Effect of Fluid Chemistry on the Interfacial Composition, Adhesion, and Frictional Response of Calcite Single Crystals—Implications for Injection-Induced Seismicity

Yijue Diao and Rosa M. Espinosa-Marzal

1Civil and Environmental Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, USA

Abstract While it has been shown that the mechanical properties and the reactivity of carbonate-bearing rocks may be influenced by the chemical composition of the fluids, little is known about how the fluid composition affects their frictional response. Here, we have used atomic force microscopy to investigate the frictional characteristics of single calcite crystals in calcium carbonate saturated solutions and in two brines, NaCl and CaCl2, at a wide range of geologically relevant concentrations. Surface forces were measured to determine the ion-specific composition of the confined fluid films and the adhesion between the confining surfaces. The effect of fluid chemistry on calcite's (dynamic) frictional response significantly depends on the normal stress. At low stresses, the confined fluid film lubricates the single-asperity contact efficiently, resulting in low friction coefficients, especially in the case of NaCl solutions. When the pressure solution of calcite is triggered at sufficiently high stress, a significant reduction of the friction coefficient was observed, and in this case, CaCl2 solutions were shown to promote this frictional weakening more significantly than NaCl. This is the first experimental investigation of the ion-specific frictional characteristics of calcite at the level of a single-asperity contact. The presence of infiltrated fluids in carbonate faults may also play a critical role in fault dynamics. Hence, the results of this nanoscale study are extrapolated to carbonate fault friction in the presence of infiltrated fluids, and they contribute to advancing our understanding of induced seismicity at geological scale.

1. Introduction

Fluid injection is often associated with an increasing rate of seismic activity (Healy et al., 1968). For instance, most induced seismicity in the Midwestern United State has been attributed to the disposal of large volumes of coproduced wastewater from oil and gas extraction (Ellsworth, 2013). In western Canada, induced micro-earthquakes have been directly related to hydraulic fracturing activities (Bao & Eaton, 2016), during which fluids are injected under high pressure to induce localized fracturing of low-permeability rock layers (Atkinson et al., 2016). There is evidence for the relation between fluid injection and nearby earthquake activities; injection rate (Weingarten et al., 2015), injection volume (Göbel, 2015; McGarr, 2014), diffusivity and permeability (Shapiro et al., 2003), and poroelasticity of the fault zones (Beeler et al., 2000; Segall & Lu, 2015) are observed to affect the evolution of the induced seismic events.

Although the nature of the hazard from wastewater injection and from hydraulic fracturing is different, the correlation between fluid injection and induced seismicity in a nearby fault is often explained via the Coulomb failure criterion, \( \tau_s = C + \mu_s (\sigma_n - P_f) \), where \( \tau_s \) is the shear stress on the preexisting fault, \( C \) is the cohesion, \( \mu_s \) the static friction coefficient (i.e., the frictional strength of the fault), \( \sigma_n \) the normal stress, and \( P_f \) the fluid pressure (Scholz, 2019). In either case, the increase of fluid pressure \( P_f \) reduces the effective normal stress \( \sigma_n' = \sigma_n - P_f \) (Rubey & King Hubbert, 1959), which shifts the stress state closer to the shear failure condition, thereby promoting fault slip. The change in the stress state during hydraulic fracturing has been also related to fault reactivation (Bao & Eaton, 2016).

Once slip commences, it is resisted by the dynamic friction coefficient. Rate-and-State Friction (RSF) constitutive equations (Dieterich, 1979; Ruina, 1983) are commonly used to describe rock friction as a function of the sliding velocity and to account for the spatial and temporal evolution of slips. In steady state, the dynamic friction of fault materials is shown to either increase or decrease with the slip velocity, which is called velocity-strengthening versus velocity-weakening friction, respectively. According to RSF equations,
if the fault stiffness is smaller than a critical value, a decrease of friction with the slip velocity will yield unstable slip (or stick-slip), which has long been associated to seismic slips. RSF equations predict that the fluid overpressure decreases this critical value, thereby promoting aseismic slip (Scholz, 1998). In contrast to this prediction, recent works suggest that the fluid overpressure can trigger a frictional instability even in velocity-strengthening fault materials (Audet & Schwartz, 2013; Scuderi et al., 2017). Although the origin of this effect has been loosely related to compaction and dilation (Scuderi et al., 2017) and to pressure solution (Verberne et al., 2010), the underlying mechanisms have not been thoroughly explained and quantified yet. Resolving these apparent inconsistencies and developing improved predictive models for earthquakes remain still important challenges (Bao & Eaton, 2016).

While the reduction in effective normal stress is still regarded as the major cause of the induced seismicity, emerging evidence suggests that the fault frictional strength can be weakened in the presence of reactive fluids (Floyd et al., 2001; Heinicke et al., 2009; Meller & Kohl, 2014; Vavryčuk & Hrubcová, 2017). For instance, in the context of enhanced geothermal systems, it has been proposed that reactive fluids may lead to the dissolution and/or the chemical alteration of the preexisting fracture plane. This may produce secondary minerals (here, clay), which cause both the friction coefficient and the cohesion at the fault plane to decrease, thereby bringing the fault closer to failure (Meller & Kohl, 2014). It was also proposed that hydrothermal alteration of crustal rocks, dissolution at fault planes and gradual fault weakening due to the interactions with the injected fluids play an important role in the evolution of induced earthquakes (Floyd et al., 2001; Heinicke et al., 2009; Vavryčuk & Hrubcová, 2017). Because host rock-fluid reactions may modify the friction coefficient and influence the induced seismicity, these studies draw attention to the influence of the chemical composition of the injected fluid on the reactivity and frictional characteristics of fault materials.

Due to the abundance of carbonate-bearing rocks in the lithosphere and their prevalence in oil reservoirs (Burchette, 2012), several laboratory studies have focused on carbonate fault materials. Calcite is regarded as the most popular model mineral for carbonate-bearing rocks, and therefore, it has been intensively investigated in the context of its interaction with water, both experimentally (Andersson & Stipp, 2012; Jordan & Rammensee, 1998; Stipp, 1999) and computationally (de Leeuw & Parker, 1997; de Leeuw & Parker, 1998; Kerisit & Parker, 2004; Wolthers et al., 2012; Wolthers et al., 2013). There is evidence for the dependence of calcite’s dissolution and precipitation on fluid chemistry (Gledhill & Morse, 2006; Wolthers et al., 2013). When a stress is applied on a mineral, its dissolution is thermodynamically driven by the higher chemical potential of the stressed mineral compared to the stress-free mineral, which leads to an increase of local solubility and to a dramatic undersaturation of the interfacial solution. The stress-induced dissolution, the subsequent diffusion of the dissolved solute through the fluid film at grain boundaries, and its reprecipitation in less stressed regions is called pressure solution (Gratier et al., 2013), a process that is influenced by the chemical composition of the fluid (Zhang et al., 2011; Zhang & Spiers, 2005; Zubtsov et al., 2005). Furthermore, recent studies have revealed that the weakening of calcite’s mechanical strength is also sensitive to the chemical composition of the fluid confined at the grain boundaries (Heggheim et al., 2005). A weakening mechanism via subcritical crack growth, which stems from the water-induced reduction of calcite’s surface energy, has been proposed (Rostom et al., 2013; Røyne et al., 2011). Such ion-specific effects on calcite’s strength and reactivity, although originated at the molecular level, are expected to influence the frictional strength of carbonate faults, as well.
during the sliding of an AFM tip along a mineral surface the wear track grows as a result of stress-induced dissolution.

In the present study, we investigate the frictional characteristics of calcite at room temperature as a function of the normal stress (Johnson & Johnson, 1987; ≤0.93 GPa) and slip rate (<10 μm/s) relevant to earthquake nucleation. Although the stress along faults in the upper Earth crust is only ~100 MPa (Sibson, 1980), it is higher at the multiasperity contacts that dictate the fault frictional strength (Johnson & Johnson, 1987; Persson, 2001; Popov, 2010), and it can even surpass the yield strength of crustal minerals (~7.5 to 15 GPa; Beeler et al., 2016; Evans & Goetze, 1979). Sodium chloride (NaCl) and calcium chloride (CaCl2) solutions with different concentrations were selected as brines to examine the influence of the fluid chemistry on the friction force between calcite and an AFM tip with a silicon oxide (silica) surface. Surface forces were also measured to determine the composition of the confined fluid films and adhesion at the selected conditions. The results of this work also contribute to advance the current understanding of the influence of the chemical composition of deep-injected brines on induced seismicity.

