Renner 2005), besides the fluid inclusion mobility two major parameters control the kinetics of fluid inclusions: firstly the \textit{dynamic wetting angle} $\psi$ of the liquid-solid interface and secondly the \textit{drag angle} $\theta$ under which the grain boundary exceeds a drag force on the fluid inclusion (Fig. 1c).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{(a) Sketch illustrating fluid inclusion drag for a grain boundary–fluid inclusions mobility ratio of $M_{FI}/(N \times M_{cal}) > 1$ and increasing grain boundary velocity $v_{1}-v_{n}$. (b) Sketch illustrating drag and drop for a mobility ratio of $M_{FI}/(N \times M_{cal}) < 1$ and increasing grain boundary velocity. The maximum fluid inclusion velocity $v_{\text{max}}$ is given for the maximum drag angle $\theta_{\text{max}}$. See text for details. (c) Schematic drawing showing parameters that control fluid inclusion–grain boundary interaction. Fluid inclusion is shaded grey with radius of curvature $a$, radius $r$, dynamic wetting angle $\psi$, and drag angle $\theta$. Mass transfer processes are illustrated as surface diffusion (s), bulk diffusion (b), and solution–precipitation (sp). Atom flux density is associated with the dynamic wetting angle, as it influences the radius of curvature of the attached fluid inclusion ($r = a \sin \psi$). Sketch modified after Svoboda and Riedel (1992).}
\end{figure}

In ceramics the concept of Zener drag describes the force and energy balance during drag and drop and the velocity of a fluid inclusions is given by $v = M_{FI} F_{d}$, where $F_{d}$ is the drag
force. The drag force can be described by $F_d = 2\pi\gamma_{GB}r \sin \theta$, with grain boundary energy $\gamma_{GB}$ and the radius of the inclusion $r$. For the maximum possible drag force and the corresponding maximum drag angle (Fig. 1b), the fluid inclusion moves at its maximum velocity. The fluid inclusion is dropped when the grain boundary velocity exceeds the peak fluid inclusion velocity at the critical drag angle (Hsueh et al. 1982; Svoboda and Riedel 1992; Petrishcheva and Renner 2005). All existing models describe the second phase to be arranged as inclusions along grain boundaries or inside the grains without change in the fluid volume. However, it has been shown that the fluid inclusions may also be incorporated into grain boundaries and re-distributed laterally (Schenk and Urai 2005).

The presence of a thin fluid film along grain boundaries, which may enhance grain boundary migration recrystallization, has been discussed in a series of papers (e.g., quartz: Tullis and Yund 1982; Kronenberg and Tullis 1984; halite: Spiers et al. 1986; Watanabe and Peach 2002; Schenk and Urai 2004; Ter Heege et al. 2005; olivine: Karato 1989), however the effect of the fluid morphology, fluid film thickness, and fluid chemistry on grain boundary mobility is not well known.

Grain boundary–fluid inclusion interaction may strongly affect fluid inclusion chemistry. Experimental data suggest that inclusions can leak along grain boundaries (Schmatz and Urai 2010) or may leak single components selectively as conditions depart from the original trapping conditions (Bakker 1992; Johnson and Hollister 1995). Kerrich (1976) and Schléder and Urai (2007) report that recrystallization has been responsible for "sweeping out" most of the primary inclusion arrays of the grains.

See-through deformation experiments with rock analogues provide a method to study the time-evolution of fluid inclusions during grain boundary migration and better understand similar fluid-rock interaction processes in the Earth’s crust and upper mantle (e.g., Urai and Humphreys 1981; Means 1989; Bons 1993; Humphreys and Hatherly 1996; Walte et al. 2003). In this paper we compare results of annealing experiments on rock analogues in the presence of different pore fluids saturated with the solid: bischofite with brine (Schenk and Urai 2005), camphor with ethanol (Schmatz and Urai 2010), and camphor with ethylene glycol. The solid–liquid systems vary in terms of wettability and solubility, whereas homologous temperatures, strain rates, annealing times and the initial textures are similar. Using this data we aim to characterize the effect of the pore fluid properties on grain
boundary–pore fluid interaction, grain boundary mobility, and the recrystallized texture. We focus on two parameters, the *grain boundary velocity* and the *fluid inclusion velocity*.

