Experimental investigation of the dissolution of quartz by a muscovite mica surface: Implications for pressure solution

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[1] Using the surface forces apparatus, which can measure small changes in thickness occurring even at essentially geological timescales, we have measured dissolution of quartz sheets when pressed against muscovite mica surfaces in aqueous electrolyte solution, but no dissolution is observed under dry conditions. It is postulated that the dissolved quartz may reprecipitate outside the contact junction as a fragile silica gel, which could be the main factor limiting the rate of further dissolution.

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1. Introduction

[2] Pressure solution has been the topic of considerable research since the pioneering work of Sorby, which suggested a relationship between mechanical and chemical forces for the origins of the microstructures that geologists observe in rocks [*Sorby*, 1863, 1908]. The term "pressure solution" encompasses such phenomena as pitting and indentation at grain contacts, stylolite formation, overgrowths, dissolution seams, cleavages, and deformation of metamorphic rocks. It is a process that requires both the presence of a solution, which has been seen to play an important role in the process, [e.g., *Hickman and Evans*, 1991, 1995; *Renton et al.*, 1969] and mass transport. The term "pressure solution" was first coined by *Sorby* [1908], based on indirect evidence for the involvement of solution as well as preliminary findings that high pressures may facilitate chemical changes in water and increase the solubility of salts [*Sorby*, 1863, 1908]. It is no longer clear, however, that high pressures are necessary for this process to take place [*Bjorkum*, 1996].

[3] Geological field studies frequently find that the presence of clays, particularly muscovite mica, enhances quartz dissolution [*Becker*, 1995; *Bjorkum*, 1996; *Fisher et al.*, 2000; *Heald*, 1955, 1956; *Houseknecht*, 1988; *Houseknecht and Hathon*, 1987; *Schwarz and Stockhert*, 1996; *Weyl*, 1959], and laboratory experiments have confirmed this effect [*Anzalone et al.*, 2006; *Hickman and Evans*, 1995;

Renard et al., 2001; *Rutter and Wanten*, 2000], although the interpretation of these results has been called into question [*Niemeijer and Spiers*, 2002]. Despite the many observations in the field, the dissolution of quartz by a mica surface has yet to be directly observed in a laboratory experiment. In the work presented here, we directly investigate the dissolution of Z-cut quartz (quartz c axis perpendicular to plane of surfaces) in contact with mica. In acidic brine, rapid dissolution is observed even at relatively low pressures while in the absence of solution, no dissolution is observed. Using the surface forces apparatus (SFA), we are able to directly observe dissolution of several nanometers of quartz over timescales of minutes to hours, allowing us to follow the changing rate of dissolution with time.

2. Methods and Materials

[4] Experiments were carried out in a surface forces apparatus (SFA) Mark III as previously described [*Israelachvili and McGuiggan*, 1990] with particular attention given to the cleanliness of the chamber and solutions used. All water used for preparing the solutions was purified by a Milli-Q (Elix-10 and Milli-Q Gradient A10) water purification system. A solution of 30 mM $CaCl_2$ (Sigma-Aldrich, Co.) was used to mimic geological conditions; however, the pH in the experiments was typically between 2.5 and 3.0 from addition of nitric acid. This pH was chosen because dissolution was most pronounced in this range. Similar dissolution is observed for surfaces immersed in $CaCl_2$ solution at pH 3 for 90 minutes before being brought into contact in $CaCl_2$ solution at close to neutral pH (pH 6), indicating that this low pH may simply play a role by initially enhancing protonation of the surfaces. All experiments were carried out at a temperature of 25°C.

[5] In SFA experiments, two transparent sheets, e.g., of mica or glass, are silvered on one side then mounted (glued) onto glass disks, silvered sides down, and positioned inside the SFA where they can be brought together in a controlled way. White light is passed normally through the surfaces

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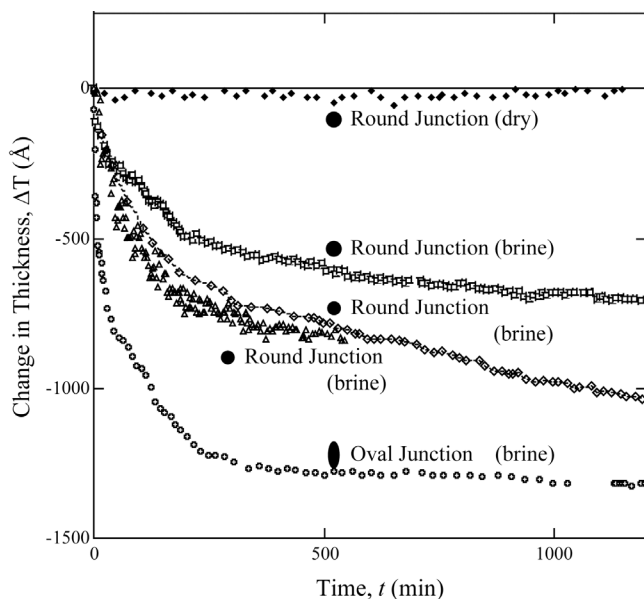
Figure 1. Five representative data from nine SFA experiments showing the change in Z-cut quartz thickness as a function of the time the quartz was in contact with muscovite mica at a mean junction pressure of 2–3 atm. The bottom four curves (open symbols) represent experiments carried out in acidic brine, while the top curve (solid symbols) represents typical data in dry conditions. The shape and relative size of each junction are indicated above each plot. Contact areas for all junctions were approximately 1.0 ± 0.5 mm^2.

