Contamination of silica surfaces: impact on water-CO_2-quartz and glass contact angle measurements

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Abstract

CO_2-wettability of sandstones is a key variable which determines structural and residual trapping capacities and strongly influences multi-phase fluid dynamics in the rock. An increasing number of researchers has now estimated this wettability by conducting contact angle measurements on quartz, however, there is a large uncertainty associated with the reported data. We demonstrate clearly that the main factor which leads to this broad data spread is due to surface contamination. It is clear that typically inappropriate cleaning methods were used which resulted in artificially high contact angle measurements. We used surface cleaning methods typically prescribed in the surface chemistry community and found that the water contact angle θ on a clean quartz substrate is low, 0-30°, and that θ increases with pressure. We conclude that quartz is strongly water-wet at high pressure conditions.

1. Introduction

We followed the recent debate about CO_2/brine quartz contact angle measurements with high interest and we would like to comment on the recent communications (Bikkina 2011, 2012, Mahadevan 2012) in the context of experimental results we acquired and also from a more general surface chemistry perspective. As a key point, we suggest a reason for the large spread in the ~~high uncertainty associated with~~ published contact angle data (Figure 1), namely surface contamination of the silica substrates. We clearly demonstrate that such contamination has a major impact on the observed contact angle θ.

2. Literature data

Figure 1 displays a compilation of published experimental CO_2-water-silica contact angle (θ is the water contact angle) data ~~(θ is the water contact angle)~~(Bikkina 2011, Broseta et al. 2012, Chiquet et al. 2007, Espinoza and Santamarina 2010, Farokhpoor et al. 2012, Jung and Wan 2012, Mills et al. 2011, Saraji et al. 2012, Sutjiadi-Sia et al. 2008, Wang et al. 2013a+b, Wesch et al. 1997), which clearly illustrate significant scattering and high uncertainties. Specifically, θ from ~7° to 92° have been reported and there is no obvious explanation for such variation. The physical and chemical parameters: temperature (range tested: 296K-396K), pressure (range tested: 0-40 MPa), and salinity (range tested: 0-7M NaCl concentration) did not show any obvious trendlines and were not able to explain the large variations. The distinction between advancing and receding θ, however, reduced data spread, and lower advancing θ (~7-42°) than receding θ (20-90°) were measured as expected, Butt et al. (2006). Nevertheless, this factor on its own cannot fully explain the large variation in measured contact angles. In our opinion, the main reason for this uncertainty is surface contamination of the substrates, and we substantiate this claim below. To capture the full picture of the influence of this variable (contamination) it is necessary to revisit standard procedures used in surface chemistry.

Fig. 1. Compilation of experimental CO_2-water-silica contact angles reported in the literature. Sessile θ: open black, advancing θ: green, receding θ: red.

3. Prescribed surface cleaning methods

In the field of surface chemistry, surface cleanliness is often of key importance. For instance, Love et al. (2006) suggest the following two methods for cleaning substrates prior to building self-assembled molecules (these are molecules which spontaneously adhere onto a substrate's surface, e.g. alkanethiols onto a gold surface):

- strongly oxidising chemicals, e.g. "piranha" solution (H_2SO_4:H_2O_2)
- oxygen plasma

Grate et al. (2012) conducted air-water and oil-water θ measurements at ambient conditions on silica surfaces, and they cleaned their substrates using standard silica wafer cleaning techniques:

- submersion in a 343K solution of 5 parts DI (deionised) water, 1 part 27% ammonium hydroxide, 1 part hydrogenperoxide for 10min, followed by DI rinse (⇒ this is a strongly oxidising chemical, see above)
- rinse with chloroform, 2-propanol, ethanol, followed by UV-ozone treatment for 30min.

In contrast, in the area of carbon geo-sequestration, and the associated CO_2-water θ measurements, the reported cleaning methods are frequently inconsistent with the methods prescribed above, Table 1. The consequence of insufficient cleaning is dramatic and will be further discussed below. We, however, think that Saraji et al. (2013) have used quite stringent cleaning procedures, i.e. sulphuric acid containing 10% Nochromix is a strongly oxidising agent (although the exact formulation is proprietary and we only assume that this is the case here), and this is probably sufficient to clean the surface properly. The use of a paper towel for absorbing water may however have compromised the cleaning, see discussion below. Chiquet et al. (2007) and Farokhpoor et al. (2013) have used diluted nitric-acid, which is also quite oxidising, but a θ around 10-20° (Farokhpoor et al. 2013) at ambient pressure is an indication of surface contamination. Mechanistically, the adsorption of molecules (particularly organic molecules), which are for instance present in the air, on the fingers of the researcher, or in the test cell itself, causes the surface contamination.