**Methods**

**Deformation rig**

The see-through deformation apparatus builds on the design of Urai (1987) (Fig. 2). It consists of a stainless steel vessel equipped with high-strength see-through windows at top and bottom. It has a pressure controlled pore-fluid system allowing pressures up to 3 MPa and controlled heating up to 200°C. Schenk and Urai (2005) give a detailed description of this generation of the Urai rig. In addition to this deformation chamber we used a simplified version that does not contain a pore fluid system (Schmatz and Urai 2010). Both assemblies consist of a stainless steel holder and a pin guide that acts as a forcing block (moving $\sigma_1$ piston). Glass plates are used to sandwich the sample holder and the sample in between. The glass plates are held in place by a precision nut and a high-precision ball bearing allows the in-situ preparation of planar samples by squeezing a pill of model material in between the two glass plates. The piston is connected to a constant speed step motor and thus serves as a $\sigma_1$–piston. The assembly is heated with heating elements outside of the pressure vessel and mantled with insulation material. The temperature is controlled by a thermocouple. An optical inverstoscope with long distance objectives is used to allow observations of the experiment. It is equipped with a high-resolution digital camera that recorded $2048 \times 1536$ px images at specific time intervals (15–900 s) with a pixel size of $1 \text{ px} = 0.9 \ \mu\text{m}$ (maximum resolution). The image sequences are converted to movies and analyzed using Adobe Illustrator CS3 and Image SXM 1.89.
Sample preparation

*Camphor–ethanol*

Sample preparation of camphor with ethanol is described in detail in Schmatz and Urai (2010). Camphor is heated together with ethanol and an accessory amount of silicon carbide (SiC, grain size = 13 µm; added as passive strain markers) to 80 °C in a closed glass vial, stirred for 30 minutes and cooled down to room temperature. The resulting camphor mush in saturated solution is squeezed inside the sample holder to the desired thickness of 100 µm (see Schmatz and Urai (2010) for further details).
Camphor–ethylene glycol

Samples of camphor with ethylene glycol are prepared by dissolving 3 g camphor in 1 ml ethanol. The solution is mixed with an accessory amount of SiC. One ml of ethylene glycol is added to precipitate a homogeneous mixture of camphor, SiC and ethanol from the solution. The result is a milky mush which is left for approximately one hour to let the ethanol evaporate from the sample. The sample setup in the deformation rig follows exactly the procedure of camphor with ethanol as described in Schmatz and Urai (2010).

Bischofite-brine

The experiments undertaken with bischofite (MgCl$_2$ · 6H$_2$O) and saturated brine are already described by Schenk and Urai (2005). Samples of synthetic, wet polycrystalline bischofite are prepared by quickly pressing the wet powder to the desired thickness of 300 µm outside of the sample holder, then cut into wafers of 14 × 8.5 mm and put into the deformation rig. Samples prepared like this can be characterized as pre-deformed.

Measurements

Solubility of the solid phase in the respective liquid is determined by dissolving the solid in the liquid phase at constant temperature until dissolution stops and a few grains are in equilibrium with the solution for one hour. The dynamic wetting angle is measured by tracing the outline of each inclusion for each time step using Adobe Photoshop CS3. Outlines are imported to Image SXM 1.89 and automated measurements on area and ellipticity are performed. The equivalent radius of the inclusion $r$ is defined as the radius of a circle with the same area (Schmatz and Urai 2010). The wetting angle $\psi$ is calculated from the best-fit ellipse ($\psi = \arctan(\text{minor axis} / \text{major axis})$) (Fig. 3a). The fluid inclusion velocity is defined by the length of the covered distance of the center of gravity of the fitted ellipse for a fluid inclusion for successive time steps (Fig. 3a, in a $xy$-coordinate system: $v_{FI} = (x_1 - x_2)^2 + (y_1 - y_2)^2$)

The drag angle $\theta$ is defined at the triple point of the two adjacent grains and the fluid inclusion (Fig. 3b). In practice it has been shown that the most accurate measurement is to fit a straight line to the grain boundary segment with a length of 3 times the fluid inclusion
radius. The drag angle is given by \( \theta = \arctan \left( \frac{h}{r} \right) \) (Fig. 3b). Measurements on grain boundary velocities are made along orthogonal trajectories inside the sample in a plane parallel to the cover glass (Urai 1983; Schmatz and Urai 2010). Measurements are only made in grain boundaries inclined more than 80° to the plane of the section. See the Appendix for error and uncertainty analyses on measurements.

Fig. 3. (a) Sketch showing measuring procedure for the dynamic wetting angle. The wetting angle is calculated from the best-fit ellipse, using \( \psi = \arctan(\text{minor axis} / \text{major axis}) \). b) Sketch showing measuring procedure for the drag angle. \( r \) is calculated from the best-fit ellipse, \( h \) is measured as shown and the drag angle is \( \theta = \arctan(h / r) \).

**General experiment protocol**

A detailed description of the experiments with bischofite–brine using the pore-fluid controlled deformation chamber is given in Schenk and Urai (2005), and Schmatz and Urai (2010) describe the experimental procedure of camphor–ethanol experiments. The procedure with camphor–ethylene glycol samples is comparable to camphor–ethanol.
For all experiments described in this study, grain size prior to annealing (late sintering stage (Schmatz and Urai 2010) or post-kinematic annealing (Schenk and Urai 2005)) is ~100 μm and the initial fluid fraction is ~20%. All samples are annealed at constant temperature of 70 °C (experiments 2s, ce0201, and cg0511, Table 1). Duration of an annealing experiment is 1 h-1 week. Occasionally, the fully annealed samples are deformed later at variable strain rates and temperatures (presented in this study: experiments 2d-2, ce0301 and cg0409, Table 1). See Schenk and Urai (2005) and Schmatz and Urai (2010) for a detailed description of dynamic experiments.

