Permeability alteration due to mineral dissolution in partially saturated fractures

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During reactive fluid flow in saturated fractures, the relative rates of dissolved mineral transport and local reactions strongly influence local aperture alterations and the resulting changes in fracture permeability (or transmissivity). In the presence of an entrapped residual nonaqueous phase (e.g., CO$_2$ or oil), the spatial distribution of the entrapped phase will influence flow and transport and thus, local aperture alterations. These aperture alterations will in turn alter the balance of forces acting on immobile regions of the trapped phase. The resulting mobilization of the entrapped phase may subsequently alter flow pathways and fracture transmissivity in a manner that defies quantification with currently used constitutive relationships. I present results from quantitative visualization experiments in which fracture aperture and entrapped phase distribution were directly measured at high spatial resolution (75 × 75 μm) during reactive fluid flow. The experiments differed only in the orientation of the fracture with respect to gravity, which influenced both the initial entrapped phase geometry and the evolution of the entrapped phase as dissolution altered fracture apertures. The presence of the entrapped phase leads to a much earlier formation of distinct dissolution channels than has been observed in saturated fractures. Compared to a similar experiment in a fully saturated fracture, dissolution in the partially saturated fractures leads to as much as a 6-fold increase in transmissivity after an equal amount of dissolution from the fracture surface (doubling of the mean fracture aperture). Furthermore, the relative influence of gravity determines whether trapped bubbles mobilize because of capillary forces (against prevailing viscous forces) or gravitational forces, which is in the direction of prevailing viscous forces for the experiments presented here.


1. Introduction

Subsurface flow of reactive fluids leads to alteration of pore spaces and changes in formation permeability. Such permeability alterations are of fundamental concern for problems such as subsurface sequestration of CO$_2$ [Ennis-King and Paterson, 2007], enhanced geothermal systems [Xu et al., 2001], enhanced oil recovery [e.g., Economides and Nolte, 2000], and development of karst systems [Dreybrodt et al., 1996; Worthington and Ford, 2009]. In many of these systems, fractures provide the dominant pathways for advective transport of fluids, and thus, the resulting geochemical alterations occur predominantly along fractures. A clear understanding of how reactive fluids alter permeability in these systems is fundamental to, for example, understanding the potential for alteration of pathways for leakage from reservoirs intended for long-term storage of CO$_2$ [Johnson et al., 2003, 2005].

Experimental and computational studies to date suggest that dissolution-induced alteration of fracture apertures is influenced by a number of parameters including initial aperture variability [Durham et al., 2001; Cheung and Rajaram, 2002; Hanna and Rajaram, 1998; O’Brien et al., 2003], mineral composition of the surfaces [Gouze et al., 2003; Nordin et al., 2007], confining stress [Polak et al., 2004; Detwiler, 2008; Yasuhara et al., 2004], reaction kinetics [Dreybrodt, 1990; Worthington and Ford, 2009], and advective-diffusive transport of dissolved minerals [Detwiler et al., 2003; Detwiler and Rajaram, 2007; O’Brien et al., 2003; Szymczak and Ladd, 2009]. In most cases, some combination of these different processes controls the evolution of fracture apertures and permeability. For example, several studies [e.g., Dijk and Berkowitz, 1998; Detwiler and Rajaram, 2007; Szymczak and Ladd, 2009] have shown the importance of the relative magnitudes of chemical reaction rates and advective-diffusive transport, which can be quantified using the dimensionless Peclet number ($Pe = Vh/D_m$), where $V$ is the mean fluid velocity in...
the fracture, \( b \) is the mean fracture aperture, and \( D_m \) is the molecular diffusion coefficient of the dissolving mineral species) and Damkohler number (\( Da = kL/V(h) \), where \( k \) is a reaction rate coefficient, and \( L \) is the length of the fracture). In a fractured rock core, fast reaction rates (high \( Da \)) and diffusive transport (low \( Pe \)) lead to dissolution at the entrance of the fracture with little alteration observed elsewhere. Conversely, slow reaction rates (low \( Da \)) and advective transport (high \( Pe \)) lead to relatively uniform dissolution throughout the length of the fracture. However, under conditions where chemical disequilibrium persists for some distance into the fracture, preferential dissolution channels, or wormholes, develop because of a positive feedback between local permeability and local reaction rates [Detwiler et al., 2003; Hanna and Rajaram, 1998; Szymczak and Ladd, 2009].