2. Experimental Setup and Data Processing

2.1. Sample Preparation

Sodium chloride and calcium chloride (purity ≥ 99.0%, Sigma-Aldrich) were dissolved at room temperature in ultrapure water (18.2 MΩ-cm resistivity) to achieve concentrations at 0 mM (no salt added), 1 mM, 10 mM, 100 mM, and 1 M and then equilibrated with excessive calcite powder (purity ≥ 99.0%, Sigma-Aldrich). The pH of the solutions was measured and can be found in Table S1 in the supporting information. Freshly cleaved Iceland Spar calcite samples were first immersed and equilibrated with calcium carbonate (CaCO3) saturated solution (labeled as 0 mM) in a home-made fluid cell for 24 hr prior to the measurements. For all sets of experiments, the fluid exchange was gently conducted using syringes from low to higher concentrations of either NaCl or CaCl2. The fluid cell was rinsed three times with the new solution to ensure a thorough exchange, and the system was then left to re-equilibrate for 1 hr. The fluid cell was covered by a membrane to minimize evaporation; the evaporation is ~5% for a 4-hr experiment, which is the maximum duration of the normal and friction-force measurements for each of the selected solution concentrations.

2.2. AFM Measurements

2.2.1. Surface Force Measurements

A Nanowizard AFM (JPK Instruments) located in an acoustic chamber was used throughout this study. Surface force measurements were performed with the AFM cantilever type (CSC38/no Al, Mikromasch) with spring constant (kver) ranging between 0.1 and 0.3 N/m, as determined by the thermal calibration
method (Hutter & Bechhoefer, 1993). The AFM tip was thermally treated at 550 °C to obtain a larger radius, which was determined to be 250 nm by Scanning Electron Microscopy imaging. After 1-hr equilibration in each solution, isothermal surface force measurements were performed at 25 °C; 256 surface force-separation curves were collected in a 5 μm × 5 μm flat area in each solution. During each measurement, the tip was approached to the surface from an initial surface separation of ~100 nm at constant speed of 20 nm/s to exclude hydrodynamic effects. Here, the deflection of the cantilever with the spring constant provides the surface force \( F \) between tip and calcite as a function of the surface separation \( D \). To quantify the adhesion between the tip and the calcite surface, a load of 5 nN was first applied on the calcite surface with the tip, and the pull-off force was measured upon retraction of the tip at 20 nm/s.

### 2.2.2. Friction-Force Measurements

Friction-force measurements were performed with the same cantilever type as surface force measurements. Figure S1a shows how the AFM tip, driven by an internal piezo motor, slides a defined distance (100 nm here) in a reciprocating fashion along the calcite surface at the selected constant load and velocity; see the trace and retrace, blue and red arrows in Figure S1b, respectively. When the AFM tip slides on the calcite surface, it experiences a lateral force due to the friction force between tip and calcite, which leads to a lateral deflection of the cantilever. The lateral force \( F_L \) is determined during both trace and retrace with the lateral deflection and the lateral spring constant \( (k_{L}) \) obtained from a noncontact thermal noise-based calibration method (Mullin & Hobbs, 2014). Figure S1c shows one friction loop that is collected from one reciprocal measurement. The friction force is calculated as the half of the difference between the lateral force during trace and retrace (Ogletree et al., 1996). The mean value of the friction force is calculated for each single friction loop. The reported friction force in this work was calculated from the mean of 8-10 friction loops at each selected applied normal load and velocity with the error bar showing the standard deviation across measurements. The normal load is defined as the force applied by the AFM cantilever on the substrate in the normal direction. The smallest normal load and friction force that can be accurately measured with our AFM is 0.01 nN.

After 1-hr equilibration in each solution, friction-force measurements were performed as a function of normal load \( L \) and velocity \( V \) at each selected concentration in an atomically smooth surface area. To measure friction at the single asperity contact given by the tip and calcite, the normal load was maintained constant, and the velocity was ramped up stepwise. The tip was then separated from the surface, and then a higher load was applied on a different location to measure friction as a function of velocity. Two sets of measurements were conducted using two tips with radii of 150 and 100 nm, respectively, as determined by Scanning Electron Microscopy imaging, to probe a wide range of normal stresses. The contact area \( A \) between the (spherical) tip and the flat surface was calculated according to the Hertz model (Johnson & Johnson, 1987), considering the radius of each tip and assuming 70 and 179 GPa as the Young’s moduli for calcite and silicon, respectively, and 0.3 and 0.2 as their Poisson ratio (Table S2). The tips used for the measurements shown in this paper and the normal stress at each applied normal load calculated with the contact area \( A \) are tabulated in Table 1. Note that we used the elastic modulus of silica (instead of silicon) to calculate the normal stress in our previous work (Diao & Espinosa-Marzal, 2018), which explains the smaller values reported there for the same normal loads and tip size. All measurements were conducted at constant temperature of 25 °C.

### 2.3. Eyring’s Model: Shear-Assisted Thermally Activated Slip

Eyring’s transition state theory (Eyring, 1935, 1936) is often applied to describe the friction force of a lubricated contact (Spikes, 2018). The theory considers that the viscous flow of a liquid is a rate process. Upon

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**Table 1**

| Tip Radius and Normal Stress in Each Experiment | Low stress (LS) | Intermediate stress (IS) | High stress (HS) |
|---|---|---|---|
| Tip radius (nm) | 150 | 150 | 100 |
| Normal load (nN) | 0.5 | 1 | 5 | 10 | 20 | 30 | 40 | 50 |
| Normal stress (MPa) | 153 | 193 | 243 | 330 | 416 | 545 | 687 | 787 | 866 | 933 |

*Note. Three regimes are distinguished in friction-force measurements, low-stress (LS), intermediate-stress (IS), and high-stress (HS) regime, whose characteristics are described in section 3.2. The normal stress \( \sigma_n \) was determined with the normal load applied by the atomic force microscopy tip divided by the contact area calculated according to the Hertz model (Johnson & Johnson, 1987); \( \sigma_n \) is equal to the Hertzian average contact stress.*
shear, layers of molecules move relative to each other. For slip to occur, it is necessary that the molecule jumps from an energy minimum over a transition state with an activation energy \( \Delta E \) before falling into the adjacent minimum (Figure 1b). The shear stress acting on a liquid molecule \( \tau \) promotes the slip rate by reducing the energy barrier by \( \tau \Omega = \Delta E / \lambda \), where \( \lambda \) is the shear force acting on the molecule, \( \Omega \) is the shear-activation volume, and \( \lambda \) and \( \lambda \) are molecular dimensions in the plane along the direction of the shear force. According to Eyring’s model, the shear-activation volume is a molecular volume given by \( \Omega = \lambda \lambda / \lambda \), where \( \lambda \) is the molecular dimension perpendicular to the plane and \( \lambda \) is the distance between the two energy minima (or equilibrium positions). This approach leads to Eyring’s sinh-law, which describes the relation between shear stress and shear rate. Since the shear rate is not known in AFM experiments, \( \Delta E \) cannot be determined with this model. Therefore, we prefer to apply a simplified approach according to Ma et al. (2015), which is described here. Considering that the slip rate of the hydrated ions and water, \( v \), is increased by the shear stress according to \( v = v_0 \exp (-\Delta E / k_0T) \), \( k_0 \) being the Boltzmann constant, \( T \) the absolute temperature, and \( v_0 \) a characteristic frequency, the following expression is derived for the friction force \( F_{L} \):

\[
F_{L} = \tau \delta = \frac{\Delta E}{\Omega/\delta} + \frac{k_0T}{\Omega/\delta} \ln(V/V_0),
\]

\( V \) being the sliding velocity, \( V_0 = \delta v_0 / v_0 \) a reference velocity, and \( \delta \) the jump amplitude of the liquid molecules in the reference state. In friction-force measurements as a function of the sliding velocity, \( \Omega/\delta \) can be unambiguously determined from the slope of \( F_{L} \) versus \( \ln (V) \) curves, while the intercept with the \( y \) axis gives \( E_s = k_0T \ln V_0 \). In a prior work, we determined a reference velocity \( (V_0) \) of 40 m/s in similar friction-force experiments but for mica and NaCl solution (Diao et al., 2019); we assume the same value here to determine the thermal activation energy \( E_s \). The shear-activation volume, \( \Omega \), is determined with the known contact area \( \delta \), which is calculated based on the Hertz model (Table S2). The normal stress \( \sigma_n \) is calculated as the normal load \( (L) \) applied by the AFM tip divided by \( \delta \), and it is equal to the Hertzian average contact stress.