Table 1
Cleaning methods used for silica surface preparation prior to contact angle measurements.

4. Contact angle measurements and influence of surface contamination

We have conducted several θ measurements, and initially we investigated three different aqueous phases: (i) DI water, (ii) 0.342 M~~20000 ppm~~ NaCl brine, (iii) 1 M $NaHCO_3$ brine. In these measurements, the water drops were dispensed onto an α-quartz surface cleaned with acetone and DI water and then the sessile water contact angle θ was measured on a magnified image captured with a video camera. The temperature was constant at 323K while the effect of pressure on the θ isotherm was measured, Figure 2. As can be seen θ was always quite high except for some of the 1M $NaHCO_3$ data, sometimes θ > 90° was observed. Theoretically, however, θ at 0.1 MPa (ambient pressure) should be ~0° (Grate et al. 2012). This discrepancy led us to a "reality check", where we cleaned an α-quartz single crystal with piranha solution (5vol:1vol H_2SO_4:H_2O_2) and measured a contact angle of approximately 0° at ambient conditions in CO_2 atmosphere. After wiping this crystal with a "clean" paper towel and repeating the test (at identical conditions) the measured angle was approximately 25°; we then measured θ (= 70°), again at identical conditions, on a crystal which was exposed to laboratory air for several weeks. This illustrates that such measurements need to

be undertaken with great care and cleanliness. We also note here that we spend a significant amount of time on cleaning all wetted parts of the contact angle measurement apparatus (three times flushed with toluene, three times flushed with acetone, three times flushed with DI water) as previously crude oil and surfactant solutions were used in that instrument. As a result,~~So~~ the apparatus itself can easily be the source of contamination, however, the above ambient condition measurements were conducted outside the apparatus.

As a next step, we procured a plasma reactor (Yocto, Diener/Germany) – note that piranha solution is a serious health and safety hazard and we recommend absolute minimal use of this dangerous chemical, and that only by trained personnel – which can clean surfaces rapidly with a low health and safety footprint (Senden, 2012). We then repeated our experiments as described above except that now the substrate was cleaned for 15min in an air plasma; and all experiments were run at room temperature (~ 296K). We note that we observed a significant increase in θ due to contamination if the CO_2 in the cell was decompressed, the cell vacuumed until the water on the quartz crystal fully evaporated, and the CO_2 pressure again raised to the experimental value. This was probably caused by residual contamination in the measurement apparatus, which cannot be removed. Consequently we had to re-clean the substrate in the air plasma after each θ measurement. In addition to measuring the sessile θ, we measured the advancing θ: we dispensed more and more water drops into the water reservoir on the quartz surface, and recorded movies for this process. The maximum θ just before the pinned three-phase line of the drop jumped forward was set to the advancing θ. We measured θ three times at 0.1 MPa CO_2 pressure and two times at 13.89 MPa CO_2 pressure, and the measurements were highly reproducible.

Results are shown in Figure 2 as blue diamonds (sessile drop θ) and squares (advancing θ), and it is clear that a) both prescribed cleaning methods result in the same θ, b) θ is relatively low, 0-30°, consistent with Saraji et al. (2013), c) advancing θ is higher than sessile drop θ as expected, and d) quartz is strongly water-wet at high pressure conditions, although higher pressures and temperatures should be tested using prescribed surface cleaning methods.

Based on the above analysis we agree with Mahadevan (2012) that surface contamination leads to a) a highly biased θ measurement, and to b) overall too high θ values. High θ however has the dramatic effect that less CO_2 can be stored permanently in the subsurface by structural or residual trapping (Iglauer et al. 2012, Naylor et al. 2011, Spiteri et al. 2008). We note for completeness that wettability can also be measured via core-flooding techniques and imbibition experiments.

Fig. 2. Sessile and advancing water contact angles θ measured on an α-quartz crystal in CO_2-atmosphere as a function of pressure. The blue diamonds (sessile θ) and blue squares (advancing θ) represent surfaces which were cleaned using the prescribed cleaning methods, i.e. piranha solution or oxygen (air) plasma.