Dissolution-induced aperture alterations are further complicated by the potential for preexisting preferential flow paths, which can result from aperture variability that occurs when two nonidentical surfaces are placed in contact. The structure of the initial aperture variability is influenced by the relative roughness of the fracture surfaces [Brown, 1995], by shear displacement of the surfaces [Durham and Bonner, 1994; Watanabe et al., 2009], and by regions of contact between the surfaces caused by stress applied normal to the fracture plane [Pyrak-Nolte and Morris, 2000; Zimmerman and Bodvarsson, 1996]. Though the relative magnitudes of \( Da \) and \( Pe \) largely control whether dissolution channels will form, the amount of aperture variability and associated preexisting preferential flow paths influence the behavior of developing dissolution patterns [Rajaram et al., 2009]. For relatively smooth surfaces, uniformly spaced dissolution channels advance along relatively straight paths. Significant aperture variability leads to more tortuous dissolution channels with less uniform spacing.

Most studies to date have investigated the influence of dissolution on the evolution of fracture permeability in fully saturated fractures. However, a number of problems of practical importance such as CO\(_2\) sequestration [Johnson et al., 2005] and enhanced oil recovery through acid injection [Bennion et al., 1994] involve reactive fluid flow in the presence of a second fluid phase. Recently, the influence of alternating flow of brine and CO\(_2\) through fractured cores [Andreani et al., 2008] was shown to cause rapid increases in permeability during gas flow because of the resulting decohesion of clay minerals from the fracture surfaces. Another scenario involving two-phase flow may occur when one phase becomes entrapped as a persistent, disconnected residual phase within variable aperture fractures [Glass et al., 2003]. When reaction kinetics at mineral surfaces are fast relative to the dissolution of the trapped nonwetting phase, such as with CO\(_2\) sequestration in carbonate formations [Ennis-King and Paterson, 2007], the presence of the entrapped phase will lead to preferential flow paths that may alter the formation and growth rate of dissolution channels.

In the laboratory experiments presented here, I directly measured changing fracture aperture and the distribution of the entrapped residual nonaqueous phase (air) in transparent analog fractures using quantitative visualization techniques. In these experiments, the initial distribution and potential mobilization of the entrapped air is controlled by the competition between capillary, viscous, and gravity forces within the fracture. A direct comparison of results from two
Figure 2. Semivariograms of the initial fracture aperture field calculated along the principle axes of anisotropy: +45° (dashed line) and −45° (solid line) from the long axis of the aperture field. The corresponding long and short correlation lengths of the fracture aperture field are $\lambda_L = 0.74$ and $\lambda_S = 0.37$, respectively.

Experiments in identical fractures at different orientations with respect to gravity and a similar experiment in a saturated fracture [Detwiler et al., 2003] demonstrates that the presence of a trapped residual phase significantly alters the dissolution-induced changes in the fracture apertures. Furthermore, the relative influence of gravity affects both the initial distribution of entrapped air and the mobilization of the entrapped air caused by dissolution-induced aperture alteration. The presence of an entrapped phase also accelerates the formation of dominant dissolution channels leading to a much more rapid increase in fracture transmissivity than has been observed in saturated fractures. These experiments were all carried out at similar values of $Pe$ and $Da$ and thus highlight the role of initial preferential flow paths caused by the entrapped air on the development of dissolution channels.

2. Experimental Methods

[7] Light transmission techniques [e.g., Detwiler et al., 1999, 2002] allow for detailed, nondestructive measurements of flow and transport processes in variable aperture fractures, provided suitable transparent analogs can be developed. For the experiments presented here, a $9.4 \times 14.5$ cm rough glass surface was mated with smooth, soluble surfaces (single KH$_2$PO$_4$ crystals) to create transparent analog fractures. This allowed both replication of the initial fracture aperture field and direct measurement of changing fracture aperture and entrapped air distribution within the fracture during each experiment.