Equation (1) led to good results in describing friction between mica surfaces in aqueous solutions at very low normal stresses (~3 MPa in Ma et al., 2015). Modifications of equation (1) have been proposed to describe the influence of the normal stress on friction of a lubricated contact through an additional pressure-dependent term (Spikes, 2018). We refrain to apply these modified models here, because, as shown later, friction can decrease with increase in normal load as a result of pressure solution, which is not accounted for by any available model. In addition to this, the change in normal stress is also responsible for the change of thickness of the confined fluid film, as described in the next section, and this also causes both \( \Omega \) and \( E_s \) to change.

Since none of the available models can describe these phenomena, we apply equation (1) to determine the two fitting parameters \( (\Omega \) and \( E_s) \) for each applied normal load (stress). Our previous work (Diao & Espinosa-Marzial, 2018) showed that equation (1) describes well the velocity-dependent friction force between calcite and the AFM tip in the absence of pressure solution. Here, we will evaluate the influence of both the chemical composition of the fluid and of the pressure solution on friction through the analysis of the fitting parameters \( \Omega \) and \( E_s \).

3. Experimental Results

3.1. Hydration Force and Pull-Off Force Measurements

In surface force measurements, the AFM tip is slowly approached to the surface and the cantilever deflects as a result of the surface force \( (F) \) acting between the tip and the calcite surface in aqueous solution; the surface force is calculated with the cantilever deflection as a function of surface separation \( D \) (see section 2.2.1). The surface separation \( (D) \) gives the thickness of the confined fluid film between calcite and AFM tip. Representative surface forces in the range of interest here \( (D \leq 3 \text{ nm}) \) are shown in Figure 2 in CaCO3-saturated solution (black), (a) NaCl and (b) CaCl2 solutions. The origin of the \( x \) axis has been defined at the hard wall, at a surface separation of ~1 nm.

The measured surface force becomes more repulsive with a decrease in surface separation in all solutions (Figures 2a, 2b, S2a, and S2b). In the context of colloidal science, the force acting between two solid surfaces in an aqueous medium is attributed to (attractive) van der Waals, electrical double layer (EDL), and
Due to the preferential dissociation of calcium ions compared to carbonate ions, calcite acquires a negative charge upon exposure to an aqueous environment (Stipp, 1999). And the surface of the silicon tip, which is oxidized, and therefore, it is silicon dioxide, that is, silica, is also negatively charged due to the dissociation of the silanol groups (Iler, 1975). According to the electrical double-layer theory, ions of opposite charge, that is, counterions, counterbalance this charge and form a Stern and a diffuse layer (Israelachvili, 2011). This higher counterion concentration between the two surfaces in comparison to the fluid reservoir induces an osmotic pressure, that is, an excessive fluid pressure in the confined film compared to the pressure of the unconfined fluid ($P_f$), which is

Figure 2. Surface forces between calcite and an atomic force microscopy (AFM) tip. Surface forces ($F$) as a function of surface separation ($D$) were measured in CaCO$_3$-saturated solution (labeled as 0 mM), (a) NaCl and (b) CaCl$_2$ solutions. Surface forces at larger surface separations are shown in Figure S2. Schematics in (c) shows how the layers of molecules are probed with an AFM tip as the surface separation $D$ decreases. The purple spheres represent co-ions, that is, ions carrying the same charge as the surface, which may also accumulate in the confined fluid film, but at a smaller concentration in comparison to counterions (green spheres). (d) Bubble diagram of the measured layer thicknesses ($\Delta$). The molecular layers are categorized into three groups, water (2–3 Å, gray background), inner sphere counterions (3–4 Å, yellow background), and outer sphere counterions (>4 Å, white), following the nomenclature by Fenter (Fenter et al., 2000). The center of each bubble gives the average layer thickness in each group, and the standard deviation is shown as an error bar. The bubble size reflects the number of layers detected with this size per concentration. As a reference, the size of the bubble pointed by the black arrow represents 30 layers. The color scheme is consistent throughout this work, black for CaCO$_3$-saturated solution (0 mM), red shades for NaCl, and blue shades for CaCl$_2$. 

(repulsive) hydration forces (Israelachvili, 2011). Due to the preferential dissociation of calcium ions compared to carbonate ions, calcite acquires a negative charge upon exposure to an aqueous environment (Stipp, 1999). And the surface of the silicon tip, which is oxidized, and therefore, it is silicon dioxide, that is, silica, is also negatively charged due to the dissociation of the silanol groups (Iler, 1975). According to the electrical double-layer theory, ions of opposite charge, that is, counterions, counterbalance this charge and form a Stern and a diffuse layer (Israelachvili, 2011). This higher counterion concentration between the two surfaces in comparison to the fluid reservoir induces an osmotic pressure, that is, an excessive fluid pressure in the confined film compared to the pressure of the unconfined fluid ($P_f$), which is
Small steps are observed in the hydration force in CaCO3 literature (Gee et al., 1990; Klein & Kumacheva, 1998).

Both calcite and silica have a high hydration energy, 94 kJ/mol (de Leeuw & Parker, 1998) and 27 kJ/mol (Iler, 1979), respectively, and therefore, water adsorbs strongly to both the surfaces (Brekke-Svaland & Bresme, 2018; Geissbühler et al., 2004). In fact, the strong affinity of water to calcite yields an unconventional Stern layer, where the calcite crystal is terminated by two strongly bound hydration layers to the surface, on top of which calcium ions and carbonate/bicarbonate ions reside (Ricci et al., 2013). When the charged calcite and silica surfaces are brought closer to each other, \( D \leq 3 \text{ nm} \), like in Figures 2a and 2b, water and counterions remain confined between the two surfaces due to their strong affinity to the surfaces. The repulsive surface force in this regime is typically called "hydration force" because it is associated with the hydration of the surfaces and of the ions present in the confined fluid film. Although hydration forces are less well understood than van der Waals and EDL forces, it is generally accepted that higher affinity of water and ions to the confining surfaces yields a stronger hydration force (Donaldson et al., 2015).

Importantly, as a result of DLVO and hydration forces, a disjoining pressure (\( \Pi \)) prevents direct contact of the two surfaces under an applied normal stress \( \sigma_n \) (Israelachvili, 2011). The effective normal stress \( \sigma_n \) acting on the two surfaces \( \sigma_n = (\sigma_n - P_f) \) is thus balanced by the disjoining pressure in the confined fluid film, \( \Pi(D) \) (Li et al., 2017). According to a recent molecular dynamics (MD) simulation study, the confined fluid film can sustain normal stresses much higher than ~1 GPa (Brekke-Svaland & Bresme, 2018), which is the maximum value applied here. This confined fluid phase thus transmits the normal stress between the two surfaces, which is often referred to as "solid-like" behavior of the confined fluid film in the colloidal literature (Gee et al., 1990; Klein & Kumacheva, 1998).

Small steps are observed in the hydration force in CaCO3-saturated solution (0 mM) and in NaCl and CaCl2 solutions at all investigated concentrations (see black arrows in Figures 2a and 2b). It is well accepted that these steps originate from the layered arrangement of molecules on smooth solid surfaces, here, the cleaved calcite surface (Diao & Espinosa-Marzal, 2016). Each step happens when the AFM tip pushes away a layer of water molecules or hydrated ions, as illustrated in Figure 2c. The thickness of these layers (\( \Delta \)) is close to the diameter of the molecules that are squeezed out (Espinosa-Marzal et al., 2012; Israelachvili & Pashley, 1983), that is, water and hydrated ions, and therefore, they provide information about the composition of the confined fluid film. Note that at the highest concentrations, an attractive force stemming from the van der Waals interaction is often observed with superposed steps (see the blue arrow in Figure 2a, 1 M NaCl). This attraction causes a rapid motion (mechanical instability) of the cantilever, which hinders resolving the size of these molecular layers with high precision; note the small number of data points in these steps. Therefore, the steps superposed to these instabilities have been excluded from the analysis.

