1 **Contact Angle Measurement Ambiguity in Supercritical CO₂-water-Mineral Systems:**
2 **Mica as an Example**

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Abstract

The current ambiguity on wettability of minerals in CO₂-brine systems under the geological CO₂ sequestration (GCS) reservoir conditions imparts the greatest uncertainty in predicting capillary behavior controlling safe-storage of CO₂. To address this issue we conducted a series of experiments using muscovite as a representative of common aluminosilicate minerals. Based on new experimental results we identified several possible causes of the ambiguity problem in contact angle (CA) measurements. We also found that reaction with water-saturated supercritical (sc) CO₂ (but not with scN₂) phase severely roughened the muscovite surfaces, largely increased CA hysteresis and CO₂ adhesion. Although some methodological influences on contact angle uncertainty can be reduced, the high surface-energy of clean and pristine aluminosilicate minerals have strong tendency to adsorb oppositely charged molecules and particles to reduce their surface energy, resulting in less reproducible CA values. Giving the fact that such clean and pristine mineral surfaces do not exist in real reservoirs, our future investigations shall focus on improving understanding of the effect of long-term CO₂-mineral-brine reactions on reservoir wettability under realistic reservoir geochemical conditions.

Graphical Abstract

Keywords: geological carbon sequestration; wettability of muscovite mica; contact angle measurement; contact angle hysteresis; adhesion; mineral-CO₂-brine reaction

1. INTRODUCTION

Geological CO₂ sequestration (GCS) has been identified as a key strategy for mitigating anthropogenic CO₂ emissions. Under the reservoir conditions of GCS, capillarity exerts large controls on the movement and distribution of CO₂ and brine, and wettability is a key factor impacting the magnitude and direction the capillary force (Anderson, 1986; Dullien, 1992; Iglauer et al., 2011; Morrow, 1990; Pentland et al., 2011; Tokunaga et al., 2013). Wetting phenomena in mineral-brine-CO₂ systems have been under active investigation in recent years, and improved understanding has been obtained in this short period of time (Bikkina, 2011; Broseta et al., 2012; Chiquet et al., 2007; Espinoza and Santamarina, 2010; Farokhpour et al., 2013; Jung and Wan, 2012; Kim et al., 2013; Kim et al., 2012; Mills et al., 2011; Shah et al., 2008; Tokunaga and Wan, 2013; Wang et al., 2013a; Wang et al., 2013b; Yang et al., 2008). However reported contact angle (denoted here as CA) values vary over a large range, and it is still unclear whether or not long-term reaction with scCO₂ changes the wettability of the reservoir minerals.

Muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F,OH})_2$) known as common mica is an ubiquitous primary mineral in the subsurface, hence in GCS reservoirs and seals. Its highly perfect basal cleavage yields remarkably thin (1.0 nm), atomically smooth, and elastic sheets. Each muscovite sheet consists of a 2:1 layered crystal structure; two tetrahedral silicate layers and an octahedral aluminum layer in between. The cleaved surfaces are negatively charged as the result of substitution of Si⁴⁺ in the silicate layer by Al³⁺ (one-fourth of Si⁴⁺ in the silicate sheets by Al³⁺). These negative charges are balanced by K⁺. Upon cleavage the structure of the aluminosilicate layers is undisturbed, but the exposed K⁺ ions can be easily displaced. Freshly cleaved muscovite

is predominantly negatively charged, has high surface energy, and is completely water-wet with zero CA (Muller and Chang, 1969).

A few groups have reported measured CAs of mica-CO₂-brine systems (Broseta et al., 2012; Chiquet et al., 2007; Farokhpour et al., 2013; Mills et al., 2011; Saraji et al., 2014; Shah et al., 2008; Wang et al., 2013a). For example, Chiquet et al. (2007) reported the CA changed from water-wet behavior at low pressure toward intermediate wet at high pressure (>10 MPa). Broseta et al. (2012) reported the receding CA, $\theta_R = 28^\circ$ increased to 45° as pressure increased from 5 to 140 bar, temperature 9-35°C and salinity low to high. They observed largely increased advancing CA θ_A up to 100° . In some cases they also observed adhesion of CO₂ when withdrawing a CO₂ droplet. Farokhpour et al. (2013) measured a set of CO₂ CAs on quartz, feldspar, calcite and muscovite. Among them only the CAs of muscovite changed from 15° to 36° with increasing pressure. They also reported increased CAs with reaction time of a CO₂ droplet in contact with mica ($\theta = 35^\circ$ to 61° from 0 to 48 days under 105 bar, 36°C). Wang et al. (2013a) measured CAs on phlogopite (Mg-mica) in brine-CO₂, and reported lower and nearly constant CAs: $\theta_R \approx 20^\circ$ and $\theta_A = 20^\circ$ - 43° (increased with P_{CO_2} from 0 to 20 MPa). They also reported decreased CAs with increased roughness.

