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CO₂-wettability of sandstones exposed to traces of organic acids; implications for CO₂ geo-storage

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Abstract

Wettability of CO₂-brine-mineral systems plays a vital role during geological CO₂-storage. Residual trapping is lower in deep saline aquifers where the CO₂ is migrating through quartz rich reservoirs but CO₂ accumulation within a three-way structural closure would have a high storage volume due to higher CO₂ saturation in hydrophobic quartz rich reservoir rock. However, such wettability is only poorly understood at realistic subsurface conditions, which

are anoxic or reducing. As a consequence of the reducing environment, the geological formations (i.e. deep saline aquifers) contain appreciable concentrations of various organic acids. We thus demonstrate here what impact traces of organic acids exposed to storage rock have on their wettability. Technically, we tested hexanoic acid, lauric acid, stearic acid and lignoceric acid and measured wettability as a function of organic acid concentration at realistic storage conditions (i.e. 25 MPa and 323 K (50 °C)). In addition, measurements were also conducted at ambient conditions in order to quantify the incremental pressure effect on wettability. Clearly, the quartz surface turned significantly less water-wet with increasing organic acid concentrations, even at trace concentrations. Importantly, we identified a threshold concentration at $\sim 10^{-6}$ M organic acid, above which quartz wetting behaviour shifts from strongly water-wet to an intermediate-wet state. This wettability shift may have important consequences for CO₂ residual trapping capacities, which may be significantly lower than for traditionally assumed water-wet conditions where CO₂ is migrating through quartz rich reservoirs.

1. Introduction

CO₂ geological storage can significantly contribute towards a green environment via permanent CO₂ immobilization in deep underground formations, e.g. deep saline aquifers and depleted hydrocarbon reservoirs (Blunt et al., 1993, IPCC, 2005, Orr, 2009;). Efficient and safe CO₂ geological storage involves a qualitative and quantitative assessment of the contribution of the different functional trapping mechanisms which prevent the buoyant CO₂ from migrating back to the surface (IPCC, 2005; Juanes et al., 2010). These trapping mechanism include structural trapping (Iglauer et al., 2015a, Arif et al., 2016a,b, 2017a;), capillary or residual trapping (Juanes et al., 2010; Iglauer et al., 2011a,b; Pentland et al., 2011; Krevor et al., 2012), mineral trapping (Gaus 2010; Golding et al., 2011; Pearce et al., 2015,) and dissolution trapping

(Iglauer 2011c; Agartan et al., 2015). In addition, adsorption trapping has been identified as another storage mechanism functional in coal seams and organic rich shales (Busch et al., 2008; Shojai Kaveh et al., 2012, 2016; Arif et al., 2016c, 2017b).

Structural and residual trapping are strongly influenced by the CO₂-brine-rock wettability (Chaudhary et al., 2013; Iglauer et al. 2015a,b; Al-Menhali et al. 2016a,b; Rahman et al., 2016; Al-Khdheewi et al., 2017; Arif et al. 2017a; Iglauer 2017; Wan et al., 2018), however, wettability is a complex parameter which is not well understood, particularly for realistic subsurface conditions. One key aspect of realistic subsurface conditions is their anoxic or reducing character, which results in the existence of organic molecules in target storage formations (Meredith et al., 2000; Watson et al. 2002).

It is shown in previous studies that water receding contact angle on the cap rock (i.e. CO₂ displacing water) is related to structural trapping (below an impermeable caprock; Broseta et al., 2012). Whereas, the advancing water contact angle (water displacing CO₂) is related to capillary trapping in the reservoir rock (Chiquet et al. 2007; and thus the amount of residually trapped CO₂; Chaudhary et al., 2013, Rahman et al. 2016, Al-Menhali et al. 2016a). Note further that dissolution trapping in the reservoir rock is significantly affected by the wettability and it is thus necessary to know the wettability for accurate reservoir simulations and storage capacity predictions (Al-Khdheewi et al. 2016, 2017).

Although the concentrations of organic molecules in deep aquifers is normally low (Stalker et al. 2013), their prevailing concentrations are potentially sufficient to significantly influence the rock's wettability characteristics (Standnes and Austad, 2003; Gomari et al., 2006; Iglauer et al., 2014). Indeed, a partial mono-molecular layer adsorbed to the mineral surface would be sufficient for this (Shafrin et al., 1962; Gaines 1966; Kuhn et al., 1971; Zasadzinski et al., 1994; Adamson and Gast 1997; Maboudian et al., 1997; Bikkina 2011; Mahadevan 2012).

These minute organic concentrations can adversely affect the storage capacities and containment security via their impact on CO₂ wettability (Iglauer et al. 2015a,b; Al-Khdheawi et al. 2016, 2017). It is therefore important to understand at what organic concentration the impact on CO₂/Water/Mineral wettability becomes significant for trapping capacities. Thus, this work aims to benchmark the influence of trace concentrations of such organics and the effect of their carbon chain length on CO₂-rock wettability.

2. Experimental Methodology

2.1. Materials

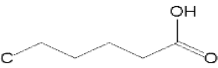
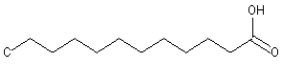
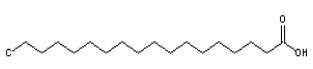
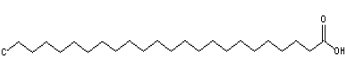
Nine pure quartz samples (Quartz (single crystals; testing chips from WARD'S Natural Science; sample range = 12 mm to 19 mm x 10 mm x 10 mm) were used as a model for sandstone storage formations. The surface roughnesses of all nine surfaces were provided by the supplier and the values ranged from 1 nm to 2 nm (root-mean-square (RMS) surface roughness, which is very smooth (Sarmadivaleh et al. 2015).

CO₂ (purity \geq 99.999 mol%; from BOC, gas code-082), N₂ (purity \geq 99.999 mol%; from BOC, gas code-234) and 10 wt% NaCl brine (NaCl purity \geq 99.9mol%; from Scharlab) were used. The NaCl was dissolved in deionized water (Ultrapure from David Gray; electrical conductivity = 0.02 mS/cm). Subsequently, the NaCl brine was equilibrated with CO₂ at experimental conditions in a high pressure mixing reactor (according to the procedure described by El-Maghraby et al. 2012). To represent organic compounds, organic acids were selected due to their presence in hydrocarbon reservoirs and aquifers; these included hexanoic acid, lauric acid, stearic acid, and lignoceric or oleic acid (Jardine et al., 1989; Legens et al., 1998; Madsen and Ida, 1998; Hansen et al., 2000; Amaya et al., 2002; Hamouda and Gomari,

2006; Kharaka et al., 2009; Stalker et al., 2013; Yang et al., 2015), Tabe 1 (purchased from Sigma Aldrich, purity ≥ 98 mol%).