The fracture cell was mounted above a uniform, near-monochromatic (633 nm peak wavelength) light source (Phlox light-emitting diode backlight) on a rotating frame that rigidly supported a $3072 \times 2048$ pixel, thermoelectrically cooled, 12-bit CCD camera (Photometrics Quantix 6303e) above the fracture cell. During experiments, injected fluids were dyed with a blue dye (1/8 g/L FD&C Blue #1), with peak absorbance at ~630 nm. Directly applying the Beer–Lambert law of light absorption to measured light intensities yields accurate, high-resolution ($75 \times 75 \mu$m pixels) measurements of the initial fracture apertures ($b \pm 3 \mu$m) and dissolution-induced changes in fracture aperture ($\Delta h \pm 5 \mu$m) over the entire flow field (see Detwiler et al. [1999] for an overview of the light transmission technique, and see Detwiler [2008] for modifications required in a fracture where the aperture field evolves with time). Figure 1 shows an image of initial fracture apertures ($b_i$) over the entire flow field. Figure 1 shows an absence of large-scale trends in fracture aperture and demonstrates a small amount of anisotropy in the fracture apertures. These qualitative observations are further supported by semivariograms of the fracture aperture field shown in Figure 2. The semivariograms are calculated along axes that are oriented at ±45° from the long axis of the fracture (i.e., aligned with the long and short correlation lengths, $\lambda_L$ and $\lambda_S$). Note that though these fractures are formed by mating a single rough surface with a smooth surface, natural fractures formed by mating two slightly offset self-affine fractal surfaces exhibit similar anisotropy in the fracture aperture field [Durham and Bonner, 1994; Mallikamas and Rajaram, 2005]. Furthermore, the statistics (mean, variance, and correlation lengths) provided in Table 1 are similar to those measured in natural rock fractures [Brown, 1995].

Measurements of light transmission also provide a means for directly quantifying the phase occupancy of individual pixels within each image. As with calculating fracture apertures, this is relatively straightforward when background images of the fracture filled with air and the dye-free solution are available. The images can then be normalized to yield sufficient contrast between the liquid and gas phases to allow use of a global thresholding routine to resolve the two phases. However, because of the changing fracture apertures and evolving entrapped air distribution, this was not possible for the experiments presented.

Table 1. Summary of Experimental Conditions

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$(b_i)$ (mm)</th>
<th>$\sigma_b$ (mm)</th>
<th>$\lambda_L$ (mm)</th>
<th>$\lambda_S$ (mm)</th>
<th>$\theta$</th>
<th>$Q_o$ (cm$^3$/s)</th>
<th>$S_o$</th>
<th>$Pe_o$</th>
<th>$Da_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.104</td>
<td>0.037</td>
<td>0.37</td>
<td>0.74</td>
<td>0°</td>
<td>0.0017</td>
<td>0.28</td>
<td>34</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td>0.104</td>
<td>0.037</td>
<td>0.37</td>
<td>0.74</td>
<td>35°</td>
<td>0.0036</td>
<td>0.86</td>
<td>67</td>
<td>18</td>
</tr>
<tr>
<td>Saturated</td>
<td>0.126</td>
<td>0.049</td>
<td>0.50</td>
<td>0.50</td>
<td>0°</td>
<td>0.0036</td>
<td>1.0</td>
<td>54</td>
<td>23</td>
</tr>
</tbody>
</table>

$^a\lambda_L$ and $\lambda_S$ calculated as the separation distance at which the semivariogram (Figure 2) reaches a value of $\sigma^2(1 - 1/exp (1))$.

$^bPe_o = V(b) / D_m$, where the mean flow velocity $V = Q/(b) W S_o$, and the molecular diffusion coefficient $D_m = 6.77 \times 10^{-6}$ cm$^2$/s [Mullin and Anantavivadhana, 1967].