and multiple beam interference fringes, commonly referred to as fringes of equal chromatic order, or FECO, can be used to accurately and unambiguously determine the absolute surface separation D between the two back-silvered surfaces, the (changing) thickness of the sheets, and the shape of the surfaces at any moment in time. For two thin (<5 μm) surfaces, distance resolution is about 1 Å, but the resolution is less in the case of the thicker quartz sheets used in the experiments carried out here. It is worth noting that the interferometric method used in SFA experiments allows measurement of changes in the absolute thickness of the quartz sheets occurring at the nanometer level over a period of several days, so that even changes in thickness as slow as 10^{-13} m/s (corresponding to 1 μm in 3 years or 1 m in 3 million years) can be measured in a laboratory experiment lasting only a few days.

[6] To prepare the surfaces (mica sheets and quartz plates) for use in these studies, a thin (2–3 μm thick) sheet of step-free, molecularly smooth muscovite (S & J Trading, Inc., New York) was glued to a spherical disk of radius $R =$ 2 cm after being back-silvered. Muscovite is the standard material used in SFA experiments, and its chemical composition was analyzed by *Israelachvili and Adams* [1978]. A piece of Z-cut quartz (MTI Corporation, both sides epi-polished) was further polished down from an original thickness of 100 μm to 10–30 μm using an Allied Multi-Prep system. The mechanically polished side was silvered, and a small piece was then glued to a flat disc, silvered side down, leaving the epi-polished side (average roughness 2–3 Å) exposed for use in the experiment.

[7] In all experiments, the two surfaces were mounted in the SFA Mark III chamber that was then sealed and purged with nitrogen gas for several hours, after which a particle-free contact (as ascertained from the flatness of the FECO fringes) between the spherical mica and flat quartz piece was found in air. For "dry" experiments, the surfaces were brought into contact and a mean junction pressure of 2–3 atm was applied. This pressure was obtained from the applied force divided by the optically measured area. For "wet" experiments, the surfaces were separated and the chamber was filled with acidic 30 mM CaCl$_2$. The surfaces were then returned to contact, where a pressure of 2–3 atm was applied. Changes in the FECO (fringe pattern) were recorded constantly over time using a video camera recording system, allowing resolution of changes in distance and/or thickness on the order of 20 Å or better, as well as changes in surface shape, to be monitored in real time. (The 10–20 Å resolution is well below the 1–2 Å resolution possible with this optical technique due to the approximately 10 times larger thickness of the quartz plate compared to that of the mica sheet.)

3. Results and Discussion

[8] Representative data taken from five separate experiments in solution and four under dry ("control") conditions are shown in Figure 1. In the case of Z-cut quartz in contact with mica in the absence of solution (dry case), no dissolution or thickness changes of the quartz are observed, indicating that the dissolution observed in the presence of
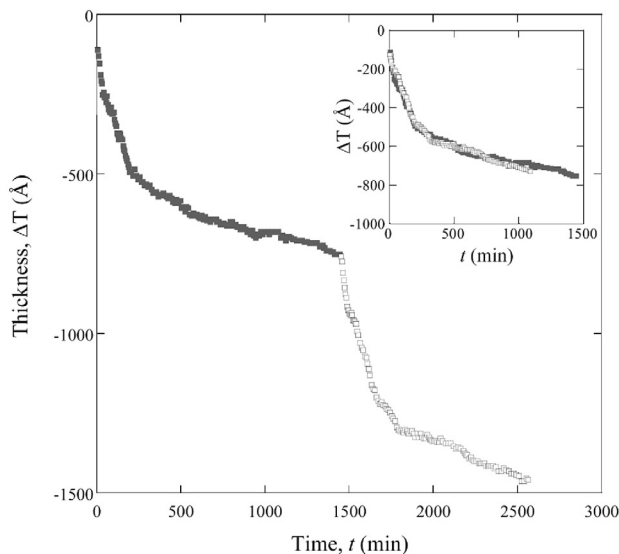
Figure 2. Representative data from an SFA experiment showing the change in quartz thickness when in contact with muscovite over longer timescales for a round contact (compare Figure 1). After the initial dissolution slowed to a steady rate, rapid dissolution began again at $t = 1450$ min when the apparatus was agitated. The time, $t = 0$, in the inset has been shifted so that the start of the second period of dissolution matches up with that of the first. The two superimposed curves are seen to be nearly identical.
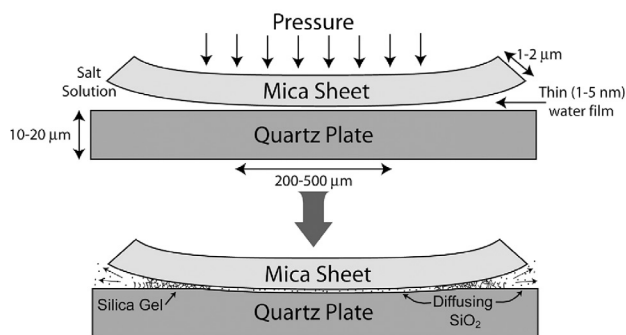
Figure 3. A schematic representation of the contact geometry and possible silica gel or precipitate formation is shown. Muscovite mica thickness remains constant, while the quartz is dissolved into solution. This dissolved silica is likely to be supersaturated just outside the contact area.