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Table 1: Properties of organic acids used in this study.

Organic Acid	Physical state	Formula	Number of C atoms	Molar mass (g/mol)	Chemical Structure
Hexanoic acid	Liquid	$C_6H_{12}O_2$	6	116.158	
Lauric acid	solid	$C_{12}H_{24}O_2$	12	200.318	
Stearic acid	solid	$C_{18}H_{36}O_2$	18	284.4772	
Lignoceric acid	solid	$C_{24}H_{48}O_2$	24	368.63	

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Acetone (≥ 99.9 mol%; from Rowe Scientific) was used as surface cleaning agent, and drops of aqueous hydrochloric acid (ACS reagent, concentration 37 vol%, Sigma Aldrich) were used to control the pH of the brine (see ageing procedure below for more details).

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2.2. Sample preparation

2.2.1 Quartz surface preparation

Initially the mineral (quartz) substrates were cleaned with DI-water to remove any dust or surface fragments from the surface. The sample was then dried in an oven at 90°C for 60 mins and exposed to air plasma (using a DiemerYocto instrument) for 15 mins to remove any organic contamination (Love et al., 2005; Iglauer et al., 2014).

2.2.2 Ageing procedure

To mimic a typical storage formation, where the rock pore surfaces were exposed to formation water over geological times we adopted the following strategy (Davis 1982; Ulrich et al., 1988; Zullig and Morse, 1988; Ochs et al., 1994; Hoeiland et al., 2001; White et al., 2003; Nordbotten et al., 2005; Karoussi et al., 2008; Birkholzer et al., 2009; Ji et al., 2015; Kleber et al., 2015):

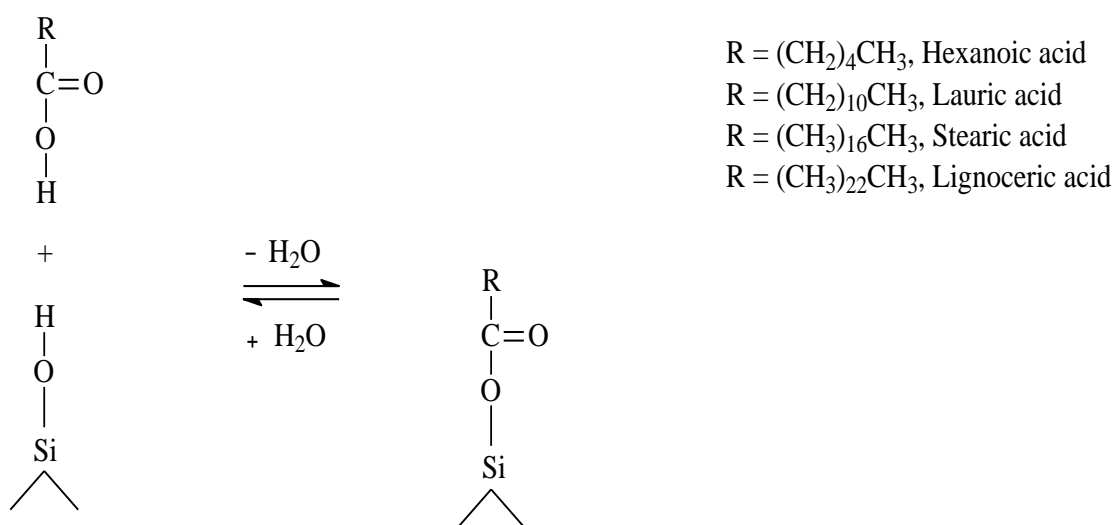
The quartz samples were immersed for 30 mins in 2 wt% NaCl brine at ambient conditions, while the acidity was maintained at pH = 4 by adding drops of aqueous hydrochloric acid; this procedure increases the adsorption rate of organics onto the substrate, and thus simulates adsorption of organic molecules over geological times (i.e. millions of years' exposure time) (Thurman 1985; Jardine et al., 1989; Madsen and Ida, 1998; Kharaka et al., 2009; Stalker et al. 2013; Yang et al., 2015). Ultraclean N₂ was then used to mechanically clean (blow away) the remaining water from the surface to avoid contamination. Subsequently the substrates were aged in different organic acid/n-decane solutions of prescribed molarity (10⁻² M to 10⁻¹⁰ M organic acid concentration) for seven days to mimic exposure to formation fluid (which contains organic molecules) over geological time (Thurman 1985; Jardine et al., 1989; Madsen and Ida, 1998; Kharaka et al., 2009; Stalker et al. 2013; Yang et al., 2015).

Previously, silanes were used to render the wettability of quartz surfaces oil-wet. Typically, different silanes have different impacts on surfaces hydrophilicity (Dickson et al., 2006, Grate et al., 2012, Hobeika et al., 2017). However, organic acids including stearic acids represent more realistically subsurface environments (Al-Anssari et al., 2016, 2018, Paterson et al., 2011, Hamouda et al., 2006, Gomari et al., 2006); while silanes do not exist in the subsurface (due to their high reactivity).

It is vital to re-create such mineral surfaces to realistically mimic the subsurface behaviour, particularly with respect to their wettability characteristics (Davis 1982; Ochs et al., 1994;

Adamson and Gast 1997; Kleber et al., 2015). Note that it is proven that carboxylic acids and hydrocarbons both exist in deep saline aquifers (Bennett et al., 1993), as a result of biodegradation and organic matter diagenesis and subsequent migration into the water zones (Jones et al., 2008).

Mechanistically, the organic acid esterifies the hydroxyl groups on the quartz surface in a condensation reaction (Scheme 1).



Scheme 1. Chemisorption of organic acids on solid quartz surface (\wedge indicates solid bulk).

Thus carboxylic components are chemically (covalently) bonded to the quartz surface, rendering them strongly hydrophobic (Al-Anssari et al., 2016).