Figure 2d shows a summary of the thickness of the resolved molecular layers (\( \Delta \)) in a bubble diagram. Based on our previous works (Diao & Espinosa-Marzal, 2016; Espinosa-Marzal et al., 2012) and on X-Ray scattering and reflectivity studies (Fenter et al., 2013; Geissbühler et al., 2004), layers with thickness \( \Delta \sim 2-3 \text{ Å} \) represent water molecules (gray background); a thickness \( \Delta \sim 3-4 \text{ Å} \) is attributed to weakly hydrated ions (yellow) and \( \Delta \geq 4 \text{ Å} \) to stronger hydrated counterions (in white), which are called inner sphere and outer sphere counterions, respectively. Layers of the size of water molecules are resolved almost at all concentrations, indicating that the confined fluid is rich in water. A much smaller number of layers is pushed away in NaCl compared to CaCl2 solutions, which is represented by the smaller bubble size. Since the two electrolytes share the same anion, this difference is mainly associated to sodium (Na\(^+\)) and calcium (Ca\(^{2+}\)) ions.

Although a higher concentration of chloride anions is expected in CaCl2 than in NaCl solutions, the concentration of co-ions close to the negatively charged surfaces is much smaller than the bulk concentration according to the EDL theory (Israelachvili, 2011), and it is neglected.

The smaller size of the NaCl-layers suggests that sodium ions are less hydrated than calcium ions. It is known, however, that fully hydrated sodium ions are larger than fully hydrated calcium ions (9 Å vs. 6 Å; Schlegel et al., 2006). A previous AFM study coupled with MD simulations (Ricci et al., 2013) suggested that calcium ions stay on top of the hydration layers of calcite, while sodium ions can penetrate into the hydration layers of calcite and are, therefore, located closer to the calcite surface. This ion-specific effect can be
attributed to the different hydration enthalpy of the two ions: Calcium has a four times higher hydration enthalpy than sodium, 1,577 kJ/mol versus 409 kJ/mol (Smith, 1977). Therefore, it is less energetically expensive for the sodium ions to lose part of their hydration shell, to penetrate into calcite’s hydration layers, and to strongly bind to the negatively charged surface. This model explains that, although fully hydrated sodium ions are larger than calcium ions, and a higher number of sodium ions would be expected in the fluid film to provide electroneutrality (as sodium is monovalent, while calcium is divalent), smaller and fewer layers are pushed away in NaCl compared to CaCl2.

The pull-off force between calcite and silica surfaces was measured upon the retraction of the AFM tip; see the inset in Figure 3. In air, the pull-off force is significant (~25 ±9 nN, ~16±6 mJ/m²; Figure S3). No pull-off force was observed at the lowest concentrations, which is attributed to the confined fluid film, which significantly reduces van der Waals forces when compared to the two dry solid surfaces in air (Israelachvili, 2011). Importantly, increasing the concentration to 10 mM CaCl2 solution led to a noticeable pull-off force (~0.5 nN, 0.3 mJ/m²). By further increasing the concentration to 100 mM, a pull-off force was measured in both brines, but higher in CaCl2 solutions. The increase in pull-off force with higher brine concentration has been reported before (Tan et al., 2014) and attributed to the presence of large amounts of ions in the confined fluid, which enhances ion-ion correlations (Kjellander & Marčelj, 1984; Kjellander & Marčelj, 1988) and leads to a more attractive surface force (Kohagen et al., 2015). In addition to this, multivalent counterions like calcium can bridge two negatively charged surfaces (Popa et al., 2009), here calcite and silica, which is consistent with the higher pull-off force in CaCl2 solutions compared to NaCl. Nevertheless, the pull-off force in each of the investigated brines is still much smaller than in air. Importantly, the yet small pull-off force between calcite and silica at all conditions (<1 nN, 0.6 mJ/m²) supports that a fluid film remains confined between the two surfaces under all investigated conditions. Our results agree well with recent measurements of the adhesion between two cleaved calcite surfaces in NaCl solution (Javadi & Royne, 2018), where a pull-off force was measured only at concentrations of at least 100 mM.

### 3.2. Friction-Force Measurements

Figures 4a–4j show representative results of the friction force (Ff) between calcite and a naturally oxidized silicon tip as a function of sliding velocity (V) and at normal stresses ranging from 153 to 416 MPa, which correspond to normal loads between 0.5 and 10 nN, in CaCO3-saturated and in NaCl and CaCl2 solutions at the selected concentrations. Under all conditions, there is no distinction between static and dynamic friction at the investigated single-asperity contact, so we call it friction in the following. The results in CaCO3-saturated solutions (0 mM) shown in panels (a) and (f) correspond to two different experimental setups, and they illustrate the deviation of results across experiments. Each of the samples was subsequently immersed either in NaCl (diagrams (b) to (e) in the first row) or in CaCl2 solutions (diagrams (g) to (j) in the second row). The same representation has been used to show the results of the friction-force measurements at higher normal stresses (Figures 4k–4t). The results were reproducible on experiments with different calcite single crystals. It is noted that due to the inherent variability of AFM measurements, a quantitative comparison of results is only possible for the same experimental setup (tip, laser position, etc.), which restrict us to compare the results in the same row in Figure 4. Nevertheless, the satisfying reproducibility across different experimental data sets proves that the observed trends are significant.

At normal stresses σn< 250 MPa, shown as the cross, circle, and square labels in Figures 4a–4j, the friction force increases only slightly with normal load (shown as stress in Figure 4) in all brines, while the increase in friction with σn becomes more obvious at higher normal stresses. This lets us distinguish two “stress” regimes: low-stress (LS), if σn<250 MPa, with only a weak influence of the normal stress, and intermediate-stress (IS), in the range ~250 to ~500 MPa. Figures 4a–4e illustrate that the friction force...
decreases significantly upon an increase in NaCl concentration to 100 mM, while friction increases with an increase in concentration to 1 M. In contrast, the friction force is much less sensitive to the concentration of CaCl₂ solutions (Figures 4f–4j). Under all conditions in Figures 4a–4j, the friction force increases logarithmically with sliding velocity, which is in good agreement with the velocity-strengthening frictional characteristics of calcite observed, for example, in gouge experiments (Carpenter et al., 2016; Verberne et al., 2014). It is important to emphasize that there is prior evidence for velocity-weakening frictional characteristics of silica (the tip’s surface) when sliding along a silica surface in aqueous solution.

Figure 4. Friction force between calcite and an atomic force microscopy tip as a function of velocity and normal stress in CaCO₃-saturated solution (0 mM) and in NaCl and CaCl₂ solutions in the low-stress (LS), intermediate-stress (IS), and high-stress (HS) regimes. The top two rows correspond to LS and IS regimes (tip radius \( R = 150 \text{ nm} \)). The bottom two rows represent HS regimes (tip radius \( R_{\text{RR}} = 100 \text{ nm} \)). The black markers are for CaCO₃-saturated solution (0 mM), red shades for NaCl, and blue shades for CaCl₂. The calculated normal stresses are 153–245 MPa, 330–416 MPa, and 545–933 MPa in the LS, IS, and HS regimes, respectively, and the corresponding applied normal loads are shown in Table 1. The pH ranges from 8.5 to 7.0 (Table S1). The error bars give the variation in friction across eight friction loops at each speed. The data for CaCl₂ were taken from (Diao & Espinosa-Marzal, 2018), with open access license http://creativecommons.org/licenses/by/4.0/.

10.1029/2018JB017252
(Diao & Espinosa-Marzal, 2018; Donose et al., 2005; Donose et al., 2006). Therefore, the velocity-strengthening friction shown in Figure 4 mainly reflects the frictional characteristics of calcite.

