

NOTICE: this is the author's version of a work that was accepted for publication in International Journal of Greenhouse Gas Control. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in International Journal of Greenhouse Gas Control, Vol. 22 (2014). DOI: 10.1016/j.ijggc.2014.01.006

1 **Contamination of silica surfaces: impact on water-CO₂-quartz and glass contact angle**
2 **measurements**

3

4 Stefan Iglauer¹, Abdulsalam Salamah², Mohammad Sarmadivaleh¹, Keyu Liu³, Chi Phan²

5

6

7 ¹Curtin University, Department of Petroleum Engineering, 26 Dick Perry Avenue, 6151

8 Kensington, Australia

9 ²Curtin University, Department of Chemical Engineering, 6151 Kensington, Australia

10 ³CSIRO, 26 Dick Perry Avenue, 6151 Kensington, Australia

11

12 **Abstract**

13 CO₂-wettability of sandstones is a key variable which determines structural and residual
14 trapping capacities and strongly influences multi-phase fluid dynamics in the rock. An
15 increasing number of researchers has now estimated this wettability by conducting contact
16 angle measurements on quartz, however, there is a large uncertainty associated with the
17 reported data. We demonstrate clearly that the main factor which leads to this broad data
18 spread is due to surface contamination. It is clear that typically inappropriate cleaning
19 methods were used which resulted in artificially high contact angle measurements. We used
20 surface cleaning methods typically prescribed in the surface chemistry community and found
21 that the water contact angle θ on a clean quartz substrate is low, 0-30°, and that θ increases
22 with pressure. We conclude that quartz is strongly water-wet at high pressure conditions.

23

24

1 1. Introduction

2 We followed the recent debate about CO₂/brine quartz contact angle measurements with high
3 interest and we would like to comment on the recent communications (Bikkina 2011, 2012,
4 Mahadevan 2012) in the context of experimental results we acquired and also from a more
5 general surface chemistry perspective. As a key point, we suggest a reason for the large
6 spread in the ~~high uncertainty associated with~~ published contact angle data (Figure 1), namely
7 surface contamination of the silica substrates. We clearly demonstrate that such
8 contamination has a major impact on the observed contact angle θ .

9

10 2. Literature data

11 Figure 1 displays a compilation of published experimental CO₂-water-silica contact angle (θ
12 is the water contact angle) data (~~θ is the water contact angle~~)(Bikkina 2011, Broseta et al.
13 2012, Chiquet et al. 2007, Espinoza and Santamarina 2010, Farokhpoor et al. 2012, Jung and
14 Wan 2012, Mills et al. 2011, Saraji et al. 2012, Sutjiadi-Sia et al. 2008, Wang et al. 2013a+b,
15 Wesch et al. 1997), which clearly illustrate significant scattering and high uncertainties.
16 Specifically, θ from $\sim 7^\circ$ to 92° have been reported and there is no obvious explanation for
17 such variation. The physical and chemical parameters: temperature (range tested: 296K-
18 396K), pressure (range tested: 0-40 MPa), and salinity (range tested: 0-7M NaCl
19 concentration) did not show any obvious trendlines and were not able to explain the large
20 variations. The distinction between advancing and receding θ , however, reduced data spread,
21 and lower advancing θ (~ 7 - 42°) than receding θ (20 - 90°) were measured as expected, Butt et
22 al. (2006). Nevertheless, this factor on its own cannot fully explain the large variation in
23 measured contact angles. In our opinion, the main reason for this uncertainty is surface
24 contamination of the substrates, and we substantiate this claim below. To capture the full
25 picture of the influence of this variable (contamination) it is necessary to revisit standard
26 procedures used in surface chemistry.

27

28 **Fig. 1.** Compilation of experimental CO₂-water-silica contact angles reported in the literature.
29 Sessile θ : open black, advancing θ : green, receding θ : red.