It is apparent that the reported data are divergent, from strongly water-wet to some even CO₂-wet, with inconsistent trends of pressure and ionic strength effects. More importantly, we do not know what the causes are for CA variations, and the hierarchy of these causes. We still have no understanding of whether or not chemical reactions with CO₂ change the wettability of the mineral/rock wettability during long term CO₂ storage. In order to improve our understanding of these issues, we conducted a series of experiments including static and dynamic CA measurements under varied conditions, and using freshly cleaved- compared with scCO₂ pre-

reacted mica, and examined these surfaces microscopically.

2. EXPERIMENTAL

2.1. Mica and other materials. Muscovite of grade V1 (the highest purity and surface smoothness mica from Electron Microscopy Sciences) was purchased. Ultra-pure DIW (resistivity $\geq 18\text{ M}\Omega$, Millipore, Milli-Q), NaCl (ACS reagent grade, Aldrich), and high-purity CO_2 (99.99%) were used. Immediately before an experiment, a mica sample was cleaved in a dust-free environment to a thickness of about 0.5 mm. A corner of each rectangular mica sheet was notched to allow identification of the freshly cleaved surfaces, and only freshly cleaved surfaces were used for CA and atomic force microscope (AFM) measurements. The freshly cleaved mica surface has high electrostatic energy due to the charge unbalance from loss or redistribution of K^+ ions, and therefore has high tendency to attract positively charged ions, organic molecules and particulates. Much attention was given to limit possible contamination. The fresh cleavage was immediately clipped onto the CA sample holder and immersed in the desired fluid phase.

2.2. Contact Angle Measurements. A high pressure and temperature (P/T) CA measurement chamber (Temco, IFT-10) was used for both the sessile drop and the captive-drop methods. The internal volume of the chamber is about 50 cm^3 , with a stainless steel plate welded at the center of the chamber to hold a horizontally oriented substrate plate. A substrate plate is clipped on without glue. Two transparent tempered glass windows allow illumination and viewing. The chamber is instrumented with a pressure transducer and a thermocouple placed in the vicinity of the droplet. Two injection ports for different fluid phases are located at the top and the bottom of the chamber. The chamber can be used for injecting water droplets top-down, and for CO_2 droplets bottom-up by turning the chamber upside down. CA images were recorded using high-

resolution time-lapse photography (16.2 Megapixel, Nikon D7000). A high P/T stirred reactor (Parr, Model 4560) was used to mutually pre-saturate brine and CO₂ at given P/T before using them in the CA chamber. Images of the droplet were recorded at up to 23 frames/second, for later analyses using ImageJ software (<http://imagej.nih.gov/ij/>) combined with DropSnake and LBADSA plug-in (Stalder et al., 2010). Before each use, the chamber was carefully cleaned with acetone (ACS reagent grade, BDH) and deionized water (DIW). Water and CO₂ were always pre-saturated with each other prior to initiating measurements. The temperature was maintained at 45°C, pressures adjusted to selected levels (up to 15.0 MPa), and tested ionic strengths were 0.0, 0.1 1.0 M NaCl.

2.2.1. Captive-drop method. In the captive-drop method, a mica plate was clipped onto the stage, the chamber was filled with water and pressurized to the desired pressure, and then the CO₂-saturated brine was used to completely displace the previously injected water. Water-saturated scCO₂ was then used to displace 10% volume of the water in the chamber in order to maintain phase equilibrium. For static CA measurements, a scCO₂ (pre-water-saturated) droplet was formed at the tip of the syringe from the bottom of the chamber and released onto the mica plate, then the dynamic images of the droplet were taken and a selected static CA was reported.

2.2.2. Sessile drop method. In the sessile drop method, the chamber was set upside down. After clip-mounting the mica sample, 5 ml DIW was injected to the chamber to insure the water saturation of CO₂, and then the chamber was filled with CO₂ to the desired pressure. About 1 hour after maintenance of stable P/T, a water droplet (estimated 8 µl) was generated and released onto the mica plate. High-resolution time-lapse photographs (video recordings for the dynamic CA measurements) were taken. The contact-line diameter and drop volume from acquired images were analyzed as described above.