2.3. Surface characterization of pure and aged quartz surfaces

The surface properties of the quartz samples were analysed via energy dispersive X-ray spectroscopy (EDS, Oxford X-act SSD X-ray detector with Inca and Aztec software) and contact angle (θ) measurements. Table 2 lists the EDS results before and after aging; these are average elemental surface concentrations (these are average over 45 data points: 5 data points

156 measured on each sample, on nine different samples) for each acid tested. Surface coverages
 157 with organic acid are also given (determined via the method defined by Dickson et al. 2006).
 158 Table 2. Surface composition of pure and aged quartz samples and associated surface coverage
 159 with all organic acids.

Concentration ion (Molarity)	Pure Quartz			After ageing			Change due to ageing			Estimated surface coverage (after Dickson et al., 2006)
	wt% Si	wt% C	wt% O	wt% Si	wt% C	wt% O	wt% Si	wt% C	wt% O	$\left(1 - \frac{\text{wt\% } C_{\text{before aging}}}{\text{wt\% } C_{\text{after aging}}}\right) \times 100$
Hexanoic Acid										
10 ⁻²	31.9	2.3	65.8	38.1	4.8	57.1	+6.2	+2.5	-8.7	52.1
10 ⁻³	33.3	4.1	62.6	30.3	7.5	62.2	-3.0	+3.4	-0.4	45.3
10 ⁻⁴	35.4	2.8	61.8	37.0	4.9	58.1	+1.6	+2.1	-3.7	42.9
10 ⁻⁵	34.7	3.2	62.1	34.2	5.1	60.7	-0.5	+1.9	-1.4	37.3
10 ⁻⁶	29.0	3.5	67.5	32.9	5.2	61.9	+3.9	+1.7	-5.6	32.7
10 ⁻⁷	29.5	4.2	66.3	29.0	5.8	65.2	-0.5	+1.6	-1.1	27.6
10 ⁻⁸	32.8	1.8	65.4	48.0	2.3	49.7	+15.2	+0.5	-15.7	21.7
10 ⁻⁹	29.9	3.4	66.7	33.1	4.1	62.8	+3.2	+0.7	-3.9	17.1
10 ⁻¹⁰	31.8	2.6	65.6	32.0	2.9	65.1	+0.2	+0.3	-0.5	10.3
0	34.0	1.5	64.5	34.0	1.5	64.5	0	0	0	0
Lauric Acid										
10 ⁻²	38.1	2.4	59.5	27.6	5.3	67.1	-10.5	+2.9	+7.6	54.7
10 ⁻³	33.8	1.8	64.4	31.1	3.5	65.4	-2.7	+1.7	+1.0	48.6
10 ⁻⁴	33.0	3.4	63.6	28.8	6.1	65.1	-4.2	+2.7	+1.5	44.3
10 ⁻⁵	38.3	4.3	57.4	35.4	7.1	57.5	-2.9	+2.8	+0.1	39.4
10 ⁻⁶	32.4	2.6	65.0	34.1	4.0	61.9	+1.7	+1.4	-3.1	35.0
10 ⁻⁷	34.5	3.6	61.9	33.5	5.2	61.3	-1.0	+1.6	-0.6	30.8
10 ⁻⁸	32.4	4.1	63.5	32.7	5.4	61.9	+0.3	+1.3	-1.6	24.1
10 ⁻⁹	32.4	1.4	66.2	36.1	1.7	62.2	+3.7	+0.3	-4.0	17.6
10 ⁻¹⁰	32.2	3.5	64.3	32.8	4.1	63.1	+0.6	+0.6	-1.2	14.6
0	31.6	2.3	66.1	31.6	2.3	66.1	0	0	0	0
Stearic Acid										
10 ⁻²	35.4	1.3	63.3	32.2	3.1	64.7	-3.2	+1.8	+1.4	58.1
10 ⁻³	34.3	3.7	62.0	26.8	7.6	65.6	-7.5	+3.9	+3.6	51.3
10 ⁻⁴	37.0	4.5	58.5	26.7	8.4	64.9	-10.3	+3.9	+6.4	46.4
10 ⁻⁵	36.8	1.6	61.6	32.3	2.8	64.9	-4.5	+1.2	+3.3	42.9
10 ⁻⁶	35.8	2.4	61.8	41.7	3.8	54.5	+5.9	+1.4	-7.3	36.8
10 ⁻⁷	36.0	4.3	59.7	22.0	6.3	71.7	-14.0	+2.0	+12	31.7
10 ⁻⁸	38.2	2.9	58.9	23.8	4.0	72.2	-14.4	+1.1	+13.3	27.5
10 ⁻⁹	34.1	4.2	61.7	23.5	5.2	71.3	-10.6	+1.0	+9.6	19.2
10 ⁻¹⁰	36.5	4.1	59.4	45.4	4.9	49.7	+8.9	+0.8	-9.7	16.3
0	36.5	2.2	61.3	36.5	2.2	61.3	0	0	0	0
Lignoceric Acid										
10 ⁻²	37.3	2.3	60.4	25.0	6.2	68.8	-12.3	+3.9	+8.4	62.9
10 ⁻³	36.3	2.0	61.7	25.4	4.6	70.0	-10.9	+2.6	+8.3	56.5
10 ⁻⁴	34.1	4.0	61.9	21.9	7.8	70.3	-12.2	+3.8	+8.4	48.7
10 ⁻⁵	35.6	3.4	61.0	24.8	6.2	69.0	-10.8	+2.8	+8.0	45.2
10 ⁻⁶	34.7	3.5	61.8	32.3	5.8	61.9	-2.4	+2.3	+0.1	39.7
10 ⁻⁷	33.9	4.1	62.0	28.9	6.1	65.0	-5.0	+2.0	+3.0	32.8
10 ⁻⁸	33.7	2.7	63.6	26.0	3.9	70.1	-7.7	+1.2	+6.5	30.8
10 ⁻⁹	39.6	1.9	58.5	27.7	2.5	69.8	-11.9	+0.6	+11.3	24.0
10 ⁻¹⁰	36.5	4.2	59.3	25.0	5.1	69.9	-11.5	+0.9	+10.6	17.6

0	34.0	3.6	62.4	34.0	3.6	62.4	0	0	0	0
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Table 3. Average Elemental surface analysis of quartz samples before and after ageing.