30

31 3. Prescribed surface cleaning methods

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

- 36 - strongly oxidising chemicals, e.g. "piranha" solution (H₂SO₄:H₂O₂)
- 37 - oxygen plasma

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

- 4 - submersion in a 343K solution of 5 parts DI (deionised) water, 1 part 27% ammonium
5 hydroxide, 1 part hydrogenperoxide for 10min, followed by DI rinse (\Rightarrow this is a
6 strongly oxidising chemical, see above)
- 7 - rinse with chloroform, 2-propanol, ethanol, followed by UV-ozone treatment for
8 30min.

9 In contrast, in the area of carbon geo-sequestration, and the associated CO₂-water θ
10 measurements, the reported cleaning methods are frequently inconsistent with the methods
11 prescribed above, Table 1. The consequence of insufficient cleaning is dramatic and will be
12 further discussed below. We, however, think that Saraji et al. (2013) have used quite stringent
13 cleaning procedures, i.e. sulphuric acid containing 10% Nochromix is a strongly oxidising
14 agent (although the exact formulation is proprietary and we only assume that this is the case
15 here), and this is probably sufficient to clean the surface properly. The use of a paper towel
16 for absorbing water may however have compromised the cleaning, see discussion below.
17 Chiquet et al. (2007) and Farokhpoor et al. (2013) have used diluted nitric-acid, which is also
18 quite oxidising, but a θ around 10-20° (Farokhpoor et al. 2013) at ambient pressure is an
19 indication of surface contamination. Mechanistically, the adsorption of molecules
20 (particularly organic molecules), which are for instance present in the air, on the fingers of
21 the researcher, or in the test cell itself, causes the surface contamination.

22

23 **Table 1**

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

25

26 **4. Contact angle measurements and influence of surface contamination**

27 We have conducted several θ measurements, and initially we investigated three different
28 aqueous phases: (i) DI water, (ii) ~~0.342 M~~ ~~20000 ppm~~ NaCl brine, (iii) 1 M NaHCO₃ brine. In
29 these measurements, the water drops were dispensed onto an α -quartz surface cleaned with
30 acetone and DI water and then the sessile water contact angle θ was measured on a magnified
31 image captured with a video camera. The temperature was constant at 323K while the effect
32 of pressure on the θ isotherm was measured, Figure 2. As can be seen θ was always quite
33 high except for some of the 1M NaHCO₃ data, sometimes $\theta > 90^\circ$ was observed.
34 Theoretically, however, θ at 0.1 MPa (ambient pressure) should be $\sim 0^\circ$ (Grate et al. 2012).
35 This discrepancy led us to a “reality check”, where we cleaned an α -quartz single crystal with
36 piranha solution (5vol:1vol H₂SO₄:H₂O₂) and measured a contact angle of approximately 0°
37 at ambient conditions in CO₂ atmosphere. After wiping this crystal with a “clean” paper
38 towel and repeating the test (at identical conditions) the measured angle was approximately
39 25°; we then measured θ (= 70°), again at identical conditions, on a crystal which was
40 exposed to laboratory air for several weeks. This illustrates that such measurements need to

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

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

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

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

34
35 **Fig. 2.** Sessile and advancing water contact angles θ measured on an α -quartz crystal in CO_2 -
36 atmosphere as a function of pressure. The blue diamonds (sessile θ) and blue squares
37 (advancing θ) represent surfaces which were cleaned using the prescribed cleaning methods,
38 i.e. piranha solution or oxygen (air) plasma.

40 5. Conclusions

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

10

11 Acknowledgements

12 The authors wish to acknowledge financial assistance provided through Australian National
13 Low Emissions Coal Research and Development (ANLEC R&D). ANLEC R&D is supported
14 by Australian Coal Association Low Emissions Technology Limited and the Australian
15 Government through the Clean Energy Initiative. We would like to thank Tim Senden for
16 helpful discussions regarding surface cleaning methods.