2.2.3. Stepwise increasing pressure. The measurements of CA as function of P are frequently done with stepwise increased pressure. In our testing of the pressure effect on CA values, the mica plate was positioned in the middle of the chamber, the chamber was filled with CO₂ pre-saturated brine, and a layer (~5 mm thick) of scCO₂ was established at the top of the chamber to ensure maintenance of CO₂ saturation in the brine. After the chamber was adjusted to the desired pressure, a CO₂ droplet was generated and captured under the substrate, the CA was measured. Then the droplet was removed by tilting the chamber, followed by increasing the chamber pressure, equilibrated for several hours and forming a new CO₂ droplet on the plate for the next CA measurements.

2.2.4. Dynamic CA measurements. For dynamic CA measurements, a fluid droplet was formed at the tip of the needle that was positioned closer to the substrate than for the static CA measurements, and the droplet was contacted with the substrate while the needle tip was still immersed in the droplet. The droplet was slowly alternated between expanding and contracting through injection and withdrawal through the needle that was connected to a motor-driven high-P syringe. The lowest and highest CA values (measured through the water phase) during this process were reported as the receding (θ_R) and advancing (θ_A) CAs, respectively.

2.3. “Pre-reacted mica”. A mica plate was sized to 50 x 19 mm using a sharp scissor and immediately blown with canned compressed clean air (AccuDuster III, Advantus) to remove possible cutting debris from mica surfaces. The mica plate then was cleaved to create a fresh surface and the fresh surface was marked and carefully protected from direct contact with any solid phase. Three identical mica plates were prepared, and each was placed vertically into one of the three compartments of a Hastelloy basket. The basket was hung inside a high P/T Parr reactor (Parr, Model 4560, 450 ml) with the pressure controlled by an ISCO pump (500D HP,

Teledyne). A small volume (5 ml) of deionized water was placed inside the vessel and below the basket to keep the N₂ or CO₂ phase water-saturated. The reactions were conducted at 12 MPa and 45°C for a desired length of time. At the sampling time, the reactor pressure was gradually decreased over 2~3 h in order to diminish the sudden phase change of CO₂ from a supercritical fluid to gas. Then the mica plates were carefully removed in a dust-free environment, and the samples were ready for CA and AFM measurements. In one treatment, deionized water-saturated scN₂ was used as the reactant for comparison under otherwise exactly the same experimental conditions.

2.4. AFM and SEM measurements. The AFM (Nanoscope IV, multimode SPM, Digital Instruments) imaging was conducted on three mica samples: a freshly cleaved plate, a plate that was pre-reacted with scCO₂ in the Parr reactor, and a plate used in brine-scCO₂ CA measurement. The AFM measurements were obtained in non-contact (tapping) mode with doped silicon tips (125 µm long with a nominal tip radius of 8 nm; Nanoworld, NCH-W). The height, amplitude, and phase images were collected simultaneously, and heights were calibrated to an ANSI B46.1 standard. The drive frequencies were 314~325 kHz, and scan rates were between 0.1 and 0.5 Hz. Images were analyzed using Vision (Veeco, version 3.44) software. Scanning electron microscopy (SEM, Zeiss Gemini Ultra-55) was used to image a freshly air-cleaved mica surface.

3. RESULTS AND DISCUSSION

3.1. Contact Angle Measurements in Mica-CO₂-Water Systems

3.1.1. Static contact angles. In this paper all the CA values are reported relative to the water phase. The majority of recently published CA data in mineral-CO₂-water systems were based on the captive CO₂ droplet method, which is easier to operate than the water droplet method for strongly hydrophilic substrates. In order to determine if there are any unexpected methodological biases, we used both the captive CO₂ droplet and sessile water droplet methods (results shown in Figures 1a and 1b, respectively), at different pressures and ionic strength. In these figures, each data point represents the average value of 3-5 repeated CO₂ or water droplets applied at the same location by removing and regenerating (limitation of the experimental apparatus and representative of the methodology used in several other laboratories). The data shown in Figure 1b as circles connected by dashed line segments were generated using one mica plate subjected to a series of measurements with stepwise increased pressure. Two duplicate runs were conducted; one started from 5.0 MPa and ended at 12.0 MPa, and another run was started at 6.5 MPa and ended at 15.0 MPa. The rest data points shown were generated from individual experiments, each on a separate freshly cleaved mica plate. Using the captive CO₂ droplet method, we obtained CA data that were scattered and poorly reproducible (Figure 1a). Scattered CA values were also observed with the water droplet method (Figure 1b). Systematic effects of pressure and ionic strength on mica CAs were clearly not identifiable. If the data from the stepwise increased P test were excluded, the CA values from the water-droplet method are within a narrower range of 30°-47°, compared to 20°-80° for the CO₂ droplet method. However, It should be noted that in about half of the tests using the water droplet method, water droplet spreading was so extensive that the CA was too small to measure. Under these circumstances, increasing the contact time of the mica plate in the chamber with water-saturated scCO₂, would then sometimes yield measurable CA, while in other cases the CA would still not be