Organic Acids	Before aging			After aging		
	Si (wt%)	C (wt%)	O (wt%)	Si (wt%)	C (wt%)	O (wt%)
Hexanoic acid	32.2 ^a ± 3.2 ^b	2.9 ^a ± 1.4 ^b	64.8 ^a ± 2.9 ^b	34.9 ^a ± 9.5 ^b	4.4 ^a ± 3.0 ^b	60.7 ^a ± 7.8 ^b
Lauric acid	33.9 ^a ± 3.4 ^b	2.9 ^a ± 1.5 ^b	63.2 ^a ± 4.4 ^b	32.4 ^a ± 4.3 ^b	4.5 ^a ± 2.7 ^b	63.2 ^a ± 4.8 ^b
Stearic acid	36.1 ^a ± 2.1 ^b	3.1 ^a ± 1.6 ^b	60.8 ^a ± 2.4 ^b	31.1 ^a ± 11.7 ^b	4.8 ^a ± 3.1 ^b	64.1 ^a ± 11.3 ^b
Lignoceric acid	35.6 ^a ± 3.0 ^b	3.2 ^a ± 1.2 ^b	61.3 ^a ± 2.6 ^b	27.1 ^a ± 6.1 ^b	5.2 ^a ± 2.7 ^b	67.7 ^a ± 4.2 ^b

^a average surface concentration is based on the arithmetic average of 45 data points measured on five different sites for each of the nine samples at all concentrations tested.

^b '±' values are the standard deviations of these observations.

Clearly, aging had a significant impact on the atomic surface concentrations irrespective of the type and concentration of organic acid (Table 3). A significant overall average increase in surface carbon concentration (+1.6 wt% C for Hexanoic Acid, +1.7 wt% C for Lauric Acid, +1.9 wt% C for Stearic Acid and +2.2 wt% C for Lignoceric Acid) was measured. These changes in atomic coverage were caused by the chemisorption of the carboxylic acid on the quartz surface, consistent with Zullig and Morse (1988); see also 2.2.2 and scheme 1 above.

Moreover, the brine contact angles on the pure quartz samples were 0° (advancing and receding) at ambient conditions, thus pure quartz was completely water-wet at ambient conditions. However, higher contact angles (advancing 56° and receding 54° ± 3°) were measured at reservoirs conditions on these pure quartz samples (323 K (50 °C), 25 MPa), consistent with literature data (Chiquet et al., 2007; Farokhpour et al., 2013; Al-Yaseri et al.

2016a,b; Arif et al., 2016d;). However, aging of the quartz surfaces caused a significant change in contact angles and thus CO₂-wettability, this is discussed in detail below.

2.4. Contact angle measurements

Contact angle measurements are a standard technique for assessing the wettability behaviour of a given rock/fluid/fluid system. Here we used the tilted plate technique, which is regarded as the most effective contact angle measurement method as it can measure advancing and receding contact angles simultaneously (Lander et al., 1993).

The schematic of the experimental setup is shown in Figure 1. It consists of a high pressure-high temperature cell, which houses the sample inside on a tilted plate. The cell is connected to two pumps (Teledyne D-500, pressure accuracy of 0.1%) used for either discharging brine or CO₂. Furthermore, a CO₂ gas cylinder and the brine pump are both connected to a mixing reactor with which CO₂ and brine can be thermodynamically equilibrated (El-Maghraby et al. 2012).

Initially, the cell was charged with CO₂ at the desired measurement pressure and temperature (0.1 MPa, 25 MPa and 323 K (50 °C)). Temperature of the pumps was controlled through heating bath and the cell temperature was controlled through heating tape around it. The brine pump was initially filled with CO₂-equilibrated brine (equilibrated at experimental conditions) and a droplet of equilibrated brine (average drop volume was 6 µL (± 1 µL) was dispensed onto the quartz surface through a needle. The advancing (θ_a) and receding (θ_r) brine contact angles were then measured at the leading and trailing edge of the droplet just before the drop started to move (Lander et al., 1993). This process was recorded by a high performance video camera (Basler scA 640–70 fm, pixel size = 7.4 µm; frame rate = 71 fps; Fujinon CCTV lens: HF35HA-1B; 1:1.6/35 mm), which was connected to a computer system to display and analyse

the results. The standard deviation of the measurements was $\pm 3^\circ$ based on replicated measurements.

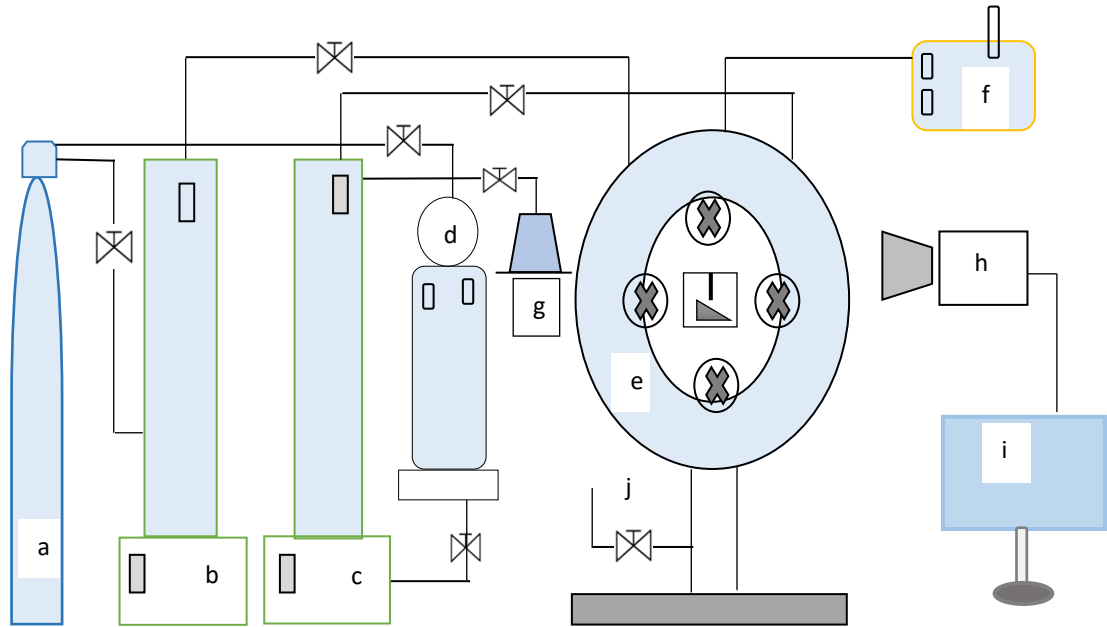


Figure 1. Experimental setting used in this study for measuring advancing and receding contact angles (modified after Arif et al., 2017a). (a) CO₂ cylinder (b) high precision syringe pump-CO₂, (c) high precision syringe pump-water, (d) High pressure Parr reactor for fluid equilibration e) high pressure cell with substrate housed on a tilted plate inside, (f) heating unit, (g) liquid feed/drain system, (h) high resolution video camera, (i) image visualization and interpretation software, (j) pressure relief valve.