5. Conclusions

Our overall conclusion is that θ on clean quartz or glass surfaces is rather low (0-30°), and that these materials are strongly water-wet at high pressure conditions. We, however, observed a significant increase of θ with pressure, and higher pressures should be tested as they are relevant for carbon geo-storage. Furthermore, it is evident that surface contamination in the context of these measurements plays a major role and can shift measured θ values to much higher ranges, which are strongly biased. We, however, acknowledge that quartz surfaces in a subsurface environment are probably not perfectly clean as they have been exposed to formation fluids over geological periods of time; this aspect, although quite challenging, should be investigated further.

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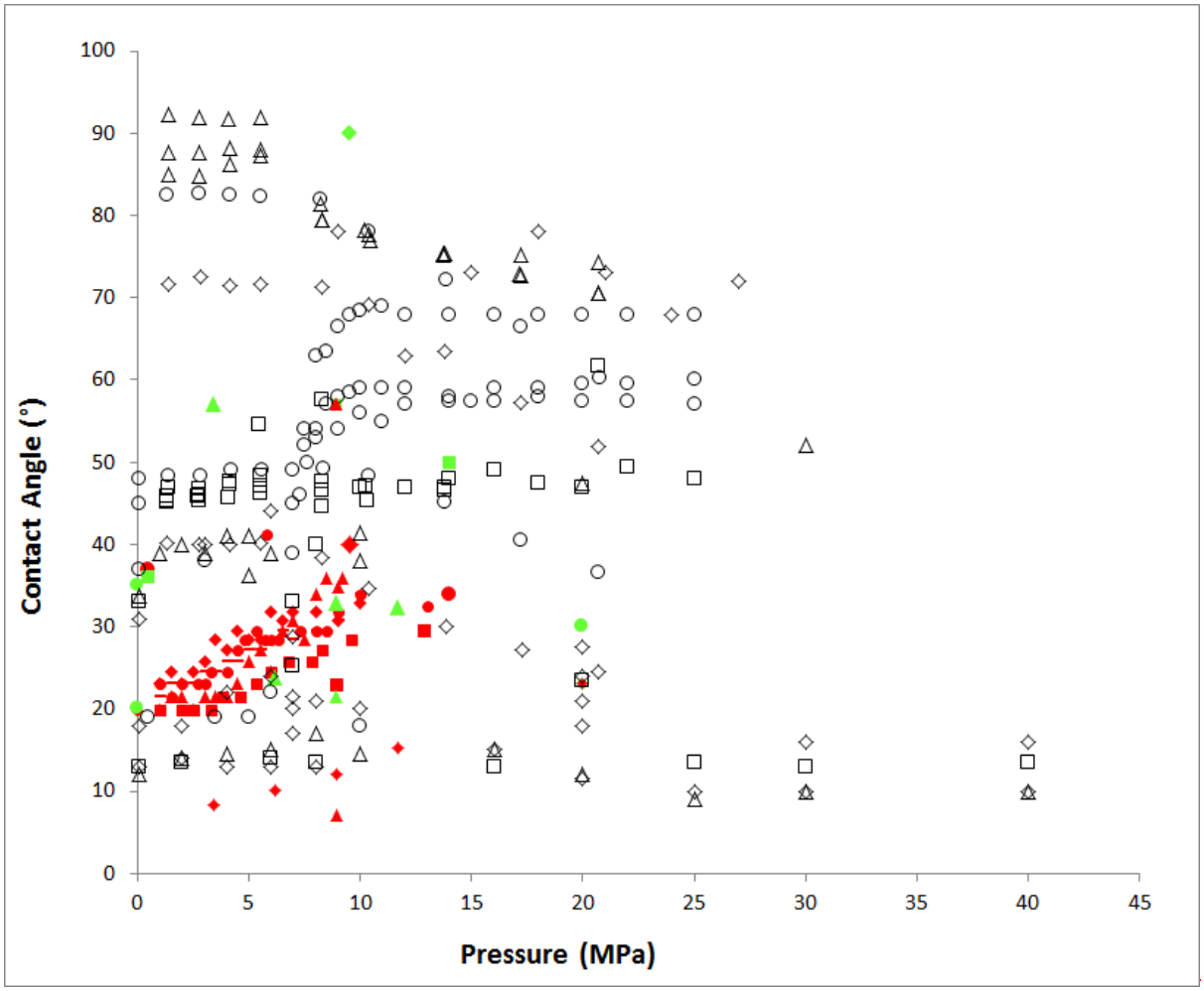
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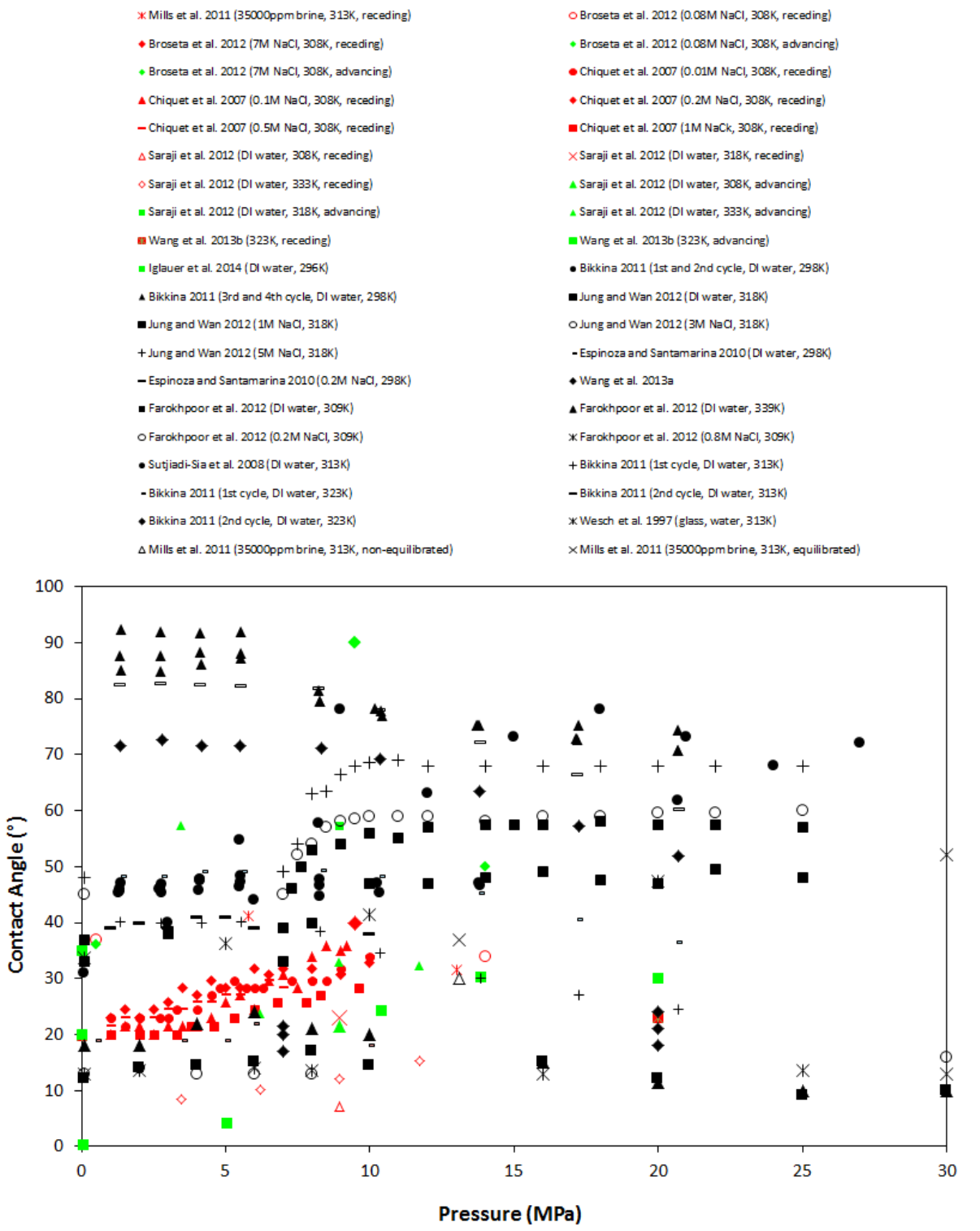