A comparison of these results with the surface force measurements shows that in the LS regime, layers of water, and ions are pushed away with the AFM tip; an increase in load thus leads to thinner films of different composition. We relate the LS regime to the so-called “hydration lubrication” that was proposed based on friction-force measurements between mica surfaces at very small normal stresses ($\sigma_n<10$ MPa; Gaisinskaya et al., 2012; Ma et al., 2015). Here, the counterions close to a charged surface (mica in that work) remain confined with their hydration shell, while the water molecules maintain their fast relaxation dynamics. The fluidity of the confined water is responsible for the reduction of the friction coefficient. Friction was associated to the viscous force stemming from the shear of a fluid film that lubricates the single asperity contact, as oil lubricates an engine. In the IS regime, the AFM tip did not push away any more layers of molecules in surface force measurements, indicating that the thickness and composition of the fluid film remained constant with an increase in load. In both LS and IS regimes, the measured friction force can be fit well by the shear-assisted thermally activated slip model (equation (1)) with $R^2>0.9$, as shown by the lines in Figures 4a–4f; the fitting parameters are discussed later.

Figures 4k–4t show the velocity-dependent friction force at normal stresses above ~500 MPa (denoted as high-stress [HS] regime and corresponding to normal loads up to 50 nN) in CaCO$_3$-saturated (0 mM), NaCl and CaCl$_2$ solutions. These data are presented in log-log scale to show more clearly the small values of the friction force. Here, although the friction force is still velocity-strengthening, it does not scale with the logarithm of the velocity. Furthermore, the friction force does not increase monotonically with applied normal load (normal stress), but a crossover of the friction force versus velocity curves is observed, which results from the remarkable decrease in friction with increase in load at slow sliding velocities.

To emphasize the significant decrease in friction at slow sliding velocities, representative load-dependent friction force measurements at the selected velocity of 0.2 $\mu$m/s are shown in Figures 5a and 5b. The change of the slope of friction versus normal load represents the transition from the IS to the HS regime. A friction coefficient $\mu$ was calculated as the slope of the friction force versus normal load in LS, IS, and HS regimes, respectively, and it is shown in Figure 5c for the different brines. The dashed lines in Figure 5c represent the results for CaCO$_3$-saturated solutions. A box chart was used to illustrate the calculated friction coefficients in NaCl (in red) and CaCl$_2$ (in blue) brines; each box includes the results obtained at all the investigated concentrations. In the LS regime ($\sigma_n<250$ MPa), the friction coefficient is very small with values ranging from ~0.001 to 0.006 over a wide range of fluid compositions at the selected velocity of 0.2 $\mu$m/s. Here, the fluid film lubricates very efficiently the single-asperity contact. In the IS regime, the confined fluid film sustains the normal stress, and friction significantly increases with normal load. This yields friction coefficients $\mu$ in the range ~0.01–0.02. The friction coefficient in IS regime is ~3 times smaller than in dry air (Diao & Espinosa-Marzal, 2018). At high normal stresses (HS regime, $\sigma_n>500$ MPa), called HS-LV from “low velocity”, friction decreases with an increase in applied normal load (Figures 5a and 5b); that is, $\mu$ becomes negative. In contrast, at fast sliding velocities in the HS regime (called HS-HV from “high velocity”), a positive friction coefficient is measured ($\mu$~0.03 – 0.07 at 5 $\mu$m/s in Figure 5c). Our previous work (Diao & Espinosa-Marzal, 2018) revealed this negative dynamic friction coefficient in CaCl$_2$ solution, and we show it here also in NaCl solutions. The frictional weakening stems from the pressure-induced dissolution of calcite while the tip slides along the calcite surface, and it is discussed later in more detail.

4. Discussion

4.1. Pressure-Solution Facilitated Slip

This study has revealed the decrease in friction with increasing normal load, resulting in a negative friction coefficient $\mu$~0.003 to ~0.005 at sufficiently slow sliding velocities and high normal stresses (HS-LV regime, Figures 5a and 5b) in all the investigated brines. Our previous work (Diao & Espinosa-Marzal, 2018) demonstrated that a negative friction coefficient is not measured (i) on dry single calcite crystals, (ii) when ethanol is used instead of the aqueous solutions, (iii) and when the tip slides along mica and silica surfaces instead of calcite and (iv) that a negative friction coefficient is measured for calcite in aqueous solution independently of the composition of the AFM tip (silicon nitride or silica). Therefore, the measured negative friction coefficient is a frictional characteristic of the calcite single crystal wetted by aqueous solution. Furthermore, AFM
images showed that the decrease in friction with increasing load is concurrent with the dissolution of calcite along the sliding path of the AFM tip. This lets us conclude that the negative coefficient of friction in the HS regime is related to the stress-induced dissolution of calcite.

The proposed frictional weakening mechanism is consistent with the estimated kinetics of pressure-induced dissolution of calcite. The pressure solution of minerals is thermodynamically driven by the increase in chemical potential ($\Delta \mu$) upon an applied normal stress, that is, $\Delta \mu = V_m \sigma_{\text{normal}}$, $V_m$ being the molecular volume of calcite. The increase in chemical potential yields an augment of the mineral solubility, and thereby a local undersaturation of the interfacial solution (Weyl, 1959a). Pressure solution includes the stress-induced mineral dissolution, the subsequent mass transfer through the confined fluid film, and the reprecipitation of the mineral, and hence, its kinetics can be limited by any of these steps (Gratier et al., 2013). If the
radius of the single-asperity contact is small enough (in the micron range or smaller), ions can rapidly diffuse in and out, and pressure solution may become interfacial limited (Anzalone et al., 2006; Greene et al., 2009); this is the case of our nanoscale studies. The interfacial-limited dissolution rate of unstressed calcite in water is \( r_{\text{cal}} = 1.8 \times 10^{-10} \text{ mol cm}^2/\text{s} \), that is, \( \approx 1.08 \text{ CaCO}_3 \) formula unit per \( \text{nm}^2 \) and per second (Cubillas et al., 2005). Taking a normal stress \( \sigma_n = 687 \text{ MPa} \), the enhanced dissolution rate of stressed calcite (\( r_p \)) increases with \( \Delta \mu \) as \( r_p \propto r_{\text{cal}} \left( \sigma_n - \sigma_0 \right) / \sigma_0 \) (Gratier et al., 2013), with \( \sigma_0 = 0.1 \text{ MPa} \). Given the area of a \( \text{CaCO}_3 \) formula unit (\( \approx 0.25 \text{ nm}^2 \)), the time required for dissolution can be estimated as \( \Delta t = 1/(r_{\text{cal}} \mu) \), and it is \( \approx 0.54 \text{ ms} \) at the selected normal stress. For the dissolved and hydrated ions to serve as lubricant in the confined fluid film, the contact time between tip and calcite must be longer than this dissolution time, that is, the sliding velocity must be sufficiently slow. Taking \( d = 6 \text{ nm} \) as the estimated diameter of the Hertzian contact area, one can estimate the maximum velocity for stress-induced dissolution to be \( V_c = d/\Delta t = 11.2 \mu\text{m/s} \). In the range of stresses in the HS regime, the estimated velocity is \( V_c < 22 \mu\text{m/s} \), which is in good agreement with our experimental results. Note that other models predict an exponential increase of \( r_p \) with \( \sigma_n \) (Gratier et al., 2013) but the linear relation seems more adequate for our experiments. Our current work aims to provide a more accurate model.

This simple estimation supports that if the sliding velocity is sufficiently slow, that is, if the contact time between calcite and tip is long enough for pressure-induced dissolution of calcite to occur, the dissolved calcium carbonate would be hydrated and released into the confined fluid film between tip and calcite while they are still in contact. We propose that these hydrated ions serve as lubricant, as an oil lubricating an engine, thereby reducing friction in a similar fashion as in the LS regime (by hydration lubrication) but at much higher normal stresses. At high sliding velocities (denoted as HS-HV regime), the contact time is too short for pressure solution to be effective. Theoretically, pressure solution should happen also at smaller normal stresses (e.g., in the IS regime), but it appears that the normal stress has to be sufficiently high for the weakening effect on the friction force to be measurable. Slower rates of dissolution in nature, for example, limited by diffusion through long and tortuous pathways in multisasperity contacts, will imply that slower sliding velocities are needed for pressure solution to be effective in reducing friction. On the other hand, larger contacts (often a few microns in size) will promote pressure solution facilitated slip at higher slip velocities.