3. Results and Discussion

Our results show that the quartz surface loses its water-wetness with increasing organic acid concentration. However, at organic acid concentrations $\leq 10^{-6}$ M, contact angles were only minimally affected, Figure 6, and thus structural trapping is not significantly affected (note:

even at low concentrations $\leq 10^{-6}$ M optimal residual trapping capacities are significantly affected). However, for concentrations $> 10^{-6}$ M, quartz wetting behaviour shifts from strongly water-wet to an intermediate-wet state (Iglauer et al., 2015b). A recent study conducted on carbonate minerals (Ali et al., 2019) showed that even at low organic concentrations ($\leq 10^{-6}$ M organic acid), optimal residual trapping capacities could be affected, which is due to the surface coverage of the mineral with organic acid and its tendency to alter the formation more CO₂-wet. Such wettability alteration changes the primary drainage capillary pressure curve (Morrow 1970, Anderson 1986, Masalmeh 2003), and thus the initial CO₂ saturation directly influencing the residual CO₂ saturation (e.g. Pentland et al. 2011; Wang et al., 2015, Heshmati et al., 2014, Akbarabadi et al., 2015).

3.1. Effect of acid concentration on quartz wettability

Advancing and receding brine contact angles increased significantly with an increase in organic acid concentration, as shown in Figures 2-5.

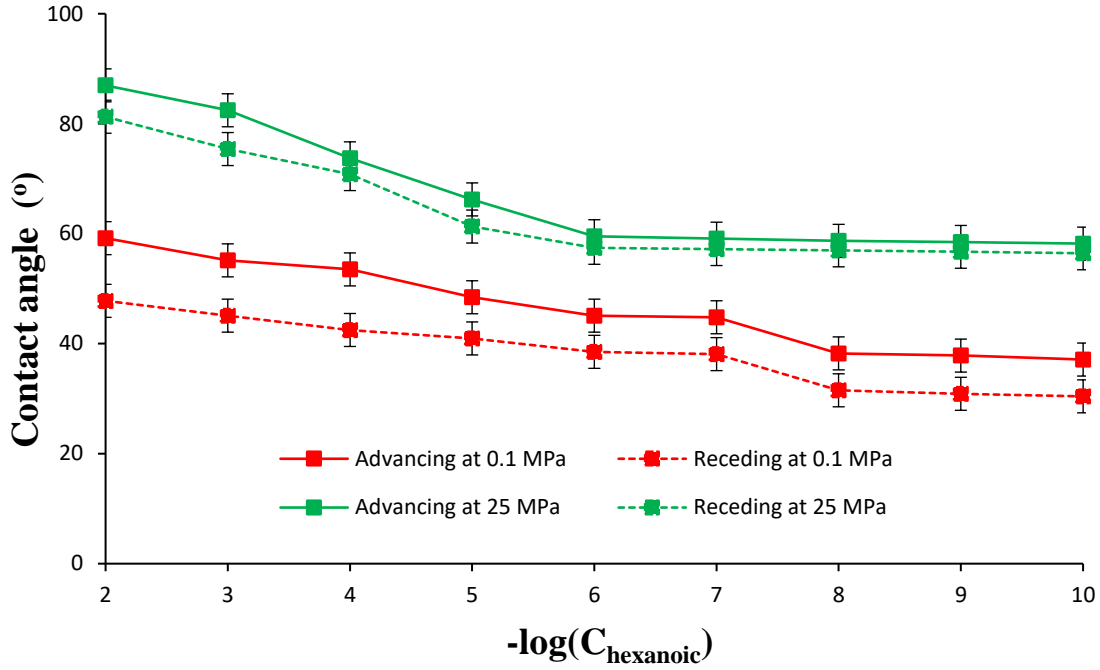


Figure 2. Quartz/CO₂/brine contact angles (measured through the water) as a function of hexanoic acid (C₆) concentration; C_{hexanoic} is the hexanoic acid concentration (molarity). Solid lines: advancing; dotted lines: receding. Red: ambient pressure; green: 25 MPa and 323 K (50 °C).

The contact angle was significantly higher at high pressure, consistent with literature data (e.g. Dickson et al. 2006; Espinoza and Santamarina 2010; Broseta et al. 2012; Shojai Kaveh et al., 2012, 2016; Chen et al, 2015; Iglauder et al., 2015a,b; Al-Yaseri et al. 2016a,b; Iglauder 2017). For example, at 25 MPa and 323 K (50 °C), for the quartz surface aged in 10⁻¹⁰ M hexanoic acid, θ_a was 58° and θ_r was 55° implying that the quartz surface is weakly water-wet under such conditions. With an increase in hexanoic acid concentration up to 10⁻⁶ M, there was an insignificant change in θ . However, further organic acid concentration increase resulted in significant contact angle increase. For instance, when the hexanoic acid concentration increased to 10⁻² M, at the same temperature and pressure (25 MPa, and 323 K (50 °C)), θ_a and θ_r increased to 87° and 82°, implying a wettability transformation from weakly water-wet to

intermediate-wet. Such a reduction in water wettability of the surface potentially leads to a reduction in residual trapping capacities where CO₂ plume is migrating in storage formation (Chaudhary et al., 2013; Iglauder et al., 2017; Al-Menhali et al., 2016a; Rahman et al., 2016). Note for instance that lower residual CO₂ saturations have been measured in more hydrophobic rock by x-ray micro-tomography (Al-Menhali et al., 2016a, Chaudhary et al., 2013, Rahman et al., 2016).

Lauric acid followed somewhat similar trends. For the quartz surface aged in 10⁻¹⁰ M lauric acid, quartz/CO₂/water contact angles were significantly lower than those measured on surfaces aged in 10⁻² M lauric acid. Thus higher organic concentrations render the surface more non-wetting to water. For example, at 25 MPa and 323 K (50 °C), for the quartz surface aged in 10⁻¹⁰ M lauric acid, θ_a measured as 61° and θ_r as 56°, which increased to $\theta_a = 89^\circ$ and $\theta_r = 84^\circ$ when lauric acid concentration increased to 10⁻² M (Figure 3).