measureable, especially when the surface became covered with thick water layer. Thus, the major differences between CA values obtained using CO₂-droplets versus water-droplets may result from which of the two phases, water or scCO₂, contacts the mica first. This consideration motivated our experiment on pre-reacting mica with water-saturated scCO₂ (section 3.2.5). Using stepwise increased pressure, the static CAs varied from 30° to 110°. The complete set of measured CAs varied over the wide range of 20°-110° (Figure 1a,b) while the expected ideal CA on a freshly cleaved mica surface is near zero. In the later sections we will discuss the possible causes of these non-unique CA values obtained under any given pressure and ionic strength conditions.

Figure 1. Static contact angles measurements for mica-CO₂-water systems using (a) captive CO₂ droplet and (b) sessile water droplet methods at various pressure and ionic strength conditions. Except for the black unfilled circles in, each of the points represents an independent experiment on a freshly cleaved mica plate. Each reported data point is an average CA value based on 3-5 repeated droplet tests, with each droplet equilibrated on the mica surface for 0.3 to 50 hours. For the interconnected black hollow circles, one mica plate was used for several stepwise increased pressures, in duplicate runs. One run started from 5.0 MPa and ended at 12.0 MPa, and the other started at 6.5 MPa and ended at 15.0 MPa. Each time the water drop was removed and the high-P chamber was pressurized to a new pressure and a new droplet was made at the same location.

3.1.2. Dynamic contact angles. The dynamic CA measurements using the captive CO₂ droplet

method are summarized in Figure 2, with the measurement dates used to identify the individual experiments. Pressure was varied and ionic strength was 0.1 M NaCl. Each experiment was repeated 3 times (3 advancing and receding cycles) on the same mica plate, and data are all presented in the inserted table. The standard deviations are from the 3 repeated measurements with each including the CA on the left and right sides of a droplet. The CA values reported here are for water receding θ_R and water advancing θ_A . The CA hysteresis value is the difference between θ_A and θ_R . The “adhesion” column denotes whether or not the some of the fluid droplet remained attached to the mica surface after the droplet was retracted back into the needle. Again, a trend for a pressure effect was not observed. Although some larger CA hysteresis values appeared in the 7.5 MPa experiments (near the CO₂ critical pressure of 7.38 MPa), reproducibility was poor. Overall, the θ_A , θ_R , and CA hysteresis values varied in the ranges of 16°-33°, 25°-93°, and 10°-60°, respectively. Images from three representative experiments are presented, showing the conditions when the advancing and receding CAs were determined, and when CO₂ receding (water advancing) was completed (showing with or without CO₂ adhesion). These 3 examples illustrated sequentially increased CA pinning (Kulinich and Farzaneh, 2009; Li, 1996), hysteresis, and CO₂ adhesion, with the contact angle hysteresis values of 12°, 28° and 62° for experiments 12-16, 11-17 and 8-5, respectively.

The greater reliability of adhesion tests over contact angle measurements for predicting wettability has long been recognized in studies of petroleum reservoirs (Buckley et al., 1989; Morrow et al., 1986). In some of these mineral-water-oil systems, DLVO theory has been shown to predict the stability of water films (Buckley, 2001; Buckley et al., 1989) Recent DLVO model calculations and measurements of brine films on mica confined by scCO₂ indicate that water film thicknesses of several nm are stable (Kim et al., 2013; Tokunaga, 2012). However, the

experimental results for contact angles and adhesion presented here indicate that other factors beyond the estimated electrostatic and van der Waals interactions used in DLVO modeling are very important. Adhesion of CO₂ demonstrates disruption of DLVO-predicted water films, but a mechanism for CO₂ sorption onto originally hydrated mica surfaces remains to be identified.

Broseta et al. (Broseta et al., 2012) reported muscovite θ_R increased from 28° to 45° as pressure increased from 5 to 140 bar and temperature increased from 9 to 35°C, and salinity increased. We did not observe the CA trends with pressure, nor with ionic strength. They observed a similar degree of largely increased advancing CA up to 100°, and also in some cases observed adhesion of CO₂ when withdrawing a CO₂ droplet. Although we did not find systematic CA trends with pressure, temperature and ionic strength, the range of our measured CA hysteresis and observed adhesion are somewhat consistent with that of the Broseta group.