Although a negative friction coefficient has been reported before for graphite due to its high adhesion to the AFM tip in air (Deng et al., 2012), the underlying mechanism is very different. The elevated adhesion of graphite to the AFM tip led to the delamination of the upper layers of graphite, which caused (i) a significant hysteresis between the friction force upon an increase and a decrease in the normal load and (ii) an increase in contact area with decrease in load. Not limited to graphite, this negative friction coefficient seems to be a more general phenomenon due to the hysteresis in the adhesive interaction between sliding bodies that are weakly anchored to the underlying substrates (Thormann, 2013). Nevertheless, this cannot occur in the case of calcite. First, the adhesion is about 3 orders of magnitude smaller than in the case of graphite (cf. 0.212 to 0.283 J/m² in Deng et al., 2012, and \( \approx 5.10^{-4} \text{ J/m}^2 \) here). Second, graphite is composed of graphene layers hold together only by weak van der Waals forces, and hence, delamination due to adhesion to the tip is possible; calcite is an ionic crystal, and the rupture of ionic bonds would require very high adhesive forces to the tip.

### 4.2. Ion-Specificity of the Frictional Characteristics of Calcite Single Crystals

In both LS and IS regimes, the friction force can be fit well by the shear-assisted thermally activated slip model (equation (1)), as shown by the lines in Figures 4a–4i. In contrast, the friction force versus velocity in the HS regime cannot be described by a single logarithmic relation (note the S shape). Figure 5d illustrates the friction force at two selected normal stresses, but now in linear-log scale. This representation reveals a transition between two different logarithmic relations between friction and velocity at 687 MPa (see red and blue lines); the black symbols represent the friction force at 330 MPa. This transition is observed at most of the loading conditions in Figures 4k–4t. Here, we propose to fit equation (1) to the two segments in the HS regime (at low and high sliding velocities) separately, considering that the stress-induced dissolution of calcite mainly affects the friction force at slow sliding velocities, and hence, two different mechanisms are responsible for the velocity-dependence of friction.

\[
\mu = 0.25 \left( \frac{\Delta \mu}{\sigma_0} \right) + 0.54 \text{ ms} 
\]
Figure 6 shows the shear activation volume ($\Omega$) in LS regime ($\leq 250$ MPa), IS regime ($250$–$500$ MPa), and HS regime ($>500$ MPa), the latter at both, high sliding velocity (HS–HV, full symbols), where no significant pressure solution was detected, and low sliding velocity (HS–LV, empty symbols, yellow background), where pressure solution took place. In CaCO$_3$-saturated solution (represented by the black and gray shaded markers linked by the dashed lines in both diagrams), $\Omega$ ranges between $\sim 3$ and $\sim 0.8$ nm$^3$, which is larger than the volume of a single water molecule or of a fully hydrated ion. Here, we invoke a previous study (Granick, 1991) that interpreted $\Omega$ as the volume of the molecules that move collectively under shear in a confined fluid film. This suggests that the “shear units” in the confined fluid films consist of multiple hydrated ions and water molecules that slip together as a result of the applied normal stress. Figure 6a shows that $\Omega$ increases with normal stress in the LS regime. This occurs when the thickness of the confined fluid film decreases with increase in normal load, because layers of ions and water are squeezed out (Figure 2c). Hence, this change in $\Omega$ not only reflects a change of the collective motion of molecules but also includes a change of the composition of the confined fluid films. With further increase in normal stress (IS and HS–HV), Figure 6a shows a remarkable decrease of $\Omega$ in the absence of pressure solution. The onset of pressure solution (empty symbols, HS–LV) coincides with an expansion of $\Omega$, which becomes similar to $\Omega$ in the LS/IS regime, when the mineral is dissolved, and the ions are released into the confined thin film. A greater $\Omega$ implies a lower friction force according to equation (1), and therefore, a better lubricious performance of...
the confined fluid. The black markers in Figure 6b show consistent results for different calcite crystals investigated in separate experiments in CaCO₃-saturated solution."

While the collective motion of several liquid molecules in the confined fluid contributes to lubricate the contact more efficiently according to this model, the thermal activation energy can be also relevant in dictating friction. Figures 6c and 6d show the thermal activation energy ($E_a/k_B T$) in CaCO₃-saturated solution as a function of normal stress (black and gray markers, 0 mM). As in the case of $\Omega$, the thermal activation energy exhibits different trends in the HS-regime. Although using different methods and experimental conditions to ours, Cafolla and Voitchovsky inferred from their friction measurements on mica that the lubricious properties of ions originate from the induced distortion of the structure (hydrogen bond network) of the hydration layers of mica upon shear (Cafolla & Voitchovsky, 2018). They associated this distortion to an empiric activation energy ($\sim 1.3k_B T$), which is about the half of the energy needed to dehydrate the mica surface per unit cell. The higher values of the thermal activation energy for calcite ($\sim 6 - 7k_B T$ in the absence of pressure solution) are consistent with the higher hydration enthalpy of calcite compared to mica and with the stronger order of the hydration layers on calcite. The observed increase in the activation energy when pressure solution happens (HS-LV regime) is also reasonable, since the probed shear-activated process includes both the energy required to dissolve the mineral and to shear the fluid film. Further, the activation energy for the dissolution of stress-free single calcite crystals in water (pH=5.5) has been estimated to be $\sim 6.5 k_B T$ (Petrov & Terzidaki, 2014), that is, in very good agreement with the value of $E_a$.

In a previous study, the stress-induced dissolution of calcite was investigated via the visualization of the wear track made with an AFM tip (Dickinson et al., 1997). This work estimated the thermal activation energy required for the growth of the wear track to be 0.6 to 0.8 eV (i.e., $\sim 23-31k_B T$) at normal stress $\geq 3.7$ GPa $k_B T$, and hence, much higher than the thermal activation energy obtained here. The authors proposed that the high tensile stress around the tip led to the nucleation of double kinks, which served as pit nuclei and accelerated the dissolution of calcite. Interestingly, the investigation of the pressure-induced dissolution of gypsum revealed a transition to an atomic wear mechanism and enhanced dissolution at normal stresses higher than 1.5 GPa, similar to Dickinson’s results (Pachon-Rodriguez et al., 2011). At smaller stresses, however, the step retraction was associated to the pressure solution of gypsum. The absence of a wear track in our experiments and the smaller applied stresses (<1 GPa) than in Dickinson’s experiments let us exclude atomic wear. This difference justifies that the thermal activation energy shown in Figure 6 is much smaller than the reported values by Dickinson. We also note that $V_0$ was assumed (without experimental support) to be $3,200$ m/s in (Dickinson et al., 1997), that is, much higher than the value that we have measured recently ($40$ m/s; Diao et al., 2019), which also contributes to the different results.

The results in Figure 4 show a subtle influence of the chemical composition of the fluid on the friction force between calcite and silica. The fitting parameters (Figure 6) are used to evaluate the influence of the fluid chemistry on friction in the different stress regimes. Note that the parameters corresponding to the same set of experiments in Figure 4 are represented in the same diagram in Figure 6 so that quantitative comparisons are possible between NaCl versus CaCO₃ and CaCl₂ versus CaCO₃ in each plot. Figures 6a and 6b show the shear-activation volume ($\Omega$) and the thermal activation energy ($E_a/k_B T$) in NaCl (in red) and CaCl₂ (in blue) solutions at the concentration of 100 mM, respectively. While only one concentration has been selected in this figure to illustrate ion-specific effects on the fitting parameters, similar trends were observed in brines with other concentrations, and they are discussed in the supporting information, Figure S4. The averaged parameters over the whole range of concentrations are shown in Figure S5. Our results demonstrate that $\Omega$ and $E_a/k_B T$ depend on brine composition, which must be associated to the different composition of the fluid films confined between calcite and silica. Figure 6a shows an increase of $\Omega$ in the LS and IS regimes upon the addition of NaCl, which coincides with the lower friction coefficient measured in NaCl solutions compared to CaCO₃-saturated solutions (0 mM). Figure S4a demonstrates that the increasing concentration of NaCl leads to a more significant increase in $\Omega$, except for 1 M. In contrast, the addition of CaCl₂ leads to a slight decrease of $\Omega$ compared to the results with CaCO₃-saturated solution (Figure 6b). These trends in $\Omega$ persist in the IS regime in both NaCl and CaCl₂ solutions. A deviation from the general trends is often observed at the highest investigated concentration of 1 M. This might result from the ion-ion correlations present at high ionic strength (Kjellander & Marcelja, 1984; Kjellander & Marčelja, 1988). It is to be noted...
that the theory of highly concentrated electrolytes is currently under debate (Gebbie et al., 2017), which requires more investigation.