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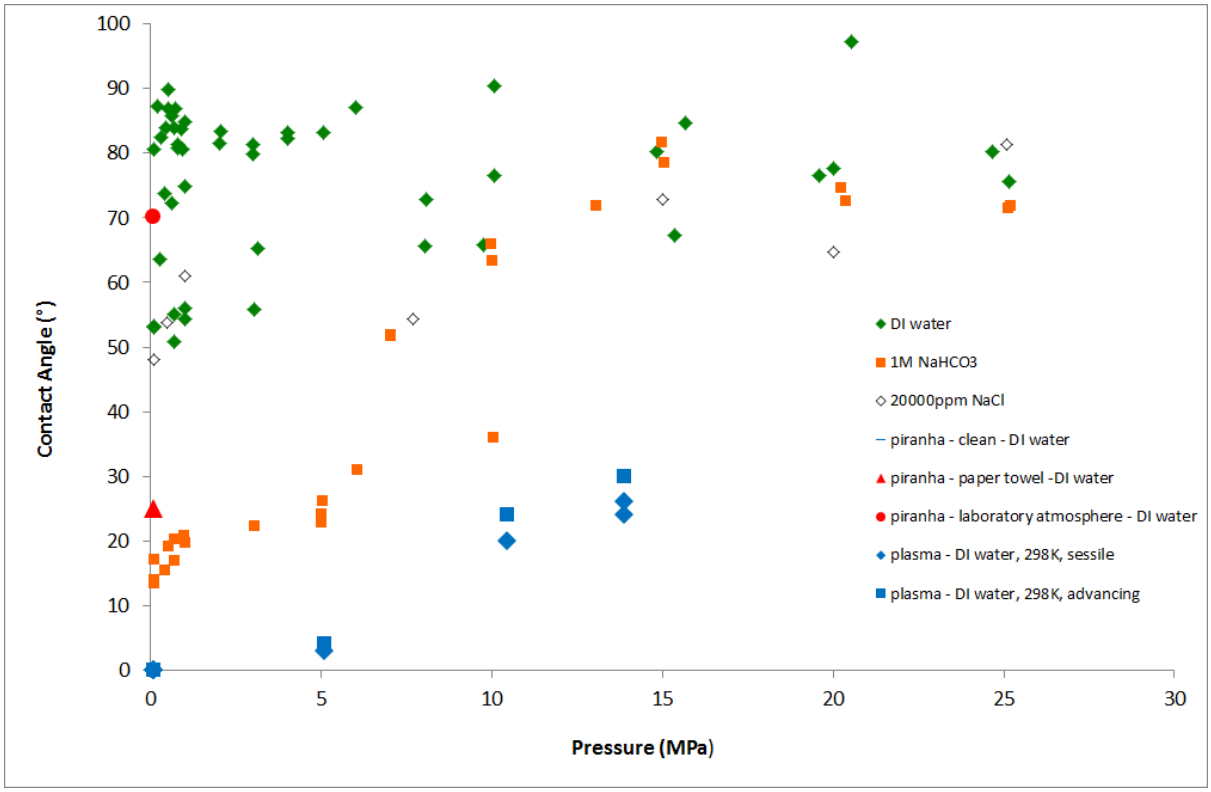