### Table 1. Summary of important experiment settings and parameters.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>solid liquid</th>
<th>$\phi$</th>
<th>$t_s$</th>
<th>$S$ at 70 °C</th>
<th>strain rate</th>
<th>process</th>
<th>Figs.</th>
<th>published</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s</td>
<td>bischofite saturated brine</td>
<td>16°</td>
<td>0.88</td>
<td>2.1 x 10^{-4}</td>
<td>-</td>
<td>post-kin. annealing, grain growth</td>
<td>4, 5, 9, 12</td>
<td>Schenk and Urai 2005, figs. 10-13</td>
</tr>
<tr>
<td>ce0201</td>
<td>camphor ethanol</td>
<td>26°</td>
<td>0.76</td>
<td>1.9 x 10^{-3}</td>
<td>-</td>
<td>annealing, grain growth</td>
<td>4, 5, 7, 12, 13, 16</td>
<td>Schmatz and Urai 2010, figs. 6 and 10</td>
</tr>
<tr>
<td>cg0511</td>
<td>camphor ethylene glycol</td>
<td>33°</td>
<td>0.76</td>
<td>1.7 x 10^{-4}</td>
<td>-</td>
<td>annealing, grain growth</td>
<td>4, 5, 7, 12</td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>bischofite saturated brine</td>
<td>0.93</td>
<td>2.1 x 10^{-3}</td>
<td>2 x 10^{-4}</td>
<td>Twinning, dyn. grain boundary migration recrystallization</td>
<td>6</td>
<td>Schenk and Urai 2005</td>
<td></td>
</tr>
<tr>
<td>ce0301</td>
<td>camphor ethanol</td>
<td>0.76</td>
<td>1.9 x 10^{-3}</td>
<td>5 x 10^{-3}</td>
<td>dyn. grain boundary migration recrystallization</td>
<td>6</td>
<td>Schmatz and Urai 2010, fig. 5</td>
<td></td>
</tr>
<tr>
<td>cg0409</td>
<td>camphor ethylene glycol</td>
<td>0.76</td>
<td>1.7 x 10^{-4}</td>
<td>8 x 10^{-5}</td>
<td>dyn. recrystallization, grain boundary sliding, subgrain rotation recrystallization</td>
<td>6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Solubility (S) of camphor in ethanol is in 8 x 10^{-5} mol g^{-1} at 24 °C with a linear increase of 1.6 x 10^{-6} mol g^{-1} °C^{-1}. S of camphor in ethylene glycol is 9.9 x 10^{-7} mol g^{-1} at 24°C with a power law ($S=2\times10^{-13}+4.85\times10^{-1}$ mol g^{-1}) increase to 1.7 x 10^{-4} mol g^{-1} at 70 °C. S of bischofite in saturated brine is 1.8 x 10^{-5} mol g^{-1} at 24 °C with a linear increase of 10^{-8} mol g^{-1} °C^{-1}. 


Results

Solubility

The three systems vary in terms of solubility, wetting behavior, and microstructural evolution. The solubility of the solid in the respective liquid is listed in Table 1 showing a similar solubility for camphor in ethanol and bischofite in brine. All experiments described in this study are undertaken at 70 °C resulting in higher solubility of camphor in ethanol \((1.9 \times 10^{-2} \text{ mol g}^{-1})\) and bischofite in brine \((2.1 \times 10^{-2} \text{ mol g}^{-1})\) (factor 100) compared to camphor in ethylene glycol \((1.7 \times 10^{-4} \text{ mol g}^{-1})\).

Wetting angle - drag angle

In camphor–ethanol the dynamic wetting angle is \(26 \pm 10^\circ\) \((n=157)\) (Fig. 4, fig 3, Schmatz and Urai, 2010) and in camphor–ethylene glycol \(\psi =33 \pm 6^\circ\) \((n=70)\). We measured a dynamic wetting angle \(\psi\) for bischofite–brine of \(16 \pm 3^\circ\) \((n=30)\).

The drag angle \(\theta_{\text{crit}}\) for fluid inclusions attached to grain boundaries is highly variable (Fig. 5) and measured values do not support a simple relation to the fluid inclusion velocity. See the Appendix for a short discussion on drag angle variability. The critical drag angle \(\theta_{\text{crit}}\) for which the fluid inclusion is dropped cannot be determined in our experiments, as drop and subsequent straightening of the grain boundary are rare events which occur in the range of a few seconds and are not often captured in our image sequences which were designed to document movement of fluid inclusions and grain boundaries over long periods.
**Fig. 4.** Histograms showing distribution of dynamic wetting angles $\psi$ in camphor–ethanol (column 1), camphor–ethylene glycol (column 2) and bischofite (column 3) with examples for high $\psi$ (row 2) and low $\psi$ (row 3).
Microstructural evolution under dynamic conditions