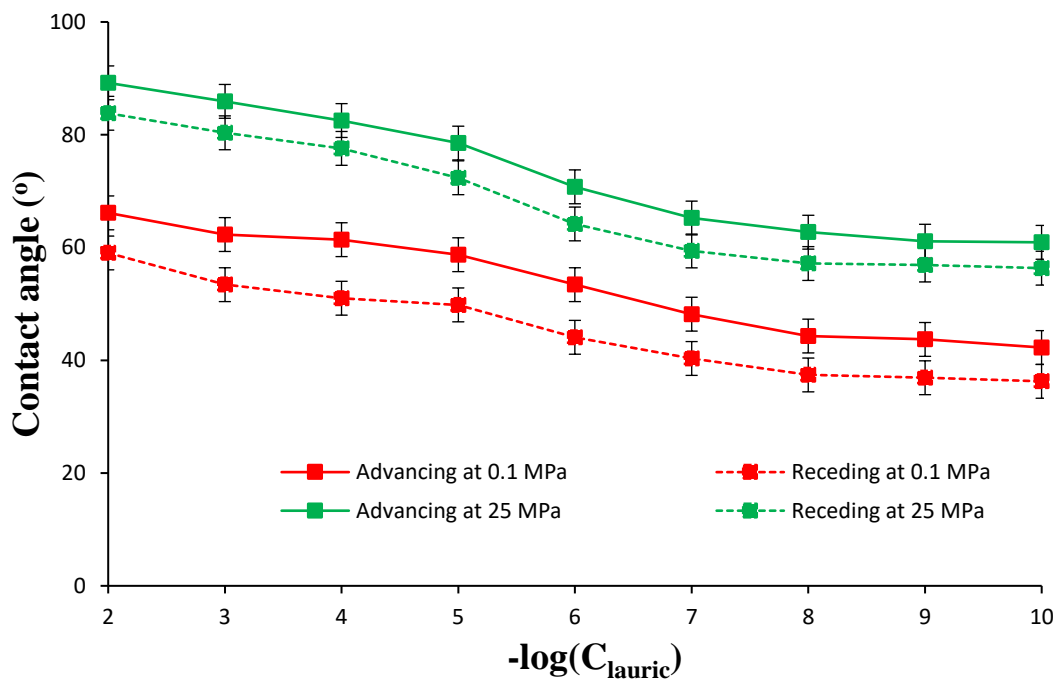


Figure 3. Quartz/CO₂/brine contact angles as a function of lauric acid (C₁₂) concentration; C_{lauric} is the lauric acid concentration (molarity). Solid lines: advancing; dotted lines: receding. Red: ambient pressure; green: 25 MPa and 323 K (50 °C).

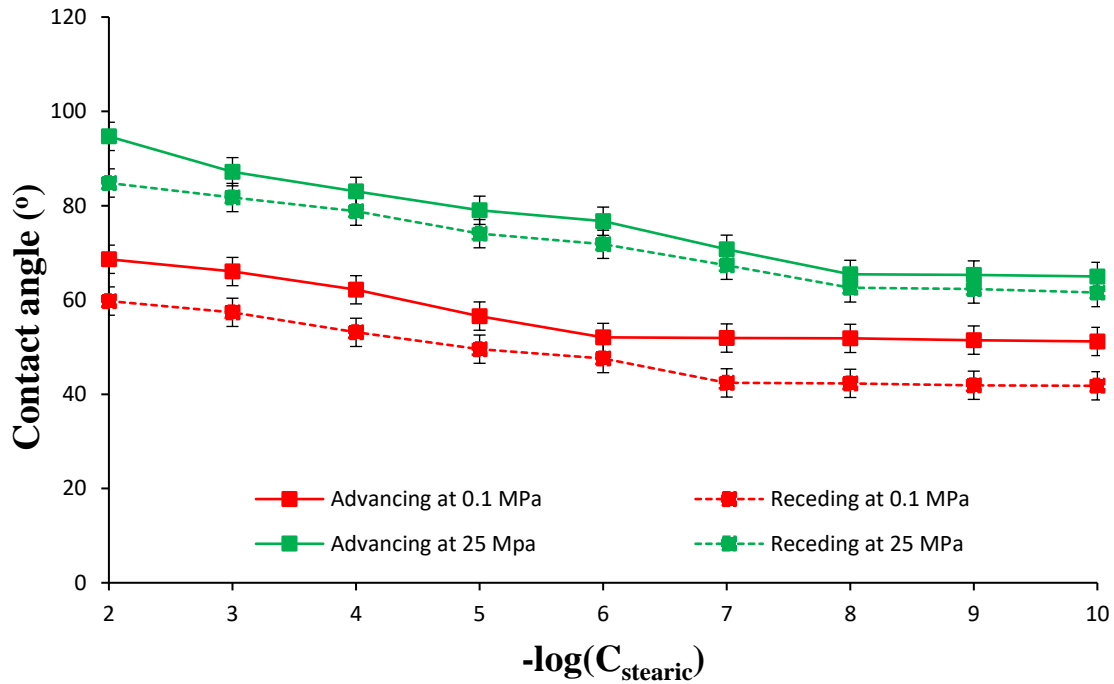


Figure 4. Quartz/CO₂/brine contact angles as a function of stearic acid (C₁₈) concentration; C_{stearic} is the stearic acid concentration (molarity). Solid lines: advancing; dotted lines: receding. Red: ambient pressure; green: 25 MPa and 323 K (50 °C).