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Table 1

Cleaning methods used for silica surface preparation prior to contact angle measurements.

Reference	Cleaning method of silica (quartz or glass) substrate
Wesch et al. (1997)	washed with acetone, then dried
Chiquet et al. (2007)	cleaned with tensioactive solution under ultrasonic agitation for 30min, then rinsed with a 10% nitric-acid solution and finally washed with DI water
Sutjiadi-Sia et al. (2008)	not specified
Espinoza and Santamarina (2010)	not specified
Bikkina (2011)	1st cycle: as received following cycles: 30 min sonicated in acetone, then 30min sonicated in ultra-pure water
Mills et al. (2011)	before first use: cleaned in toluene, methanol, acetone, 2-propanol thereafter:

	rinsed in methanol, DI water and placed in an ultrasonic bath (in a beaker)
Broseta et al (2012)	not specified
Jung and Wan (2012)	ethanol
Saraji et al. (2013)	rinsed with 2-propanol, then immersed in sulphuric acid containing 10% Nochromix and sonicated for 30min, soaked in this solution overnight; washed thoroughly with water and boiled in DI water for 2h, rinsed and stored in DI water. Prior to test the substrates were dried by absorbing their bulk water with a filter paper and blow-dried with ultrahigh purity nitrogen.
Farokhpoor et al. (2013)	washed and sonicated in Deconex cleaning detergent solution for 20min, then washed with DI water, then rinsed with 6% nitric-acid solution while heated to 303K, then washed with DI water.
Wang et al. (2013a)	soaked in acetone for 3h, heated to 393K for 2h, sonicated in DI water, flushed with nitrogen to dryness.
Wang et al. (2013b)	soaked in acetone for 3h, heated to 393K for 2h, sonicated in DI water, flushed with nitrogen to dryness.

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