$^cDa_o = kV(b)$, where the reaction rate coefficient $k = 5.6 \times 10^{-4}$ cm/s, and $L$ is the fracture length. Note that for the case where both fracture surfaces are dissolving, $Da_o$ must be multiplied by 2 to reflect the increased reaction rate caused by two reacting surfaces [Detwiler and Rajaram, 2007].
here. Instead, light reflection at the curved air-liquid interfaces (Figure 3) aided in delineating individual regions of residual trapped air. A global-thresholding routine identified a subset of the pixels in each air bubble, and a region-growing algorithm [Gonzalez et al., 2003] identified the remainder of the pixels within each air bubble. The results give very good visual agreement between the original gray-scale images and the processed binary fields (Figure 3).

3. Overview of Experiments

[10] To initiate each experiment, the fracture was first saturated with water pre-equilibrated with KH$_2$PO$_4$ ($c_s = 22.0\%$ by weight) at the temperature of the water in the fracture ($18.5^\circ\mathrm{C} \pm 0.2^\circ\mathrm{C}$). For each experiment, the fracture was then drained and refilled, leaving residual entrapped air bubbles present at the initiation of the dissolution phase. Rotating the test stand to orient the fracture plane at an angle ($\theta$) of $35^\circ$ from horizontal sufficiently increased the influence of gravitational forces to stabilize the air-water interface during the primary drainage cycle. After the initial drainage phase, the water-air distribution for the two fractures was nearly identical, supporting the reproducibility of the experimental procedure. Slow flow rates (0.02 ml/min, which corresponds to a Capillary number, $Ca = \mu V/\tau$, of $5 \times 10^{-7}$, where $\mu$ is the dynamic viscosity, $V$ is a mean flow velocity in the fracture, and $\tau$ is the interfacial tension) during drainage and subsequent imbibition ensured that capillary and gravitational forces controlled the displacement process. Prior to imbibition and initiation of the dissolution phase for experiment 1, the fracture plane was rotated to horizontal, negating the influence of gravity. For experiment 2, the fracture plane remained at $\theta = 35^\circ$ for the duration of the experiment, and water flowed upward through the fracture.

[11] After the imbibition phase, the fracture contained air bubbles that were completely surrounded by flowing water (Figure 4) and exhibited a small amount of anisotropy as a result of the correlation structure of the fracture aperture field. Capillary forces immobilized the air bubbles such that increasing the flow rate to 0.2 ml/min resulted in negligible air bubble mobilization. Because the initial fracture aperture fields were identical, there are strong similarities in the initial entrapped air distribution for the two experiments. However, the differing influence of gravity during imbibition in experiment 2 reduced the average size of the entrapped air bubbles and led to higher initial aqueous phase saturation ($S_a$) (Table 1), which has been shown to strongly influence relative permeability in variable aperture fractures despite fairly significant differences in the relative size, shape, and distribution of trapped regions [Detwiler et al., 2005, 2009].

[12] The dissolution phase of the experiments was initiated by closing the outflow manifold, slowly filling the inflow manifold with undersaturated solution ($c_o = 0.95c_s$), and opening the outflow manifold to allow the undersaturated fluid to flow through the fracture. A constant head inflow reservoir 4 cm above the outlet provided a constant hydraulic gradient during each experiment. Approximately 2 m of 1.6 mm inner diameter tubing connected the inflow and outflow to the fracture, and a balance recorded the cumulative mass outflow from the fracture. The CCD camera acquired images at 2 min intervals.