The microstructural evolution under dynamic conditions for the systems bischofite–brine (Schenk and Urai 2005) and camphor–ethanol (Schmatz and Urai 2010) is described in earlier publications. The dynamically recrystallized microstructure in bischofite–brine at high strain rates and high temperatures (Fig. 6a, T=90°, strain rate=1.7×10⁻⁴ s⁻¹, experiment 1d, Schenk and Urai (2005)) features intracrystalline defects indicated by undulose extinction and twinning. Camphor-ethanol under similar conditions (T=70 °C, strain rate=5×10⁻⁵ s⁻¹) shows
dynamic grain boundary migration recrystallization between grains without visible lattice distortion and with highly lobate grain boundaries accompanied by dynamic grain growth (Fig. 6b, experiment ce0301). In camphor–ethylene glycol we observe grain boundary sliding, kinking and subgrain rotation recrystallization as additional microstructural processes at high temperatures (70 °C) and high strain rates \((8\times10^{-5}\ s^{-1})\) (Fig. 6c, experiment cg0409).

Fig. 5. Images showing (a) bischofite–brine, (b) camphor–ethanol, and (c) camphor–ethylene glycol under dynamic conditions. See text for further description.
Observations during annealing

*Grain boundary-fluid inclusion interaction*

Schmatz and Urai (2010) defined a classification of principle modes of interaction of fluid inclusions with grain boundaries: i) motion of fluid inclusions with grain boundaries and ii) change of fluid inclusion shape. Further subdivisions of these modes can be classified as follows: fluid inclusions that are passed by migrating grain boundaries without interaction (figs 7 and 8, Schmatz and Urai (2010), regime 1a), fluid inclusions that are dragged and dropped without shape change (regime 1b), fluid inclusions that are dragged and dropped with shape change (regime 2b), fluid inclusions that pin a migrating grain boundary without shape change (regime 1c) or with shape change (regime 2c). Regime 2d covers the incorporation of fluid inclusions into the migrating grain boundary.

**Camphor–ethanol**

In the system camphor-ethanol grain growth is dominant (Fig. 7, experiment ce0201, Table 1). Here, for different grain boundary migration rates and fluid inclusion sizes we observe that (i) fast migrating grain boundaries (>2×10⁻⁷ ms⁻¹) pass fluid inclusions without interaction (regime 1a), (ii) grain boundaries migrating with moderate velocities (~2×10⁻⁷ -10⁻⁹ ms⁻¹) drag and drop fluid inclusions with shape change (regime 2b) and that (iii) fluid inclusions pin slowly migrating grain boundaries (<1×10⁻⁹ ms⁻¹) (regime 2c). Fluid inclusions being attached to a migrating grain boundary usually change their shape and become elongated during separation. Large fluid inclusions (r>7 µm) are seen to neck down while being dropped, leaving behind a smaller fluid inclusion at the migrating grain boundary (regime 2b, figs. 6c and 11, Schmatz and Urai 2010).
Camphor–ethylene glycol

During annealing of camphor–ethylene glycol we observe grain growth (Fig. 8, experiment cg0511, Table 1). Dominant features in the interaction of migrating grain boundaries with fluid inclusions are (i) the passage of fluid inclusion without any interaction for grain boundaries being faster than \( \sim 8 \times 10^{-7} \text{ ms}^{-1} \) (regime 1a) and (ii) pinning of grain boundaries by immobile fluid inclusions (grain boundary velocity \(<1 \times 10^{-9} \text{ ms}^{-1}\) ) (regime 1c). Drag and drop (regime 1b) is also observable for grain boundary velocities in the range of \(~1 \times 10^{-9} \text{ ms}^{-1}\) but only measureable for small inclusions (\(r<10 \mu\text{m}\)) for the duration of an experiment. Usually, the fluid inclusions keep their shape when in contact with a grain boundary.
Bischofite–brine

Deformation and subsequent annealing of bischofite at high homologous temperatures ($t_h$~0.7) leads to rapid recrystallization. The dynamically recrystallized texture of wet bischofite samples (Fig. 9, experiment 05010, fig 10, Schenk and Urai 2005, Table 1) predominantly consists of small grains (100 µm) (Schenk and Urai 2005). Grain growth during post-kinematic annealing overprints the texture with new, strain-free grains. At this stage variable interaction of fluid inclusions with migrating grain boundaries is observed: (i) For very high grain boundary migration rates (>5×10⁻⁸ ms⁻¹) we observe no interaction of fluid inclusions with passing grain boundaries (regime 1a). (ii) At high grain boundary velocities (1×10⁻⁹-9×10⁻⁹ ms⁻¹) the fluid inclusions are dragged and affected in shape (regime 2b). After the grain boundary has dropped fluid inclusions they re-equilibrate to spheres in a few minutes; (iii) for moderate grain boundary velocities (<5×10⁻¹⁰ ms⁻¹) the fluid inclusions are dragged involving (iv) the incorporation of fluid inclusions into the migrating boundary (regime 2d). Incorporation involves the re-distribution of fluid along the grain boundaries resulting in a fluid film which is often associated with local thickening of the grain boundary.
Critical grain boundary velocity