The proposed conceptual model in Figure 7 associates \( \Omega \) to the composition of the confined fluid film. As the electrical double layer theory (Israelachvili, 2011) predicts, the counterions (Na\(^+\) and Ca\(^{2+}\)) populate the vicinity of the (negatively charged) calcite surface in aqueous environment, and the near-surface concentration of co-ions, here Cl\(^-\) and CO\(_3^{2-}\), is negligible. The concentration of counterions is much higher than the nominal brine concentration in this confined fluid film according to the electrical double layer theory. In the LS-regime, both sodium and calcium ions populate the confined fluid film, as multiple layers are resolved in surface force measurements. Since the much higher hydration enthalpy of Ca\(^{2+}\) makes it energetically more unfavorable to dehydrate, Ca\(^{2+}\) ions are situated on top of the hydration water of calcite, while Na\(^+\) ions can easily dehydrate and penetrate into the calcite's hydration layers. This turns the structured (ice-like) hydration layer into a more liquid-like, that is, more mobile film, which results in a larger stress-activation volume. In IS- and HS-HV regimes, only the most strongly adsorbed ions remain in the contact. While the majority of Ca\(^{2+}\) ions are removed, Na\(^+\) ions are still embedded in the hydration layer. In HS-LV regime, when the pressure solution is triggered, the contact is enriched with freshly dissolved and hydrated calcium and carbonate ions, and the confined fluid film lubricates in a similar manner as in the LS-regime, but at much higher normal stresses.

Figure 7. A conceptual model for the confined fluid film under shear in the proposed low-stress (LS), intermediate-stress (IS), and high-stress (HS)-high velocity (HV), and HS-low velocity (LV) regimes. Red, green, and blue circles represent sodium, chloride, and calcium ions. As the electrical double layer theory (Israelachvili, 2011) predicts, the counterions (Na\(^+\) and Ca\(^{2+}\)) populate the vicinity of the (negatively charged) calcite surface in aqueous environment, and the near-surface concentration of co-ions, here Cl\(^-\) and CO\(_3^{2-}\), is negligible. The concentration of counterions is much higher than the nominal brine concentration in this confined fluid film according to the electrical double layer theory. In the LS-regime, both sodium and calcium ions populate the confined fluid film, as multiple layers are resolved in surface force measurements. Since the much higher hydration enthalpy of Ca\(^{2+}\) makes it energetically more unfavorable to dehydrate, Ca\(^{2+}\) ions are situated on top of the hydration water of calcite, while Na\(^+\) ions can easily dehydrate and penetrate into the calcite's hydration layers. This turns the structured (ice-like) hydration layer into a more liquid-like, that is, more mobile film, which results in a larger stress-activation volume. In IS- and HS-HV regimes, only the most strongly adsorbed ions remain in the contact. While the majority of Ca\(^{2+}\) ions are removed, Na\(^+\) ions are still embedded in the hydration layer. In HS-LV regime, when the pressure solution is triggered, the contact is enriched with freshly dissolved and hydrated calcium and carbonate ions, and the confined fluid film lubricates in a similar manner as in the LS-regime, but at much higher normal stresses.

that the theory of highly concentrated electrolytes is currently under debate (Gebbie et al., 2017), which requires more investigation.

The proposed conceptual model in Figure 7 associates \( \Omega \) to the composition of the confined fluid film. Calcite acquires a negative charge upon exposure to aqueous environment. As the EDL theory predicts (Israelachvili, 2011), the near-surface concentration of co-ions, the ions with the same charge sign as the surface (Cl\(^-\)), is negligible, and counterions (Na\(^+\) and Ca\(^{2+}\)) and water mainly populate the vicinity of the calcite surface. We thus propose that the variation in the stress-activation volume \( \Omega \) originates from the “hydration-driven” interaction of calcite with the counterions (sodium and calcium). Such hydration-driven interaction relies on the strong hydrophilicity of calcite, which leads to the adsorption of two highly ordered water (“ice-like”) layers (Kerisit & Parker, 2004). The term “ice-like” implies the pronounced order of the water molecules in the calcite’s hydration layers and the prominent slow-down of the diffusivity. Based on MD simulations and the visualization of the calcite-solution interface by AFM (Ricci et al., 2013), the strongly hydrated calcium ions stay on top of calcite’s hydration layers and do not directly reside at the calcite’s surface, also under applied pressure with an AFM tip. In contrast, more weakly hydrated sodium ions lose part of their hydration shell, which helps them penetrate through (at least one of) calcite’s hydration layers. The
abundance of sodium ions in the confined film leads to the distortion of the structure of calcite’s hydration layers, which is referred to as “liquid-like” behavior. The distortion of the ice-like structure of the hydration layers should be more prominent with increase in the population of surface-adsorbed sodium ions, which coincides with the gradual increase of Ω in the LS-regime with concentration (Figure S4a) so that the confined fluid becomes easier to shear. In contrast, the addition of CaCl2 does not affect the composition of the fluid film, Ω and the friction force as dramatically as the addition of NaCl.

The variation of Ω upon addition of NaCl is opposite in the IS and HS-HV regimes, which indicates the action of two competing mechanisms (Figure 6a). On one hand, the increase in Ω compared to CaCO3-saturated solution in the IS-regime is interpreted as the increasing presence of hydrated sodium ions within the hydration layers, which disturbs the water structure, like in the LS regime. Increasing NaCl concentration allows more sodium ions to penetrate through the hydration layers, and thereby a more pronounced distortion of the hydration layer of calcite with concentration (Figure 7b). On the other hand, the shear units might become more compressed and smaller with increasing normal stress, perhaps causing Ω to decrease in the HS-HV regime, as in CaCO3-saturated and CaCl2 solutions (Figure 6b). It is possible that the much lower $E_s$ required to shear the NaCl films in the HS-HV regime reflects the distortion of the ice-like hydration layers due to the embedded sodium ions.

When pressure solution is triggered at sufficiently HS and slow sliding velocity (HS-LV regime), a decrease in the friction force with increase in normal load (i.e., a negative friction coefficient in Figure 5e) was observed in both NaCl and CaCl2 solutions, but more prominently in CaCl2. In the HS-LV regime, Ω increases with normal stress at all solution conditions and eventually becomes comparable to the magnitude in the LS regime (Figure 6a and 6b). This supports that pressure-solution leads to a more lubricious confined fluid film with the dissolved and hydrated ions (Figure 7c). A larger Ω is, again, observed in NaCl in comparison to CaCO3-saturated in the HS-LV regime, indicating the presence of sodium ions in the recovered fluid film as in the LS regime.

Importantly, the activation energy $E_a$ is higher in NaCl compared to CaCO3-saturated solution in the HS-LV regime, while the opposite is observed in CaCl2 brines, where a significant decrease of $E_a$ is observed. Since the activation energy in the absence of pressure solution (HS-HV regime) is smaller in NaCl, this implies that the activation energy for stress-induced dissolution of calcite is remarkably higher in NaCl brines compared to CaCl2. Note that the lower coefficient of friction in CaCl2 solutions compared to NaCl in the HS-LV regime is, in fact, mainly dictated by this smaller activation energy. A possible explanation for this difference can be related to the influence of the fluid composition on the reactivity of calcite. As Table S1 shows, the addition of calcium ions reduces the pH dramatically, while the addition of sodium ions increases the pH slightly. This leads to a higher acidity of the CaCl2 brine in the vicinity of calcite compared to NaCl. It is well known that the dissolution rate of calcite is affected by the pH of the solution (Sjöberg & Rickard, 1984). In particular, a decrease of the dissolution rate of calcite has been reported above a pH of ~8 (Shiraki et al., 2000) and with an increase in pH from 7 to 9 (Dolgaleva et al., 2005). This might be because the dissolution of calcite is mediated by hydronium ions, which simultaneously hydrolyze calcium-carbonate bonds and rapidly transfer a proton to fully hydrate the calcium (Shiraki et al., 2000). This pH dependence of the dissolution rate is consistent with the higher activation energy for stress-induced dissolution of calcite in the NaCl brines (pH>8.3) inferred from our work.