4. Experimental Results

[13] Despite identical initial hydraulic gradients, the initial flow rates ($Q_o$) for the two experiments differed because of the difference in $S_a$ (Figure 5). In addition, at early times ($t < \sim 4$ h), $Q$ changed at different rates for the two experiments (as apertures began to increase because of dissolution). During experiment 1, which began with a lower $Q_o$, $Q$ initially increased more quickly than in experiment 2. However, after a period of dissolution channel initiation, both experiments exhibited a period of rapid increase in $Q$ followed by a period of relatively uniform $Q$ at later times. The rapid increase in $Q$ (between approximately 4 and 8 h) for both experiments was due to the breakthrough of dissolution channels that gradually developed at early times.
ments, the fracture surfaces were fixed in space (that is, dissolution did not lead to closure of the fracture), so \((b)/\langle b_o \rangle\) is directly related to the mass of minerals dissolved from the fracture surfaces. At early times \((b)/\langle b_o \rangle < 1.1\), see dynamic content), the influence of the entrapped air on dissolution is not strongly evident, yet for experiment 1, a larger value of \(D_o\) resulted in more focused dissolution tendrils forming from the inflow end of the fracture. Experiment 2 exhibited more uniform dissolution with preferential dissolution of small aperture regions. These early time results are similar to the observations in the saturated experiment.

As dissolution proceeded farther into the fracture, the influence of preferential flow paths caused by the entrapped air became increasingly evident (Figure 6). At early times, dissolution occurred predominantly along these flow paths leading to the formation of distinct channels. In experiment 1, the resulting channels are deeper and more focused, as seen by the light blue and green colors that propagate farther into the fracture (Figure 6). In experiment 2, the combined influence of a larger \(S_o\) (i.e., more space between air bubbles) and a lower \(D_o\) results in more diffuse dissolution channels, with more gradual aperture increases along their length. Because aperture growth propagates farther into the fracture for experiment 1, there is less pressure loss along the length of the primary dissolution channel, leading to higher pressure at the tip of the channel [Cheung and Rajaram, 2002; Szymczak and Ladd, 2009]. This results in a larger pressure gradient (and larger \(Q\)) through the unaltered region of the fracture, which explains the more rapid increase in \(Q\) at early times during experiment 1. At later times \((b)/\langle b_o \rangle = 2.2\), significant dissolution channels extended to the outflow end of the fracture, whereas for the saturated fracture, the longest of the several channels only caused small increases in fracture aperture at the outflow end of the fracture (Figure 6).

During growth of the dissolution channels, the relative rate of aperture growth along channels influenced the alteration of local capillary forces. The resulting imbalance between capillary, viscous, and gravity forces along air-water interfaces caused mobilization of some of the air

Figure 5. Evolving flow rate plotted against time for experiments 1 (squares) and 2 (triangles). The elevation of inflow and outflow reservoirs was the same for both experiments; differences in initial flow rates reflect the different initial saturation for the two experiments.

4.1. Aperture Alteration and Bubble Migration

Different distributions of entrapped air and the resulting variation in \(Q_o\) (and thus, \(D_o\)) led to noticeable variations in the dissolution process for the two experiments. In the absence of entrapped air, lower values of \(D_o\) lead to more diffuse dissolution patterns [Detwiler and Rajaram, 2007; Szymczak and Ladd, 2009], which are also evident at early times in the partially saturated experiments presented here. Figure 6 shows frames from animations (see dynamic content) of the changing fracture aperture and entrapped air distribution for experiments 1 and 2 and an experiment in a similar fully saturated fracture [Detwiler et al., 2003].\(^1\) The saturated experiment was carried out at a similar value of \(D_o\) to the partially saturated experiments presented here (Table 1). The frames in Figure 6 show the state of each experiment at a sequence of relative changes in mean fracture aperture, \((b)/\langle b_o \rangle = 1.4, 1.8, \text{ and } 2.2\). During these experiments, the fracture surfaces were fixed in space (that is, dissolution did not lead to closure of the fracture), so \((b)/\langle b_o \rangle\) is directly related to the mass of minerals dissolved from the fracture surfaces. At early times \((b)/\langle b_o \rangle < 1.1\), see dynamic content), the influence of the entrapped air on dissolution is not strongly evident, yet for experiment 1, a larger value of \(D_o\) resulted in more focused dissolution tendrils forming from the inflow end of the fracture. Experiment 2 exhibited more uniform dissolution with preferential dissolution of small aperture regions. These early time results are similar to the observations in the saturated experiment.