Above a certain critical grain boundary velocity grain boundaries do not interact with fluid inclusions (see Schmatz and Urai 2010) as observed in all three systems. During annealing the critical grain boundary velocity measured in camphor–ethanol is around $1 \times 10^{-7}$ ms$^{-1}$ (for fluid inclusion radius = 5 µm) (Fig. 10a). For camphor–ethylene glycol the critical velocity is $\sim 8 \times 10^{-9}$ ms$^{-1}$ (Fig. 10b). The critical grain boundary velocity for bischofite–brine is in between is around $2 \times 10^{-8}$ ms$^{-1}$ (Fig. 10c). A number of observations for large fluid inclusions in camphor–ethanol show that the critical grain boundary velocity is dependent on the fluid inclusion size (Schmatz and Urai 2010).
Maximum fluid inclusion velocity

In Figure 11 we concentrate on fluid inclusion velocity, plotting all data (all modes of interaction, except regime 1a) where fluid inclusions moved and their velocity could be measured.

For camphor–ethanol and bischofite–brine there is a clear maximum above which no fluid inclusion velocities were measured, and this maximum decreases by almost two orders of magnitude for fluid inclusion size of 1 to 20 µm in camphor–ethanol and 1-10 µm in bischofite–brine. For camphor–ethylene glycol data are comparable to camphor–ethanol for fluid inclusions size and velocity, but there are not sufficient data to allow testing the hypothesis of size-dependent maximum velocity.

Fig. 5.10. Diagrams showing grain boundary velocity vs. fluid inclusion size for (a) camphor–ethanol, (b) camphor–ethylene glycol, and (c) bischofite–brine. In all three systems grain boundaries do not interact with fluid inclusions above a certain grain boundary velocity. See text for details.
**Fig. 5.11.** Diagram showing fluid inclusion velocity vs. fluid inclusion size for dragged fluid inclusions in (a) camphor–ethanol, (b) camphor–ethylene glycol, and (c) bischofite–brine. Gray shading indicates data field above the critical grain boundary velocity with no grain boundary–fluid inclusion interaction. Red line shows limiting grain boundary velocity above which no measurements exist. Graphs show peak fluid inclusion velocities calculated with mobility term for (i) surface diffusion, (ii) bulk diffusion, and (iii) solution–precipitation. Assumed values (Table 5.2) are selected to fit the graphs as close as possible to the data without intersecting.

### Discussion

**Solubility**

Solubility is one of the key parameters controlling fluid–rock interaction (e.g., Kronenberg and Tullis 1984; Karato 1989). Bauer et al. (2000) compare solubility of the rock analogue norcamphor in water (20 °C, 0.1 MPa) with the solubility of quartz in water at 600 °C and 500 MPa, neglecting the effect of anisotropic stress conditions. Solubility of camphor in ethanol at 70 °C is in comparable range to quartz in water at 800 °C and 1 GPa (Manning 1994) and the solubility of camphor in ethylene glycol at 70 °C is similar to solubility of quartz in water at 500 °C and 1 GPa (Manning 1994). Tullis and Yund (1982) show that grain boundary velocity in quartz increases with increasing solubility of quartz in water. We compare results of camphor–ethanol (high solubility) with results of camphor–ethylene glycol to describe the
effect of the type of pore fluid on the microstructural processes (Figs. 6-8). With the maximum measured grain boundary velocity of $1 \times 10^{-6}$ m s$^{-1}$ camphor–ethanol shows two orders of magnitude higher grain boundary migration rates compared to camphor–ethylene glycol at equivalent experimental conditions. However, maximum fluid inclusion velocities were comparable in camphor–ethanol and camphor–ethylene glycol for the same fluid inclusion size which suggests that solubility does not affect the fluid inclusion mobility pointing to self diffusion through the solid being the rate controlling mechanism for the mobility of fluid inclusions in these systems (see paragraph on peak fluid inclusion velocity for further discussion).

Wetting behavior of grain boundaries

As described in the results, the fluid phases in our samples show a considerably different wetting behavior with respect to the co-existing solid phase. The effect of the dynamic wetting angle during drag and drop can be described comparing the two systems bischofite–brine and camphor–ethanol. Both samples have a similar solubility in the respective fluid phase and both are deformed and annealed at similar homologous temperatures ($T_h \sim 0.8$). The average dynamic wetting angles, however, differ by 10° (Figs. 4a and c, bischofite–brine $\psi \sim 16°$, camphor–ethanol $\psi \sim 26°$), and the experiments show that the pore fluid in bischofite samples is much more frequently incorporated into the migrating grain boundary, while grain boundaries in camphor can deform and/or drag the pore fluid but never incorporate it completely. Grain boundaries in bischofite slow down while incorporating the pore fluid and redistributing it along the grain boundary (Fig. 9). As a result the pore fluid is mainly found along grain boundaries. The observed slowing down for thicker films may point to diffusion being rate controlling if grain boundary migration rates are dependent on the fluid film thickness (Urai et al. 1986; Watanabe and Peach 2002; Schenk and Urai 2005).