Figure 2. Data and example images of dynamic contact angle measurements of muscovite-scCO₂-water using captive CO₂ droplets under three different pressures, 45°C, and 0.1 M NaCl conditions. The measurement dates were used to label specific experiments. Freshly cleaved muscovite surface was used for each experiment. The contact angle values refer to water receding θ_R and water advancing θ_A . CAH refers contact angle hysteresis; the difference between θ_A and θ_R .

3.2. Possible Causes of Ambiguity in Measured Contact Angles

3.2.1. Initially different and imperfect substrate surfaces. Substrates used by different researchers can be significantly different. For examples both quartz and amorphous silica (Bikkina, 2011; Jung and Wan, 2012; Mills et al., 2011; Saraji et al., 2013; Wang et al., 2013a)

have been used to represent reservoir silica. Although various forms of silica are known to have different surface energies (Parks, 1984) and dissolution kinetics (Icenhower and Dove, 2000) we do not know if they have the same reactivity with CO₂ and with other components that can alter wettability, especially under elevated P/T and acidic conditions. Different grades of muscovite have been used in CA measurements (Broseta et al., 2012). While it is common to cleave mica along its basal plane to obtain large flat surfaces, this procedure can generate variation in surface properties. We examined our carefully cleaved mica plates using AFM and SEM, and observed imperfections including edge steps (Figure 3a) and deposition of particulate debris (Figure 3b). Although the muscovite was cleaved in a dust-free environment, stored in covered containers, and blown with clean compressed air before examination, dust particles were still seen on the freshly cleaved mica plate (Figure 3b). Mica plates were usually scissor-cut to the desired size, and handled using tweezers. These processes of cutting and handling unavoidably leave debris and scratches along edges and on surfaces of the prepared mica (Israelachvili et al., 2004; Ostendorf et al., 2008). The SEM image shown in Figure 3c is from a mica sample before loading into the CA chamber. The debris from the cut edges and scratches can redistribute later when immersed in water, and some can reattach onto the mica surface. It has been realized that unless the mica is cleaved and maintained in ultrahigh vacuum, it is impossible to avoid adsorption of particles and low molecular weight organic gases on this high-energy solid surface (Israelachvili et al., 2004). Israelachvili et al. developed a hot-wire cutting procedure combined with flowing clean air to avoid deposition of oppositely charged particles, ions, and mica flakes upon cleaving (Israelachvili et al., 2004).

Various cleaning methods to prepare substrates for CA measurements have been used by different researchers, and some can alter surface properties. For examples, NOCROMIX

[(NH₄)₂S₂O₈] (Saraji et al., 2013), Piranha solution (H₂SO₄:H₂O₂ in a 5:1 volume ratio) and air plasma (Iglauer et al., 2014) can chemically increase surface charge density to artificially make the substrate more hydrophilic, as pointed by Saraji et al. (2014). All of these aforementioned differences in surface preparation methods may contribute to the variation in measured CAs, pinning and hysteresis.

Figure 3. Images of muscovite basal surfaces showing some possible sources of contact angle uncertainty. NC-AFM amplitude images of a freshly cleaved mica with (a) an edge step created during cleaving and with (b) deposited dust particles. (c) SEM image shows scratches (near the edge of the mica plate) and the resulting debris that can redistribute and supply abundant particles for contact angle pinning and hysteresis. These defects are difficult to avoid in the laboratory tests, and ubiquitous in the subsurface reservoirs for CO₂ storage.

3.2.2. Contamination and surface alteration during CA measurements. Using the NC-AFM we examined the mica surfaces after they were used in CA measurements. Surprisingly significant surface contamination by adsorption of particles was observed. A few typical images are shown in Figure 4. Some of the particles clearly originated from cutting mica (Figure 4a, b), but the nanoparticles shown in Figure 4c appear to be different and of unknown origin. Although these selected images are from areas with more abundant surface features, not a single image obtained over regions spanning tens of micrometers on surfaces after use in CA measurements was completely clean and smooth like the original fresh mica surfaces. We also observed formation of small blisters (tens of nm) such as those shown in Figure 4d, occurring in some areas of the surface only after measurements in scCO₂-water. These blisters are possibly the

result of scCO₂ diffusion into the interlayer from the edges of the mica plate, and gas expansion upon depressurization.

Figure 4. NC-AFM flattened amplitude images of mica after the contact angle measurements conducted in scCO₂-water, showing (a-c) contaminant particles and (d) blisters.