acidic brine (wet conditions) is not due to slow aging effects or plastic deformations of the quartz surface. In the presence of acidic brine we find initially rapid dissolution of the quartz surface, which slows down considerably after a few hours (typically around 500 min). Similar decay curves were observed by Hickman and Evans in the case of halite-silica interfaces [*Hickman and Evans*, 1995].

[9] In experiments run on the wet quartz-mica systems, the rate of initial, rapid dissolution is seen to vary quantitatively from junction to junction, presumably reflecting the different shapes and pressure distributions within these junctions, which all had comparable total areas ($\sim 1.0 \pm 0.5$ mm^2) and mean pressures ($2-3$ atm). For example, the larger rate of initial dissolution in the case of the oval junction may be due to the shorter path for diffusion along the narrower dimension of the oval. The FECO optical technique requires two surfaces to be in or close to contact. Any dissolution immediately appears as a movement of both the even and odd order fringes, which gives information both on the change in thickness of the mica or quartz, and of the refractive index of the aqueous medium between them [*Israelachvili*, 1973]. For well-separated surfaces the fringes were curved (reflecting the undeformed roundness of the mica surface) while for compressed surfaces they were elastically flattened. In the former case, even with the two surfaces held apart, we saw no movement of the fringes, indicating no dissolution (of either surface); rapid movement only occurred when the surfaces were in flattened contact.

[10] After the initial rapid dissolution, further dissolution settles to an approximately constant rate of ~ 0.1 Å/min for all contact junctions. Atomic force microscopy (AFM) imaging performed on the quartz surfaces before and after these experiments showed no change in the overall surface roughness. Because of the large (~ 1 mm^2) area of the contact junction, the large radius (~ 2 cm) of the mica surface "indenter," and the relatively small (~ 1000 Å) depth of the dissolution "pit," imaging of this very shallow depression is not possible with AFM or scanning electron microscope (SEM) techniques.

[11] The slowing of the rate of dissolution after several hours might be taken to indicate saturation of the solution by the dissolved quartz, but saturation of the bulk solution in the SFA chamber (volume ~ 200 mL) by dissolution from such a small area would not be possible. Even a high-end estimate of the volume of quartz dissolved results in a bulk concentration of less than 5 µg/L, or 4 orders of magnitude less than the concentration required for saturation [*Iler*, 1979]. In fact, the rapid dissolution was seen to restart after agitation of the surfaces and to follow a trend almost identical to that of the initial dissolution (see Figure 2). This hints at the possibility that it may in fact be the local diffusion and possible reprecipitation of the supersaturated silica, in the form of a silica gel or other complex precipitate structure [*Iler*, 1979; *Hayrapetyan and Khachatryan*, 2004], in the thin gap or just outside that contact junction that is responsible for limiting the rate of dissolution. A schematic of this scenario is shown in Figure 3, in which we postulate that a silica gel may be forming at the edge of the quartz-mica contact.

[12] The SFA data presented here offer preliminary results of the direct observation of the dissolution of a quartz surface in contact with muscovite mica, and provide some qualitative and quantitative details on the pressures, rates and time evolution of dissolution. That such rapid dissolution occurs even at pressures of just a few atmospheres is not inconsistent with the idea presented by *Bjorkum* [1996] that pressure serves primarily to bring the grains together to allow dissolution to occur. With our current data, however, it is not possible to distinguish pressure effects from proximity effects, as the two parameters are intrinsically related. Further investigations are needed to determine the physics and (electro)chemistry underlying the whole process, the role that crystallographic orientation, muscovite mica, and solution chemistry and conditions play in this process.

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