In camphor–ethanol drag and drop of fluid inclusions is frequent. Fluid inclusions change in shape but are never fully incorporated into the migrating boundaries. Fluid inclusions in camphor–ethanol show preferential leakage, pointing to lateral transport of which the mechanism, however, is not visible in the microscope (Schmatz and Urai 2010). After long periods of dynamic or static recrystallization the majority of fluid inclusions is found in bulk grains and not along grain boundaries. The effect of different wetting angles may also play a role in quartz-H$_2$O-CO$_2$ systems which show the preferential entrainment of CO$_2$ inclusions on
grain boundaries and in bulk grains during grain boundary migration recrystallization, while aqueous fluids are re-distributed along grain boundaries (Boullier et al. 1989; Bakker 1992; Holness 1993; Johnson and Hollister 1995; Drury and Urai 1990).

Peak fluid inclusion velocity

Our results show a maximum fluid inclusion velocity which is dependent on the fluid inclusion size for camphor–ethanol and bischofite–brine (Fig. 11). In Figure 11 we also plotted the limit of measured grain boundary velocities – based on this it is possible that very small fluid inclusions could move faster (there is a grain boundary fast enough to drag). During drag and drop the fluid inclusion velocity is proportional to its mobility and the drag force exerted by the migrating grain boundary (e.g., Svoboda and Riedel 1992).

We measured fluid inclusion velocities for fluid inclusions attached to grain boundaries with a wide range of velocities ($10^{-11}$ – $10^{-6}$ ms$^{-1}$). The velocity of a grain boundary (driven by a reduction of surface energy, grain boundary energy, dislocation density) is given by its mobility and the driving force. This may vary for different grain boundaries in our experiments even though grain growth is the dominant microstructural process during annealing.

Analyzing the velocity of an individual fluid inclusion as a function of grain boundary mobility (Raabe 1995) and drag angle is not possible using our data. We did not measure grain orientations and drag angle data do not show systematic trends (see Appendix). Also it was not possible to observe individual fluid inclusions with progressively increasing drag angle until they are dropped. However, we propose to interpret the maximum fluid inclusions’ velocities to represent those fluid inclusions which were moved by the “optimal grain boundary” (i.e., the grain boundaries with the highest mobility and the largest driving force). If we make the assumption that the properties of this “optimal” boundary were the same for all fluid inclusion sizes, existing models suggest that the maximum fluid inclusion velocity is only dependent on fluid inclusion mobility. Therefore, the large number of measurements on fluid inclusion velocities ($n=154$, in camphor–ethanol) for the whole range of grain boundary velocities allows comparison to the existing models for the influence of inclusion size on fluid inclusion mobility:
Changes in the shape of an inclusion attached to a grain boundary and also drag and drop can be accomplished by self-diffusion along the surface, by bulk diffusion through the lattice, and by solution–precipitation (Anthony and Cline 1971; Chuang et al. 1979; de Meer and Spiers 1999); in most studies which discuss drag and drop of inclusions surface diffusion is assumed to be rate controlling (e.g., Hsueh et al. 1982; Svoboda and Riedel 1992; Petrishcheva and Renner 2005).

Assuming surface diffusion to be rate controlling the mobility of the fluid inclusion is given by $M_{FI(s)} = A \frac{1}{r^4}$, with $A = \frac{\Omega D_s}{2\pi kT}$, Table 2), being a material and temperature dependent constant. In case of bulk diffusion being rate controlling the mobility term is $M_{FI(b)} = B \frac{1}{r^3}$, with material and temperature dependent constant $B = \frac{\Omega D_b}{2\pi kT}$, Table 2).

Mobility of inclusions migrating by solution–precipitation is $M_{FI(sp)} = C \frac{1}{r^2}$, where $C = \frac{\Delta p \Omega^2}{(2\pi m)^{\frac{1}{3}}(kT)^{\frac{1}{2}}}$, Chuang et al. 1979, Table 2) is the material, pressure and temperature dependent constant.

We plotted these three functions in each of the graphs of (Fig. 11a, Table 2), choosing reasonable values and adjusting the parameter A, B and C so that the lines were as close as possible to the maximum fluid inclusion velocity.

Although this is not a well defined best-fitting procedure, the maximum fluid inclusion velocity trend seems to be best explained by bulk diffusion being rate controlling for camphor–ethanol and bischofite–brine.

Obviously, parallel operation of all three processes is possible (Chuang et al. 1979). It could be speculated that for very small inclusions solution-precipitation is rate limiting, enabled by higher pressures inside the inclusion (Young-Laplace equation), while for larger inclusions the mobility is controlled by diffusion. However, our data are not sufficient to test this hypothesis. The bulk diffusion model for camphor is supported when comparing camphor–ethanol with camphor–ethylene glycol. Despite the large difference in solubility, both systems show the same range of maximum fluid inclusion velocities which is explained by diffusion through the lattice. Results of camphor–ethylene glycol are not sufficient to
distinguish between dominant mechanisms (Fig. 11b, Table 2), but, results in bischofite–brine (Fig. 11c, Table 2) show a similar trend as results in camphor–ethanol (except for a lack of data for large fluid inclusions) and thus support the bulk diffusion model.