3.2.3. Effect of CO₂ droplet dissolution. The solubility of CO₂ in water has strong pressure-dependence (Spycher and Pruess, 2010). Thus, true phase equilibrium following a pressure increase applied in captive CO₂ droplet CA measurements may take longer than assumed. Slight phase disequilibrium in a pressure chamber (usually tens of cm³ in volume) can have a large impact on sizes of much smaller CO₂ droplets (few mm³). Greater solubility with increased P drives CO₂ from captive droplets into the water phase, decreasing droplet contact line diameter and droplet volume. Typical time trends of CA with contact line diameter, and with droplet volume are shown in Figures 5a and 5b, respectively. The system phase equilibrium is achieved only when contact line diameter and droplet volume both reach constant values. The most rapid changes occurred within the first ~3 hours following increased P, with CA increases from 60° to ~80°, accompanied with droplet volume decrease from 11 to 7.5 mm³ under practically constant contact line diameter (Kulinich and Farzaneh, 2009; Li, 1996). The constant contact line diameter condition held for 35 hours, during which the CA continuously increased from 60 to 115°. At 35 hours, the contact-line retracted and the CA appeared to stabilize at a high value of 120° (with decreased contact line diameter). When the experiment was stopped at 50 hours, the droplet volume was still decreasing showing that the system had not yet reached phase equilibrium. These results demonstrate that phase disequilibrium can be a common source of CA

measurement uncertainty, especially when CA is measured as a function of P, and the experimental pressure was increased stepwise. Because this phenomenon is amplified in the vicinity of the critical pressure for CO₂ (7.38 MPa), where its compressibility is highest, largest contact angle hysteresis is observed near the critical pressure.

Figure 5. An example of contact angle changes caused by CO₂ droplet dissolution as pressure increased. Shown here are the time dependents of contact angle vs. (a) contact line diameter and (b) droplet volume. The inserted illustrations show that initially as the CO₂ drop volume decreases, the contact line diameter remained nearly constant while the contact angle increased from 60° to ~120° over time (a-1). However, at later times (a-2), the contact line diameter decreased while the contact angle remained nearly constant (~120°).

3.2.4. Effect of repeated contact of scCO₂ droplets with the substrate. We reproducibly observed progressive increases in CA upon repeating measurements on the same area of a mica surface. This experiment was conducted on a freshly cleaved mica plate, at 10 MPa and 45°C, using captive scCO₂ droplets. Each time after completing a measurement, the CO₂ droplet was removed by tilting the pressure chamber, then placing a new droplet onto the same location on the mica surface. The measured CA value increased in the sequence of 22°, 27°, 37°, and 42°, as summarized in data and associated images presented in Table 1. Note that the droplet contact line diameter and droplet volume were constant, indicating that the system was in phase equilibrium, and CO₂ dissolution was not a factor. Similar CA behavior was observed in other experiments involving water droplets in bulk scCO₂ presented earlier (Figure 1b, interconnected black hollow circles); where repeated use of the same mica surface region resulted in CA increases from 30° to

110° (phase disequilibrium may have influenced this result). The phenomenon of increasing CA values over time was also sometimes observed during dynamic measurements. In some repeated cycles of advancing and receding the CO₂-water interface, increased apparent CAs were associated with adhering CO₂ droplets. Possible factors related to the observed increased CA include increased contact/reaction time between altering mica surfaces, and gradual contamination through sorption. Recall that our system was thoroughly cleaned prior to experiments, so that the nature of putative contamination is unknown, and would likely exist in other studies as well.

Table 1. Contact angles increased with repeated measurement on the same region of a freshly cleaved mica surface

3.2.5. Does reaction with scCO₂ alters mica wettability? To simulate longer-term exposure of the mica surface to scCO₂, freshly cleaved muscovite plates were reacted with water-saturated scCO₂ in a Parr reactor at 7.5 and 12 MPa for 4 and 8 days (45°C). In order to isolate possible wettability change attributable to reaction with CO₂, a separate muscovite plate was reacted for 12 days with water-saturated scN₂ at 12 MPa and 45°C. The reacted mica plates were measured for static CAs in ambient air by using sessile DIW droplets. The images in Figures 6(I) (a, b) show water (DIW) droplets on the scN₂ pre-reacted mica and on scCO₂-pre-reacted mica, respectively. The water droplet spread extensively on the N₂-reacted mica, showing that it remained nearly completely water-wet. It should be noted that water droplets spread even thinner and faster on freshly cleaved mica surfaces (no image taken). Distinctly different from the scN₂ reacted mica, the average static CA in air-water from the three scCO₂ pre-reacted mica plates is