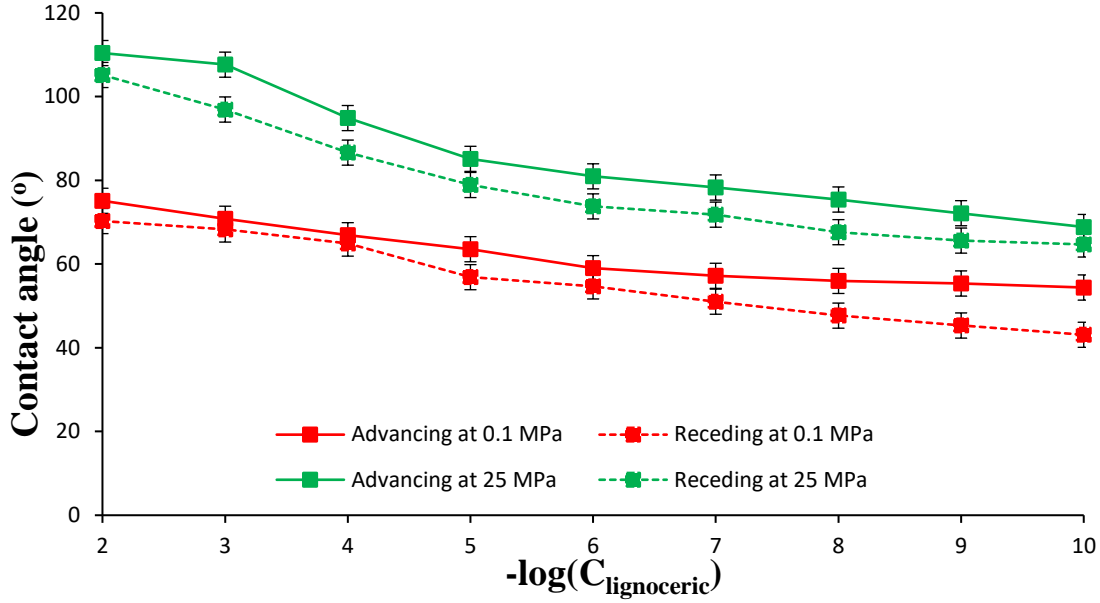


Figure 5. Quartz/CO₂/brine contact angles as a function of lignoceric acid (C₂₄) concentration; C_{lignoceric} is the lignoceric acid concentration (molarity). Solid lines: advancing; dotted lines: receding. Red: ambient pressure; green: 25 MPa and 323 K (50 °C).

The results showed the same trend for quartz surfaces aged in stearic acid and lignoceric acid (Figures 4 and 5). In summary, the higher the organic acid concentration was, the higher were the values of both the advancing and receding water contact angles irrespective of the type of organic acid used for aging. Our results are consistent with literature data on wettability of calcite/oil/brine systems in the presence of organic acids (Hansen et al., 2000; Standness and Austad, 2003; Gomari et al., 2006). Mechanistically, carboxylic acid adsorbs onto the quartz surface leading to a wettability modification towards less water-wet surface conditions, see above.

When compared with CO₂-wettability of pure quartz surfaces, we find that higher contact angles are found, even at the lowest organic acid concentration (10⁻¹⁰ M, which is very low). For instance, for pure quartz/CO₂/brine system, at 20 MPa and 323 K (50 °C), θ_a was reported to be approximately 40° (Sarmadivaleh et al., 2015), whereas the lowest θ_a in the presence of

lowest chain organic acid (Hexanoic acid, C_6) was 57° (Figure 6). It is thus clear that even minute amounts of organic acid significantly increase the CO_2 -wettability of mineral surfaces. As such minute concentrations always exist in the subsurface, even in aquifers (Bennett et al., 1993; Jones et al., 2008; Stalker et al. 2013), lower residual trapping capacities than previously thought are expected (Ali et al., 2019).

3.2 Influence of organic acid alkyl chain length on quartz wettability

It is clear that all organic acids influence the quartz wettability in a similar fashion i.e. both water advancing and receding contact angles increase with an increase in organic acid concentration and quartz rapidly loses its water-wetness, Figure 6. However, at a fixed organic acid concentration, the absolute values of contact angles were different for different acids (which differ in their alkyl chain length and their coverage on the quartz surface, as showed in Figure 6); surfaces aged in hexanoic acid (C_6) exhibited the lowest contact angles values, while surfaces aged in lignoceric acid (C_{24}) exhibited the highest contact angles values. Lauric acid and stearic acid fell in between. For instance, at 25 MPa and 323 K ($50^\circ C$), and a fixed organic concentration 10^{-2} M of hexanoic, lauric, stearic and lignoceric acid, $\theta_r = 81^\circ$, $\theta_r = 84^\circ$, $\theta_r = 85^\circ$ and $\theta_r = 105^\circ$, respectively. Such a wettability transformation from intermediate-wet to CO_2 -wet is attributed to the number of carbon atoms present in the acid, Table 1. Clearly, longer alkyl chains in the organic acid renders the surface more hydrophobic.

These effects have dramatic impact on the optimal residual trapping limit, which we consider here as the point where primary drainage is unaffected by wettability, i.e. at $\theta_a = 50^\circ$ (Morrow 1970, Morrow 1976). For example, at 25 MPa and 323 K ($50^\circ C$) and a fixed trace organic concentration of 10^{-10} M, $\theta_a > 50^\circ$ for all acids (note that this is a very minute concentration, and much higher organic concentrations were measured in deep saline aquifers (e.g. Thurman

1985; Jardine et al., 1989; Madsen and Ida, 1998; Kharaka et al., 2009; Stalker et al. 2013; Yang et al., 2015)); Figure 6.

Overall it is clear that a detailed knowledge of organic acids and its relative concentrations in storage formations is very important for assessing the feasibility of long-term geological storage projects.