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Figure 4. Initial distribution of the entrapped air (white) for experiments 1 and 2. Drainage and imbibition were from the left-hand edge of the fracture, and flow was from left to right during the dissolution experiment. The thin vertical lines inset from the left and right edge of the fracture are artifacts caused by the clear gaskets that separated the fracture surfaces from the transparent test frame. These regions were removed from each measured field prior to carrying out flow simulations.

During both experiments. At later times (and higher \(Q\)), head losses through the inflow and outflow plumbing surpassed the head losses through the fracture, such that increases in the fracture aperture had a diminishing influence on \(Q\).
bubbles as dissolution proceeded. In the absence of buoyant forces (experiment 1), capillary and viscous forces alone drove the mobilization of air bubbles. Even near the end of the experiment, when fracture apertures were relatively large (small capillary forces) and flow velocities were relatively high (large viscous forces), capillary forces still dominated air bubble mobilization as demonstrated by air bubbles in the middle of the dominant channel migrating toward the inflow manifold (opposite the viscous pressure gradient) at late times. Because the location of air bubbles strongly influenced the location of conductive flow paths within the fracture, the mobilization of air bubbles created a feedback mechanism that altered the path of dissolution channels. During experiment 1, air bubbles migrated into incipient secondary channels, effectively blocking further flow and further focusing the primary dissolution channel (see dynamic content).

To quantify the conditions under which bubbles are mobilized by buoyant forces, it is useful to define the Bond number (ratio of buoyant to capillary forces) as

\[
Bo = \frac{\langle b \rangle L \Delta \rho g \sin \theta}{\tau},
\]

where \(L\) is a bubble length scale, \(\Delta \rho\) is the difference in density between the trapped and flowing phases, \(g\) is gravitational acceleration, and \(\tau\) is the interfacial tension of the air-water interface. For experiment 2, bubbles began to migrate upward when local values of \(Bo\) exceeded the range of 0.1–0.2. Once bubbles were mobilized, they typically followed the center of the dissolution channel where they sometimes coalesced to form larger bubbles, increasing \(L\) and the buoyancy of the bubble, further enhancing upward migration. The result is that unlike experiment 1, where bubbles accumulated in and adjacent to the dissolution channel, buoyant forces tended to remove bubbles from the channel over time, further enhancing the width of the dissolution channel during experiment 2.

4.2. Transmissivity Alteration

[18] Observations of fracture dissolution in the two partially saturated fractures highlight the interplay between entrapped phase distribution and mobilization on the evo-
solution of fracture apertures during reactive fluid flow. Because large-scale numerical models often rely upon simple relationships between fracture aperture and permeability (or transmissivity) alterations, it is also useful to consider the influence of aperture alterations and redistribution of entrapped phase on fracture transmissivity ($T$), where flow rate through the fracture is

$$Q = T \frac{D_h}{L} W,$$

where $D_h$ is the change in hydraulic head across the fracture, and $W$ and $L$ are the width and length, respectively, of the fracture. Note that in saturated fractures, the cubic law is often invoked to estimate a fracture-scale saturated transmissivity, $T_{\text{sat}} = \frac{b_{\text{eff}}^3 g}{12 \nu}$, where $b_{\text{eff}}$ is effective hydraulic aperture of the entire fracture, $g$ is gravitational acceleration, and $\nu$ is the kinematic viscosity of the fluid. In partially saturated fractures, $T = k_i T_{\text{sat}}$, where $k_i$ is the relative permeability, which depends strongly on saturation [e.g., Detwiler et al., 2005]. Because head losses in the experimental plumbing were comparable or, at later times, greater than head losses through the fracture, it is not possible to directly calculate $T$ from measured $Q$ during the experiments. Instead, we used the measured fracture aperture fields and entrapped air distribution as input for computational flow simulations using the depth-averaged Reynolds equation. Despite limitations of the Reynolds equation [e.g., Adler and Thovert, 1999; Brush and Thomson, 2003], it provides excellent estimates of relative changes in fracture transmissivity caused by an entrapped phase [Nicholl et al., 2000] and allows direct comparison of results to our previous experiment in the fully saturated fracture. For the simulations presented here, the fracture was discretized by assigning each pixel in the $\Delta h$ images (Figure 6) the measured aperture and by assigning zero transmissivity to pixels occupied by entrapped air [e.g., Detwiler et al., 2002; Nicholl et al., 1999]. Note that this assumes that the air bubbles completely span the fracture, because in the absence of contacting fracture surfaces, the bubbles would be spherical; this is a reasonable assumption when the diameter of the bubble in the fracture plane is larger than the local fracture aperture (most bubbles in the experiments presented here). This approach for modeling flow in the vicinity of air bubbles neglects the possible role of thin films of water between the air and fracture surface [Tokunaga and Wan, 1997; Or and Tuller, 2000], but these films are likely to be at least an order of magnitude thinner than the fracture aperture (with transmissivity at least 3 orders of magnitude smaller than water-filled locations).