17

18 References

- 19 Bikkina, P.K. 2011. Contact angle measurements of CO₂-water-quartz/calcite systems in the
20 perspective of carbon sequestration. *Int. J. Greenh. Gas Con.* (5), 1259-1271.
- 21 Bikkina, P.K. 2012. Reply to the editor. *Int. J. Greenh. Gas Con.* (7), 263-264.
- 22 Broseta, D., Tonnet, N., Shah, V. 2012. Are rocks still water-wet in the presence of dense
23 CO₂ or H₂S? *Geofluids* (12), 280-294.
- 24 Butt, H.-J., Graf, K., Kappl, M. 2006. *Physics and chemistry of interfaces*. Weinheim: Wiley-
25 VCH.
- 26 Chiquet, P, Broseta, D, Thibeau, S. 2007. Wettability alteration of caprock minerals by
27 carbon dioxide. *Geofluids* (7), 112-122.
- 28 Espinoza, D.N., Santamarina, J.C. 2010. Water-CO₂-mineral systems: Interfacial tension,
29 contact angle, and diffusion – Implications to CO₂ geological storage. *Water Resour Res* (46),
30 W0753.
- 31 Farokhpoor, R., Bjørkvik, B.J.A., Lindeberg, E., Torsæter, O. 2013. Wettability behaviour of
32 CO₂ at storage conditions. *International Journal of Greenhouse Gas Control* (12), 18-25.
- 33 Grate, J.W., Dehoff, K.J., Warner, M.G., Pittman, J.W., Zhang, C., Oostrom, M. 2012.
34 Correlation of oil-water and air-water contact angles of diverse silanized surfaces and
35 relationship to fluid interfacial tensions. *Langmuir* (28), 7182-7188.

- 1 Iglauer, S., Mathew, M., Bresme, F. 2012. Molecular dynamics computations of brine-CO₂
2 interfacial tensions and brine-CO₂-quartz contact angles and their effects on structural and
3 residual trapping mechanisms in carbon geo-sequestration. *Journal of Colloid and Interface*
4 *Science* 386 (1), 405-414.
- 5 Jung, J.-W., Wan, J. 2012. Supercritical CO₂ and ionic strength effects on wettability of silica
6 surfaces: equilibrium contact angle measurements. *Energy and Fuels* (26), 6053-6059.
- 7 Love, J.C., Estroff, L.A., Kriebel, J.K., Nuzzo, R.G., Whitesides, G.M. 2005. Self-assembled
8 monolayers of thiolates on metals as a form of nanotechnology. *Chem. Rev.* (105), 1103-
9 1169.
- 10 Mahadevan, J. 2012. Comments on the paper titled "Contact angle measurements of CO₂-
11 water-quartz/calcite systems in the perspective of carbon sequestration": a case of
12 contamination?. *Int. J. Greenh. Gas Con.* (7), 261-262.
- 13 Naylor, M., Wilkinson, M., Haszeldine, R.S. 2011. Calculation of CO₂ column heights in
14 depleted gas fields from known pre-production gas column heights. *Marine and Petroleum*
15 *Geology* (28), 1083-1093.
- 16 Saraji, S., Goual, L., Piri, M., Plancher, H. 2013. Wettability of supercritical carbon
17 dioxide/water/quartz systems: simultaneous measurement of contact angle and interfacial
18 tension at reservoir conditons. *Langmuir* (29), 6856-6866.
- 19 Senden, T. 2012. Private communication.
- 20 Spiteri, E.J., Juanes, R., Blunt, M.J., Orr, F.M. 2008. New model of trapping and relative
21 permeability hysteresis for all wettability characteristics. *SPE Journal* (13)3, 277-288.
- 22 Sutjiadi-Sia, Y., Jaeger, P., Eggers, R. 2008. Interfacial phenomena of aqueous systems in
23 dense carbon dioxide. *Journal of Supercritical Fluids* (46), 272-279.
- 24 Wang, S., Edwards, I.M., Clarens, A.F. 2013a. Wettability phenomena at the CO₂-brine-
25 mineral interface: implications for geologic carbon sequestration. *Environmental Science and*
26 *Technology* (47) 234-241.
- 27 Wang, S., Tao, Z., Persily, S., Clarens, A.F. 2013b. CO₂ adhesion on hydrated mineral
28 surfaces. *Environmental Science and Technology* (47), 11858-11865.
- 29 Wesch, A., Dahmen, N., Ebert, K., Schön, J. 1997. Grenzflächenspannungen, Tropfengrösse
30 und Kontaktwinkel im Zweiphasensystem H₂O/CO₂ bei Temperaturen von 298 bis 333K und
31 Drücken bis 30 MPa. *Chemie Ingenieur Technik* (69), 942-946.