It is also worth noting that the conceptual picture shown in Figure 7 significantly advances the understanding of aqueous lubrication compared to previous studies on mica surfaces (Ma et al., 2015), where it was only proposed that hydrated ions are more lubricious than pure water because they enrich the confined fluid film with highly mobile water molecules that they carry in their hydration shells (Klein, 2013). Here, we have observed that ion specific effects, the competition between water and ions to adsorb on the surface, and the reactivity of the surface in the specific aqueous environment need to be considered to reliably predict the frictional characteristics of mineral surfaces and lubrication.

4.3. Geological Implications

The friction coefficients measured in this work (μ<0.1) are much smaller than those corresponding to calcite-rich fault gouge in macroscopic experiments (μ~0.6 under saturated conditions) (Carpenter et al., 2014; Carpenter et al., 2016; Verberne et al., 2014). A similar discrepancy between the friction coefficients
measured at different length scales has been reported before for other materials, such as mica (Horn & Deere, 1962; Ma et al., 2015), quartz (Chester, 1994; Donose et al., 2006), and graphite (Liu et al., 1998). Ruths, Berman, and Israelachvili explained how the low (dynamic) friction between two atomically smooth surfaces in water ($\mu \approx 0.02$ for mica single-asperity contact) transitions to a much higher friction coefficient of $\approx 0.3$ after damage occurs; in this case, the surface becomes rough, and the friction coefficient of the multi-asperity contact is much higher as a result of asperity interlocking and failure (Ruths et al., 2005). The higher values of macroscopic rock friction compared to our results are thus attributed to additional processes occurring at the macroscale, for example, asperity interlocking and failure, plastic deformation, and granular flow, which are absent in our single-asperity (AFM) measurements. Note that at the level of a lubricated single-asperity contact, we have found no difference between static and dynamic friction coefficients, that is, $\mu_s = \mu_d$, and hence, we have not made any distinction in this work.

The measured frictional characteristics of single calcite crystals in contact with an aqueous fluid reveal two main pathways that may influence the frictional strength of faults. First, the presence of the confined brine lubricates asperity contacts at the fault plane, and it reduces the friction coefficient, thereby facilitating fault slip. In this case, the abundance of sodium ions in the confined fluid films should reduce the friction coefficient of calcite more significantly than calcium ions. These results are in line with a hydration-driven adsorption of ions on calcite (Ricci et al., 2013). Accordingly, monovalent counterions can more readily dehydrate and perturb the hydration layers of calcite compared to multivalent ions due to their lower hydration enthalpies (Smith, 1977). We propose that this leads to more mobile confined fluid films, that is, easier to shear (larger $\Omega$), and thereby to lower friction coefficients. Calcium ions, in contrast, do not modify the hydration layers of calcite. There are still open questions, though. For example, MD simulations have proved the electrostatic-driven adsorption of magnesium ions on calcite, whereby fully hydrated magnesium ions penetrate through the hydration layers of calcite (Kerisit & Parker, 2004). Previous theoretical work has indicated that multivalent ions may enhance the dipole moment of the neighboring water molecules at the solid-liquid interface (Ruckenstein & Huang, 2003). It is thus possible that the presence of multivalent ions in the fluid films like magnesium could enhance the structure and ice-like behavior of the hydration layers at the calcite's surface and thereby lead to a significant increase in friction, but this requires further investigation. Further, while these results can be extended to other fluid chemistries, competitive adsorption of ion species will happen in the complex brines in nature, and it is not clear yet how this will affect the friction coefficient.

The second pathway involves the weakening of the frictional strength of calcite fault gouge due to its stress-induced dissolution. In this case, the higher basicity of the NaCl brines in our study mitigates the decrease in the friction coefficient induced by pressure solution, and therefore, slip is less favored. The brine composition has been shown to influence the pressure-induced dissolution of calcite (Zhang et al., 2011; Zhang & Spiers, 2005; Zubtsov et al., 2005), and our results suggest that brines promoting dissolution will lead to lower friction coefficients when pressure-solution is triggered. The observed inhibitive effect of NaCl on pressure-solution facilitated slip seems contradictory to a previous laboratory study of the compaction rate of calcite grains, which showed enhanced compaction in NaCl solutions compared to CaCO$_3$ saturated solution (Zhang & Spiers, 2005). However, there are major differences between these two studies. First, pressure solution was diffusion and precipitation limited in that work, while it is interfacial limited in our AFM nanoscale studies. The authors observed significant grain boundary roughening in NaCl solutions, which could have accelerated pressure solution, while no surface roughening was observed in our experiments. Further, it could not be excluded that the compaction rate was partially originated by other mechanisms such as grain fracture and subcritical crack growth (Gratier et al., 2013). Finally, the overall compaction rate included the contribution of both the dissolution and reprecipitation of grains of multiple geometries and sizes, grain fracture, and granular flow, and therefore, the role of pressure solution cannot be deconvoluted in that previous work.

Fluid injection through hydraulic fracturing and disposal wells may bring faults closer to failure as a result of multiple mechanisms, including the decrease in effective normal stress (Healy et al., 1968), the change of the state of stress (Bao & Eaton, 2016), hydrothermal alteration of faults (Floyd et al., 2001; Heinicke et al., 2009; Vavryčuk & Hrubcová, 2017), and precipitation of secondary minerals that modify the frictional strength of faults (Meller & Kohl, 2014). In addition, we propose that stress-induced mineral dissolution coming along
with the injected reactive fluid can lead to a significant reduction of the friction coefficient at the level of the single-asperity contacts at the fault plan and, thereby, favor the nucleation of earthquakes. Our studies also provide evidence for the effect of the fluid composition on the frictional behavior of carbonate minerals. To the best of our knowledge, the current numerical models forecasting induced seismicity barely consider the effect of fluid chemistry on the friction coefficient (Baisch et al., 2010; Norbeck & Horne, 2018; Rutqvist et al., 2013, 2015). The results of this work suggest that the composition of injected fluids should also be considered, when evaluating induced seismicity.

Our study has clarified the frictional characteristics at the level of a single asperity contact between calcite and silica. We emphasize that we do not attempt to extrapolate our results to the behavior of a bimaterial fault in nature, where unstable slippage (Weertman, 1980) and dynamic rupture (Shi & Ben-Zion, 2006) may occur and can be influence by the different elastic constants of the fault materials. Our previous work (Diao & Espinosa-Marzal, 2018) proved that our experimental method mainly probes the frictional behavior of calcite and therefore the obtained fundamental insight from this work contributes to advance the understanding of the properties of carbonate-bearing rocks. Furthermore, we note that the effect of temperature might be critical. Not only the solubility of carbonate-bearing rocks is temperature dependent (Weyl, 1959b) but also the proposed pressure solution facilitated slip is a thermally activated process, and hence, it is affected by changes in temperature (equation (1)). In fact, the temperature of the regions in the Earth crust reached by the injected fluid may be high, for example, 260 °C in Zoback and Harjes (1997), and the retrieved reservoir fluid from a geothermal well can be hot (Sanchez-Alfaro et al., 2016). Studies also suggest that the temperature of the fluid may increase due to flushing heating at much higher slip rates (Rice, 2006), while the elevation of temperature at the asperity level can be significantly influenced by the thermophysical properties of the fluid (Acosta et al., 2018; Chen et al., 2017). The increase of temperature in our AFM experiments is estimated to be extremely small (1.42·10⁻⁷ to 5.5·10⁻⁴ °C; Cowan & Winer, 1992; Rabinowicz & Tanner, 1966). Nevertheless, the effect of temperature may be critical, and it calls for further studies.

5. Conclusions

This nanoscale study has revealed the effects of the fluid composition on the frictional response of calcite single crystals in presence of aqueous solutions. At relatively low normal stress, the presence of the confined fluid film lubricates the single asperity contact efficiently. Here, the interfacial composition plays a key role; specifically, the addition of sodium ions reduces friction more than calcium ions, likely due to the distortion of the hydration layers of calcite by the sodium ions. When pressure solution is triggered at a sufficiently high normal stress, the presence of sodium ions, however, increases the energy barrier for slip to occur, which is likely attributed to the lower reactivity of calcite at the higher pH of these brines. This study reveals one possible mechanism underlying the weakening of fault frictional strength by reactive fluids and emphasizes the influence of the chemical composition of injected brines, which poses implications for the injection-induced seismicity of carbonate-based faults. The relative contributions of subcritical crack growth, crystal plasticity, multiasperity interlocking, lubrication, and pressure solution to macroscopic friction still remain to be quantified.

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