31°±0.3° (data presented in the upper inserted table in Figure 6). Although the magnitude of the static CA increases is moderate compare to the non-pretreated surfaces (data reported in Figure 1), it is remarkable how very reproducible the CAs became; suggesting that the reacted muscovite surfaces are more charge balanced than the freshly cleaved surfaces. The results of dynamic CA measurements are presented in Figure 6(II). Pre-treating with scCO₂ largely increased the hysteresis and adhesion of the mica surfaces relative to the dynamic CAs measured on the freshly cleaved micas (Figure 2). The two pressures and two reaction times tested did not result in obvious CA differences. The θ_R values are around 40°, and θ_A values are in the range of 95° to 112°. Adhesion was observed in all three samples. Adhesion was so strong that the static CAs of the adhered CO₂ droplets were all greater than 90°. As shown in the last images in Figure 6, scCO₂ became the wetting phase. Thus, reaction with water-saturated CO₂ altered the mica surface to become more CO₂-wet.

Figure 6. Contact angles on muscovite plates pre-reacted with water-saturated scCO₂. (I) Static CAs measured in ambient air-DIW. (II) Dynamic CA of the same mica plates as in 6(I), measured in scCO₂-water (45° and 0.1 M NaCl).

3.2.6. Reaction with scCO₂ increased surface roughness. Surface deformation of muscovite was measured using the non-contact model AFM. Figure 7 shows example AFM images of CO₂-prereacted muscovite surfaces (used for CA measurements and data shown in Figure 6). One of the main features are blisters, visible in all the images, but especially evident in Figure 7a. Although very small blisters were also observed on some samples of the freshly cleaved mica after the CA measurements (e.g. Figure 4d), the extent of the blistering greatly increased in these

scCO₂ pre-reacted samples, with much larger populations and wider size distributions. In these images the original sizes of some of the blisters may have been larger; apparently collapsing when trapped gas escaped, and leaving impressions of the original blisters as shown in images 7b-d. A few particles of varying size (likely mica debris) adsorbed/deposited on the surface appear in images 7b, c. It should be noted that the scN₂ pre-reacted mica surfaces remained relatively unaltered (not shown). Recent investigations of biotite reacted with scCO₂ and brines (Hu and Jun, 2012; Hu et al., 2013) have revealed not only surface deformation but precipitation of secondary mineral as well (experiments with concentrated salts in brine).

Figure 7. NC-AFM amplitude images of scCO₂-reacted mica surface (12 MPa, 45°C, 8 days; the scCO₂ was saturated with DIW). **(a)** CO₂-induced blisters; **(b, c)** remnants of blisters after collapse, along with dissolution and precipitation features; **(d)** close-up image of blisters in various stages of apparent collapse, and resulting rough surface.

4. Summary

Based on the new experimental data presented here and supporting literature, we identified several possible common causes for the divergent CA values. These include (1) starting substrates of nominally same composition can have very different intrinsic surface chemical properties and reactivity, variably altered surface chemistry resulting from cleaning methods, or different initial surface roughness; (2) different types and amounts of “contaminants” can preferentially adsorb onto the substrate surfaces, and some are difficult to avoid; (3) phase disequilibrium induced CO₂ droplet dissolution, especially for measurements conducted along

with stepwise pressure increase, and also especially in the vicinity of the critical pressure; (4) CO₂ and substrate contact time, procedures, and repetition may affect water film or CO₂ stability on the substrate (water or CO₂ to first contact the substrate). Although some of these causes can be avoided or reduced, giving the fact that the perfectly clean and pristine mineral surfaces do not exist in real reservoirs, focusing on the realistic reservoir geochemical conditions in the future wettability studies is a better stratagem. Measurements on pre-reacted mica surfaces with water-saturated scCO₂ revealed remarkably increased surface roughness and surface affinity for the CO₂ phase. These results suggest that the mineral-CO₂-water reactions require longer equilibration times than used in many of the published studies on CA measurements.

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Figure

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Figure 1. Static contact angles measurements for mica-CO₂-water systems using (a) captive CO₂ droplet and (b) sessile water droplet methods at various pressure and ionic strength conditions. Except for the black unfilled circles in, each of the points represents an independent experiment on a freshly cleaved mica plate. Each reported data point is an average CA value based on 3-5 repeated droplet tests, with each droplet equilibrated on the mica surface for 0.3 to 50 hours. For the interconnected black hollow circles, one mica plate was used for several stepwise increased pressures, in duplicate runs. One run started from 5.0 MPa and ended at 12.0 MPa, and the other started at 6.5 MPa and ended at 15.0 MPa. Each time the water drop was removed and the high-P chamber was pressurized to a new pressure and a new droplet was made at the same location.