32

33

34

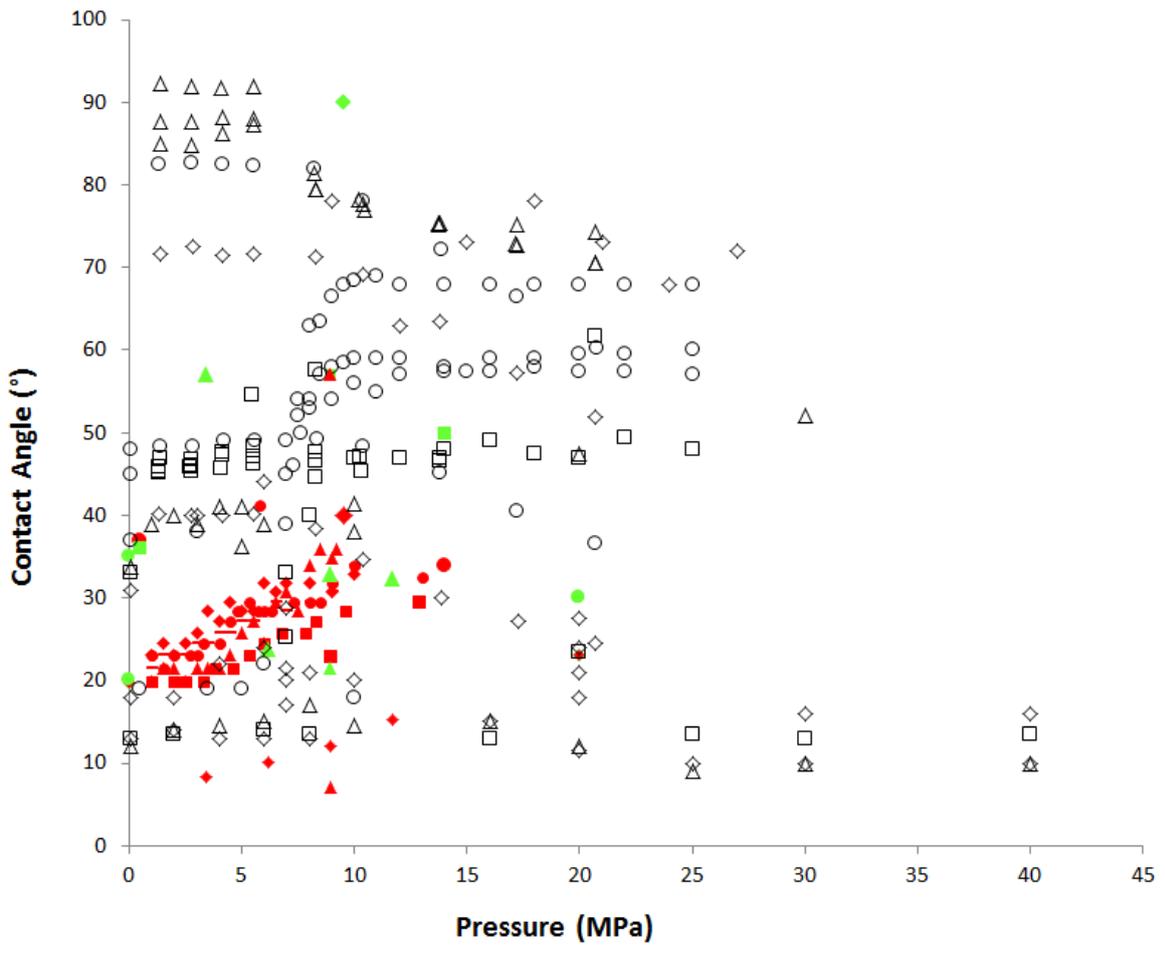
1

2

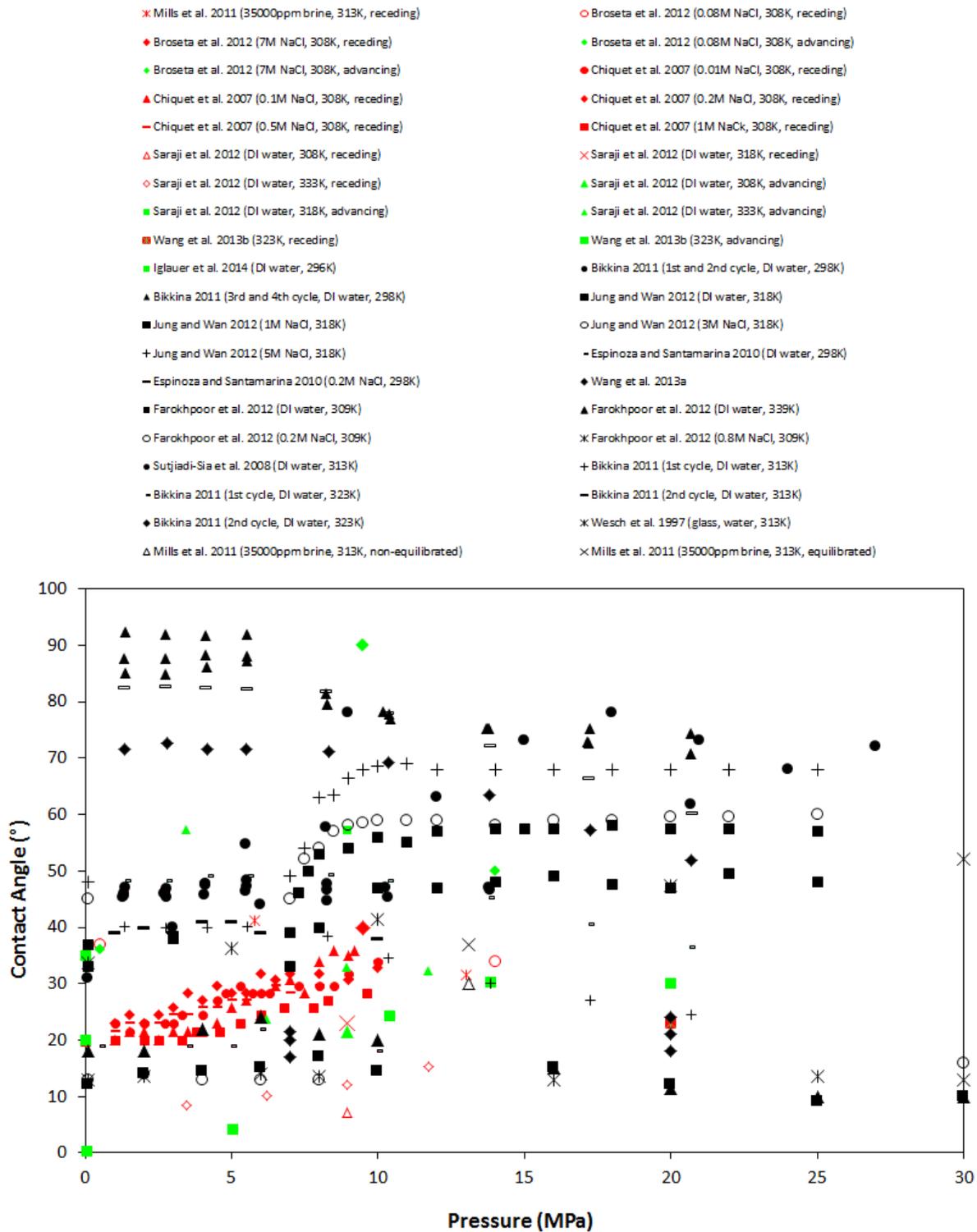
3

4

5

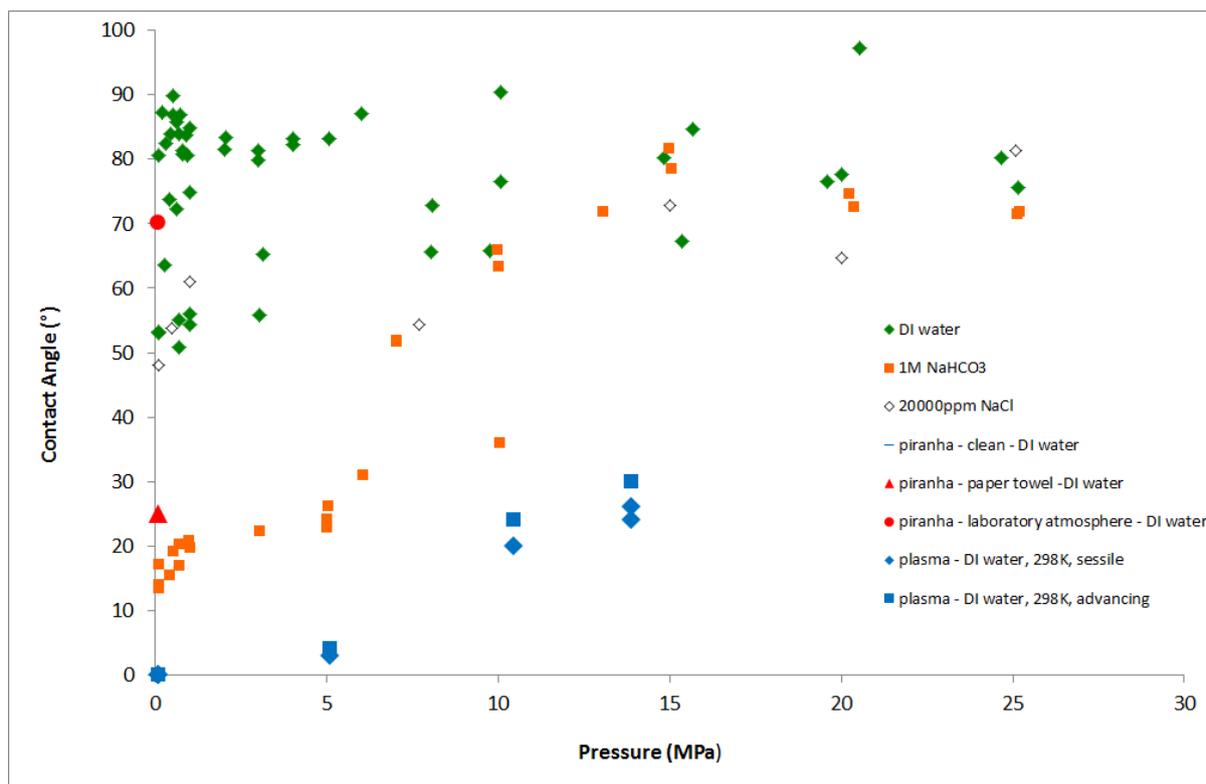


1



1
2
3
4
5

Fig. 1. Compilation of experimental CO₂-water-silica contact angles reported in the literature. Sessile θ : open or closed black, advancing θ : green, receding θ : red.



1
2 **Fig. 2.** Sessile and advancing water contact angles θ measured on an α -quartz crystal in CO_2 -
3 atmosphere as a function of pressure. The blue diamonds (sessile θ) and blue squares
4 (advancing θ) represent surfaces which were cleaned using the prescribed cleaning methods,
5 i.e. piranha solution or oxygen (air) plasma.

6
7
8

9 **Table 1**

10 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)	1 st 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:

Broseta et al (2012)	rinsed in methanol, DI water and placed in an ultrasonic bath (in a beaker)
Jung and Wan (2012)	not specified
Saraji et al. (2013)	ethanol 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.

1

2