Figure 7 shows simulated estimates of local flow rates, $q$, normalized by the mean flow rate through a single grid block in the initial aperture field under fully saturated conditions, $\langle q_{\text{sat}} \rangle$. The frames shown in Figure 7 (taken from the animations provided as dynamic content) show each experiment at $\langle b \rangle / \langle b_o \rangle = 1.4, 1.8$, and 2.2, which corresponds to the $\Delta h$ fields shown in Figure 6. Note that to facilitate visualization of $q/\langle q_{\text{sat}} \rangle$ over the full range of observed fluxes, the color scale is applied to log ($q/\langle q_{\text{sat}} \rangle$). In addition, to clarify the relative magnitudes of $q/\langle q_{\text{sat}} \rangle$ in...
transmissivity (at the outflow (Figure 7, + 1.4) in experiments 1 and 2, ∼ T_{0.11}) than experiment 1 (ffii 1.3), the = 2.5. Though (3) is a simplified model in 2. Johnson et al. were predominantly became similar for both experiments.

due to changes in fracture aperture [e.g., w T_{o} D is the width of the channel relative to the fracture, for experiment 1 was significantly less than for increased more quickly for due to growth of the primary dissolution channel. Once the dissolution channels

dissolution progressed, T increased more quickly for experiment 1 than either experiment 2 or the saturated experiment owing to the relative long development period for the primary dissolution channel. The result is that unlike in the partially saturated fractures, even after

![Figure 8](image1.png)

**Figure 8.** Transmissivity (T) normalized by the transmissivity through the fully saturated initial fracture aperture field (T_{o, sat}) plotted against the normalized mean aperture during dissolution experiments in partially saturated fractures (experiment 1, squares; experiment 2, triangles) and a similar saturated fracture (crosses). The solid line shows the transmissivity predicted by the cubic law.

the evolving dissolution channels, the right plots in Figure 7 show profiles of simulated q/(q_{o, sat}) at the outflow (Figure 7, right) end of the fractures for each experiment. Initially, for both experiments 1 and 2 (dynamic content), the entrapped air bubbles act to focus flow through several nondistinct preferential flow paths. This contrasts with the saturated fracture, where the numerous preferential flow paths are completely defined by the small-scale aperture variability. At relatively early times ((b)/(b_{o}) ∼ 1.4) in experiments 1 and 2, preferential dissolution channels extend from the inflow end of the fracture to the outlet. In both of these experiments, once the dominant channel forms, additional dissolution occurs predominantly along this channel. In the saturated fracture at early times, dissolution channels begin to form but only become clearly evident at the outflow end of the fracture when (b)/(b_{o}) ∼ 2.

[20] Figure 8 compares T normalized by the initial transmissivity of the fully saturated fracture (T_{o, sat}) over the duration of experiments 1 and 2 and the saturated experiment. Also shown is the cubic law prediction, which relates T to the cube of the aperture for parallel-sided fractures; despite known limitations of applying the cubic law to rough-walled fractures, it is often used to estimate changes in T due to changes in fracture aperture [e.g., Gherardi et al., 2007; Johnson et al., 2005]. The results show that, as expected, T_{o} for experiment 1 was significantly less than for experiment 2 because of the difference in S_{o}. However, as dissolution progressed, T increased more quickly for experiment 1 than either experiment 2 or the saturated experiment owing to the more focused growth along the primary dissolution channel. Once the dissolution channels reached the outflow end of the fracture ((b)/(b_{o}) ∼ 1.3), the rate of change of T became similar for both experiments. This is because further increases in T were predominantly due to growth of the primary dissolution channel.