Figure 2. Data and example images of dynamic contact angle measurements of muscovite-scCO₂-water using captive CO₂ droplets under three different pressures, 45°C, and 0.1 M NaCl conditions. The measurement dates were used to label specific experiments. Freshly cleaved muscovite surface was used for each experiment. The contact angle values refer to water receding q_R and water advancing q_A . CAH refers contact angle hysteresis; the difference between q_A and q_R .

Exp. ID	Pressure (Mpa)	$\square_R$ (degree)	$\square_A$ (degree)	CAH (degree)	Adhesion (Y or N)
8-5	7.5	31.0 $\pm$ 14.6	92.5 $\pm$ 12.7	61.5	Y
11-11	7.5	33.2 $\pm$ 11.7	76.8 $\pm$ 7.3	43.6	N
12-17	7.5	33.4 $\pm$ 2.1	38.5 $\pm$ 0.8	5.1	N
11-5	10	24.5 $\pm$ 1.9	40.3 $\pm$ 1.8	15.8	N
11-7	10	23.9 $\pm$ 1.6	51.5 $\pm$ 20.7	27.6	Y
12-16	10	26.0 $\pm$ 0.5	38.1 $\pm$ 1.8	12.1	N
8-2	15	22.1 $\pm$ 4.0	31.6 $\pm$ 7.7	27.6	N
8-7	15	15.5 $\pm$ 0.9	25.4 $\pm$ 2.3	9.9	N

Experiment 12-16

Experiment 11-7

Experiment 8-5

Figure 3. Images of muscovite basal surfaces showing some possible sources of contact angle uncertainty. (a, b) NC-AFM amplitude images of a freshly cleaved mica with (a) an edge step created during cleaving and with (b) deposited dust particles. (c) SEM image shows scratches (at the near edge of the mica plate) and the resulting debris that can redistribute and supply abundant particles for contact angle pinning and hysteresis. These defects are difficult to avoid in the laboratory tests and ubiquitous in the subsurface reservoirs for CO₂ storage.

Figure 4. NC-AFM flattened amplitude images of mica after the contact angle measurements conducted in scCO₂-water, showing (a-c) contaminant particles and (d) blisters.

Figure 5. An example of contact angle changes caused by CO₂ droplet dissolution as pressure increased. Shown here are the time dependents of contact angle vs. (a) contact line diameter and (b) droplet volume. The inserted illustrations show that initially as the CO₂ drop volume decreases, the contact line diameter remained nearly constant while the contact angle increased from 60° to ~120° over time (a-1). However, at later times (a-2), the contact line diameter decreased while the contact angle remained nearly constant (~120°).

Table 1. Contact angles increased with repeated measurement on the same region of a freshly cleaved mica surface

Droplet #	Time h	CA°ave. degree	CD mm	DV mm ³	Image
1st. droplet	0.2	21.5	2.18	9.23
	1.0	22.8	2.21	9.26	
	4.0	21.1	2.19	9.19	
	8.0	20.9	2.19	9.2	
Average:		21.6			
2nd droplet	0.2	25.1	2.21	6.07
	0.5	28.3	2.22	6.06	
	1.0	28.2	2.22	5.98	
	2.0	27.4	2.22	5.96	
Average:		27.3			
3rd droplet	0.2	38.5	2.54	7.25
	0.5	36.7	2.55	7.21	
	1.0	36.4	2.54	7.21	
	2.0	39.2	2.54	7.22	
Average:		37.2			
4th droplet	0.2	41.4	2.53	9.73
	5.0	43.5	2.52	9.72	
	10.0	42.2	2.52	9.74	
	20.0	42.4	2.52	9.51	
Average:		42.3			

CD: contact-line diameter; DV: droplet volume. Note, when both CD and DV are constant the CO₂-water phase equilibrium is achieved. Experiment conditions: 10 MPa, 45°C, 0.1 M.

Figure 6. Contact angles on muscovite plates pre-reacted with water-saturated scCO₂. (I) Static CAs measured in ambient air-DIW. (II) Dynamic CA of the same mica plates as in 6(I), measured in scCO₂-water (45° and 0.1 M NaCl).

Figure 7. NC-AFM amplitude images of scCO₂-reacted mica surface (12 MPa, 45°C, 8 days; the scCO₂ was saturated with DIW). (a) CO₂-induced blisters; (b, c) remnants of blisters after collapse, along with dissolution and precipitation features; (d) close-up image of blisters in various stages of apparent collapse, and resulting rough surface.