### Table 2. Symbols, units and assumed values for mass transfer models.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>SI unit</th>
<th>Camphor–ethanol (Fig. 11a)</th>
<th>Camphor–ethylene glycol (Fig. 11b)</th>
<th>Bischofite–brine (Fig. 11c)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Omega$</td>
<td>Atomic volume</td>
<td>$m^3$mol$^{-1}$</td>
<td>$1.50 \times 10^{-20}$</td>
<td>$1.50 \times 10^{-21}$</td>
<td>$1.50 \times 10^{-24}$</td>
</tr>
<tr>
<td>$m$</td>
<td>Atomic mass</td>
<td>kgmol$^{-1}$</td>
<td>0.152</td>
<td>0.152</td>
<td>0.203</td>
</tr>
<tr>
<td>$D_s$</td>
<td>Diffusion coefficient for surface diffusion</td>
<td>$m^2$s$^{-1}$</td>
<td>$8.9 \times 10^{-9}$</td>
<td>$8 \times 10^{-9}$</td>
<td>$4 \times 10^{-9}$</td>
</tr>
<tr>
<td>$D_b$</td>
<td>Diffusion coefficient for bulk diffusion</td>
<td>$m^2$s$^{-1}$</td>
<td>$2.5 \times 10^{-10}$</td>
<td>$4.5 \times 10^{-11}$</td>
<td>$2.5 \times 10^{-12}$</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>Pressure on the fluid inclusion wall</td>
<td>Pa</td>
<td>$7.5 \times 10^{-3}$</td>
<td>$7.5 \times 10^{-3}$</td>
<td>3</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant</td>
<td>$m^2$kg$s^{-1}$K$^{-1}$</td>
<td>$1.38 \times 10^{-23}$</td>
<td>$1.38 \times 10^{-23}$</td>
<td>$1.38 \times 10^{-23}$</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
<td>343</td>
<td>343</td>
<td>343</td>
</tr>
<tr>
<td>$\gamma_{GB}$</td>
<td>Grain boundary energy</td>
<td>kg/$s^1$</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Dynamic wetting angle</td>
<td>$^\circ$</td>
<td>26</td>
<td>33</td>
<td>16</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Drag angle</td>
<td>$^\circ$</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
</tbody>
</table>

#### 1.1 Mobility ratio

Early models (e.g., Brook 1969) discuss the effect of the boundary-inclusion mobility ratio on the recrystallized grain size. They show that the microstructure is controlled by the grain boundary mobility for a mobility ratio of $M_{JI} / (N ^* M_{GB}) \geq 1$. Results for camphor-ethanol
with highly mobile fluid inclusions support their considerations as grain boundary velocity is relatively stable during drag and drop (Fig. 7). However, it is necessary to distinguish between boundary controlled textures with and without interaction of fluid inclusions and grain boundaries for grain boundaries above the critical grain boundary velocity. Firstly, because a pronounced chemical exchange of inclusion fluids with grain boundary fluids is expected for long dwell periods which may influence e.g., filling temperatures. Secondly, because passing without interacting leads to an intragranular porosity, whereas interaction leads to intergranular porosity (Fig. 12).

**Fig. 12.** Examples of annealed textures in (a) camphor–ethanol, (b) camphor–ethylene glycol, and (c) bischofite–brine. In (a) fluid inclusions are mainly found in bulk grains, only a few rest along grain boundaries. In (b) fluid inclusions are found in bulk grains and also at grain boundaries. In (c) besides areas with fluid inclusions large fluid free areas a visible. See text for discussion.

**Conclusions**

In agreement with theory, the three model systems with different wetting angles and solubility show strongly different interactions of fluid inclusions and mobile grain boundaries, such as fluid inclusions can act either as immobile phase slowing down grain boundary migration by Zener pining, as mobile phase which is dragged and dropped by the migrating grain boundary. Fluids from inclusions were also incorporated into and redistributed along the grain boundary.

In all three systems, fluid inclusion velocities fall in a comparable range, suggesting that solubility has no strong effect on fluid inclusion mobility in these experiments. However, the
dynamic wetting angle has a strong influence on the types of interaction. For a low wetting angle in bischofite-brine the fluid redistribution and incorporation of fluid into the grain boundaries is much more prominent than in the other systems with higher dynamic wetting angle.

In all three systems the maximum possible velocity of a fluid inclusion being dragged by a moving grain boundary. Fluid inclusion velocity is dependent fluid inclusion mobility, which is – according to our experimental measurements – inclusion size dependent. The analysis allowed prediction of the rate-limiting processes. The analysis allowed prediction of the rate-limiting processes. Even though surface diffusion, bulk diffusion and solution-precipitation can operate parallel, our results suggest that bulk diffusion is rate limiting factor.