[21] The influence of aperture growth along the primary dissolution is clarified by considering the idealized case of a saturated parallel-sided fracture with aperture, b, through which a single dissolution channel passes. If dissolution occurs only along the channel, a simple expression for the fractional increase in transmissivity can be derived from (2) applied to this idealized geometry

$$\frac{T}{T_{o, sat}} = 1 + w \left( \frac{1 + \Delta b}{b} \right)^{3} - 1,$$

where w is the width of the channel relative to the fracture, and Δb is the change in aperture within the channel. This simple model (Figure 9) provides a reasonable approximation of the rate of transmissivity increase in experiments 1 and 2, because during most of the experiment, dissolution occurs predominantly along the main dissolution channel. Because the channel is almost 40% wider in experiment 2 (w ∼ 0.11) than experiment 1 (w ∼ 0.08), the final transmissivity is approximately 2.25 times larger in experiment 2 at (b)/(b_{o}) = 2.5. Though (3) is a simplified model in that it does not consider the influence of the entrapped air on changing transmissivity, it predicts the relative difference in transmissivity for the two partially saturated experiments remarkably well. However, this simplified model poorly predicts the evolution of transmissivity in the saturated fracture owing to the significant aperture alteration across the width of the fracture at early times, which is in turn due to the relative long development period for the primary dissolution channel. The result is that unlike in the partially saturated fractures, even after

![Figure 9](image2.png)

**Figure 9.** Transmissivity (T) normalized by the transmissivity through the unaltered fracture aperture field (T_{o}) plotted against the normalized mean aperture during dissolution experiments in partially saturated fractures (experiment 1, squares; experiment 2, triangles) and a similar saturated fracture (crosses). The solid lines show predictions of a simplified model (equation (3)) of an idealized saturated fracture in which a dissolution channel of width (w) extends along the length of the fracture. Width is estimated from right plots in Figure 7.
the primary dissolution channel breaks through to the outflow end of the fracture, the secondary channels continue to contribute to the overall flow through the fracture.

5. Concluding Remarks

[22] Results from two dissolution experiments in partially saturated fractures demonstrate the complicated interaction between local dissolution-induced aperture alterations and the resulting mobilization of residual entrapped air. In the absence of buoyant forces, the entrapped air migrates in the opposite direction of flow owing to the changes in local capillary forces, resulting in a narrower, faster growing dissolution channel. Introduction of buoyant forces causes bubbles to migrate upward when Bo exceeds a value of approximately 0.2 and eventually exits the fracture resulting in a broader more open dissolution channel. Though initial values of T are less than those observed in a similar saturated experiment, the relatively rapid formation of a dominant dissolution channel in the partially saturated experiments causes T to quickly surpass both the results from a saturated experiment and estimates based on the cubic law.

[23] The experiments presented here demonstrate the importance of the initial distribution of an entrapped phase on the early development of dissolution channels in fractures. These results suggest that the presence of preferential flow paths in the initial flow field can dramatically affect both time to breakthrough of dissolution channels and the relationship between mean fracture aperture and transmissivity. In the absence of an entrapped phase, large-scale preferential flow paths may also be caused by the initial fracture aperture distribution, particularly in fractures with regions of contact between the surfaces. Increasing contact area by adding randomly distributed contact points has been shown to have a weak effect on the formation of dissolution channels [Szymczak and Ladd, 2009]. However, in fractures composed of mated self-affine surfaces, contact areas may exhibit spatial correlation that leads to the formation of preferential flow paths [Watanabe et al., 2009] that are more similar to those observed in the partially saturated experiments presented here.

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