Application of our results to natural systems depends on the rate limiting process in these. However our results suggest that there are clear differences between systems with different solubilities and wetting angles in natural tectonites.

Acknowledgements

We thank F.-D. Scherberich for constructing the deformation cell. P.D. Bons and J.K Becker are acknowledged for inspiring discussions on our experiments. M. Jessell and an anonymous reviewer are acknowledged for thorough reviews. The project was funded by the German Science Foundation (DFG, UR 64 / 8-1) and was part of the European Science Foundation (ESF)-funded the collaborative research project EuroMinSci.

References


Smith CS (1948) Grains, Phases, and Interfaces - an Interpretation of Microstructure. Transactions of the American Institute of Mining and Metallurgical Engineers 175:15-51


Appendix

Fluid inclusion size

Fluid inclusion size is measured by focusing onto the center of the inclusion. As fluid inclusions move up or down in the sample the measurements may contain an error. Schmatz and Urai (2010) tested this measuring the size of an inclusion in different levels. They found the maximum uncertainty in measurement to be 4% for the radius of a fluid inclusion.

Wetting angle

We calculate the dynamic wetting angle from the fitted ellipse to the outlined fluid inclusion which is also used to determine the size of the fluid inclusion. Accordingly, the uncertainty in measurement for the fluid inclusion radius also accounts for the wetting angle. With upper and lower approximation of the ellipse’s axes length the uncertainty is ±8 %. To determine the error in measurement we compare measurements undertaken directly on image captures with calculated values from the best-fit ellipse for 25 fluid inclusions in camphor–ethanol (Fig.13). The maximum differences for calculated and measured values are 4° and -3° (measured wetting angle minus calculated wetting angle) with no trend to over- or underestimate the dynamic wetting angle and no size depended inaccuracy (Fig.14). Additional small inaccuracies resulting from 3D effects cannot be excluded.
Drag angle

As illustrated in Figure 5 drag angle measurements show a high variability. We find no correlation of drag angle and fluid inclusion velocity (Fig. 15) as predicted by basic theory. At least two important features influence our drag angle measurements: Firstly, feedback processes for closely spaced fluid inclusions may affect the drag angle (Fig. 16a). Secondly, we do not expect the grain boundaries to be perfectly planar. Measurements, however, are only undertaken in two-dimensional sections parallel to the cover glass. Drag angle variations in the third dimension influencing the fluid inclusion velocity cannot be excluded (Fig. 16b).
Fig. 5.15. Diagram showing calculated drag angles (Fig. 5.3b) vs. the fluid inclusion velocity for four fluid inclusion size classes.

Fig. 5.16. Sketches showing that variations of the calculated (or measured) drag angle result from (a) the spacing of fluid inclusions arrays attached to grain boundaries and (b) from 3D effects along non-planar grain boundaries.

Velocities

To determine the uncertainty in measurement for the grain boundary velocity we repeat the measurement on grain boundary velocity 30 times for a fast grain boundary, a medium fast grain boundary and a slow grain boundary (Table 3). The covered distance measured along
orthogonal trajectories gives the grain boundary velocity. The maximum uncertainty in measurement is found for the medium fast grain boundary with 11%.

**Table 3. Measurements on grain boundary velocity.**

<table>
<thead>
<tr>
<th>Grain boundary</th>
<th>min</th>
<th>max</th>
<th>points</th>
<th>mean</th>
<th>median</th>
<th>std dev</th>
<th>std error</th>
<th>max error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>fast</td>
<td>2.4017E-07</td>
<td>2.9171E-07</td>
<td>30</td>
<td>2.6411E-07</td>
<td>2.643E-07</td>
<td>1.3875E-08</td>
<td>2.5333E-09</td>
<td>5.253492863</td>
</tr>
<tr>
<td>medium</td>
<td>7.7863E-08</td>
<td>1.2063E-07</td>
<td>27</td>
<td>9.7766E-08</td>
<td>9.87E-08</td>
<td>1.0722E-08</td>
<td>2.0635E-09</td>
<td>10.96700284</td>
</tr>
<tr>
<td>slow</td>
<td>2.632E-08</td>
<td>3.948E-08</td>
<td>30</td>
<td>3.2608E-08</td>
<td>3.2352E-08</td>
<td>3.4791E-09</td>
<td>6.352E-10</td>
<td>10.66946762</td>
</tr>
</tbody>
</table>

We calculate the fluid inclusion velocity from the covered distance of the center of gravity of the fitted ellipse in a certain time step. The uncertainty in measurement is ±8%, determined from the accumulated error of the fluid inclusion radius.

For both, grain boundary and fluid inclusion velocity we use displacement not distance. This method bears an increasing uncertainty with the increasing time step. However, for most measurements, we have a number of image captures in between the images used for measurements, from which we can exclude large variations in velocity during grain growth.