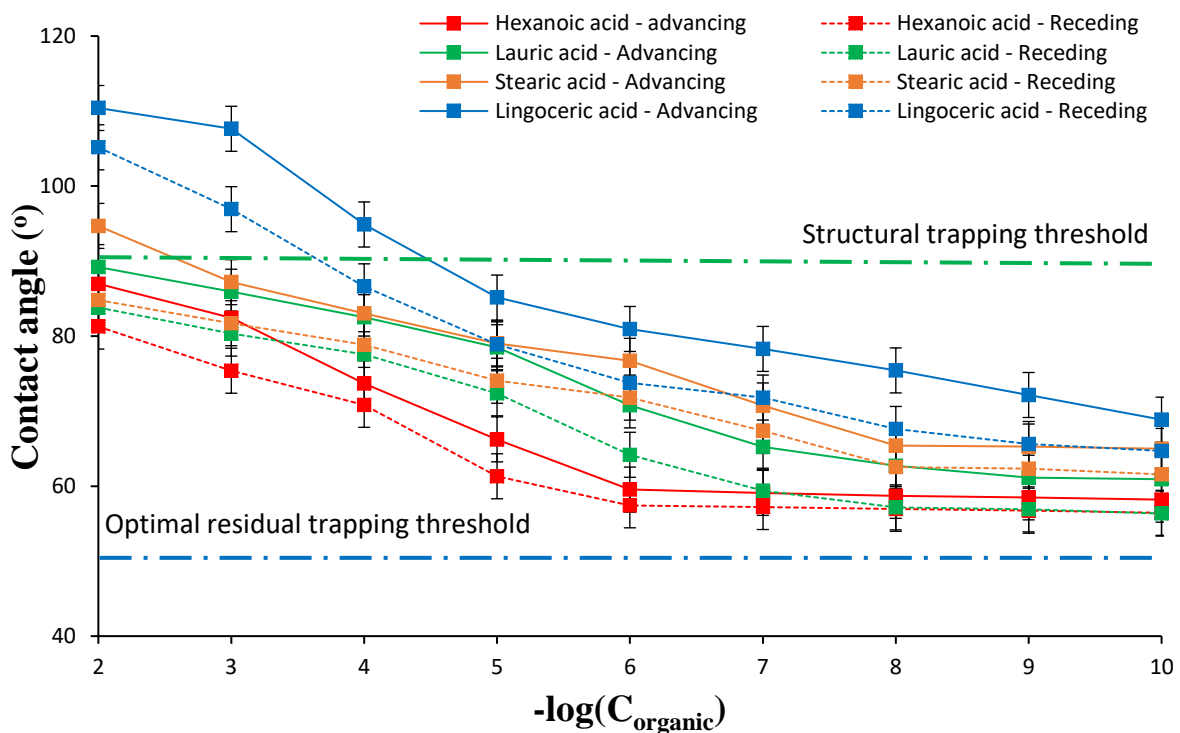


Figure 6. Quartz/CO₂/brine contact angles as a function of organic acid concentration and alkyl chain length at 25 MPa and 323 K (50 °C); C_{organic} is the organic acid concentration (molarity).

Dotted blue horizontal lines in the graph define the capillary trapping threshold ($\theta = 50^\circ$), and dotted green horizontal lines in graph define the structural trapping ($\theta > 90^\circ$) threshold.

4. Conclusions

Deep saline aquifers contain organic acids, which have a direct impact on the interfacial phenomena at the fluid/rock interface due to chemisorption. These effects are, however, only poorly understood; thus we measured the wettability of quartz/CO₂/brine systems in the presence of various organic acids. Four acids (hexanoic acid, lauric acid, stearic acid, lignoceric acid) were considered for a wide range of concentrations (10^{-9} M to 10^{-2} M), and advancing and receding contact angles were measured at typical storage conditions (25 MPa and 323 K (50 °C), as well as at ambient pressure) in order to mimic a realistic subsurface behaviour. We found that both advancing and receding contact angles increased with an increase in organic acid concentration throughout the tested experimental matrix. In addition, at a fixed organic acid concentration, the highest contact angles values were measured for lignoceric acid (C24), while relatively least values were recorded for hexanoic acid (C6). This behaviour is attributed to the number of carbon atoms in the organic acids alkyl chain, and hence a higher number of C atoms, resulting in more CO₂-wet/hydrophobic surfaces, which causes a reduction in residual trapping capacities.

We thus conclude that CO₂ geological storage capacities in certain geological scenarios (aquifers as an example) may be lower than previously thought. Reservoir-scale models thus need to take these effects into account so that accurate storage predictions are obtained thus de-risking carbon geological storage (CGS) projects.

Conflicts of Interest

There are no conflicts to declare.

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References

- A. W. Adamson, & A. P. Gast, Physical Chemistry of Surfaces, 6th ed., Wiley-Interscience, N. Y, 1997.
- Agartan, E., Trevisan, L., Cihan, A., Birkholzer, J., Zhou, Q., & Illangasekare, T. H. (2015). Experimental study on effects of geologic heterogeneity in enhancing dissolution trapping of supercritical CO₂. *Water Resources Research*, 51(3), 1635-1648, doi: 10.1002/2014WR015778
- Akbarabadi, M., & Piri, M. (2015). Co-sequestration of SO₂ with supercritical CO₂ in carbonates: An experimental study of capillary trapping, relative permeability, and capillary pressure. *Advances in water resources*, 77, 44-5, doi: 10.1016/j.advwatres.2014.08.011
- Al-Anssari, S., Barifcani, A., Wang, S., Lebedev, M., & Iglauer, S. (2016). Wettability alteration of oil-wet carbonate by silica nanofluid. *Journal of Colloid and Interface Science*, 461, 435-442. doi:http://dx.doi.org/10.1016/j.jcis.2015.09.051
- Al-Anssari, S., Arif, M., Wang, S., Barifcani, A., Lebedev, M., & Iglauer, S. (2018). Wettability of nanofluid-modified oil-wet calcite at reservoir conditions. *Fuel*, 211, 405-414. doi:https://doi.org/10.1016/j.fuel.2017.08.111
- Al-Khdheawi, E. A., Vialle, S., Barifcani, A., Sarmadivaleh, M., & Iglauer, S. (2016). Influence of CO₂-wettability on CO₂ migration and trapping capacity in deep saline aquifers. *Greenhouse Gases: Science and Technology*, 7(2), 328-338, doi: 10.1002/ghg.1648
- Al-Khdheawi, E. A., Vialle, S., Barifcani, A., Sarmadivaleh, M., & Iglauer, S. (2017). Impact of reservoir wettability and heterogeneity on CO₂-plume migration and trapping capacity. *International Journal of Greenhouse Gas Control*, 58, 142-158, doi: 10.1016/j.ijggc.2017.01.012
- Al-Menhali, A. S., Menke, H. P., Blunt, M. J., & Krevor, S. C. (2016a). Pore Scale Observations of Trapped CO₂ in Mixed-Wet Carbonate Rock: Applications to Storage in Oil Fields. *Environmental Science & Technology*, 50(18), 10282-10290, doi: 10.1021/acs.est.6b03111
- Al-Menhali, A. S., & Krevor, S. (2016b). Capillary trapping of CO₂ in oil reservoirs: Observations in a mixed-wet carbonate rock. *Environmental science & technology*, 50(5), 2727-2734, doi: 10.1021/acs.est.5b05925
- Al-Yaseri, A. Z., Lebedev, M., Barifcani, A., & Iglauer, S. (2016a). Receding and advancing (CO₂+ brine+ quartz) contact angles as a function of pressure, temperature, surface roughness, salt type and salinity. *The Journal of Chemical Thermodynamics*, 93, 416-423, doi: 10.1016/j.jct.2015.07.031
- Al-Yaseri, A. Z., Roshan, H., Lebedev, M., Barifcani, A., & Iglauer, S. (2016b). Dependence of quartz wettability on fluid density. *Geophysical Research Letters*, 43(8), 3771-3776, doi: 10.1002/2016GL068278
- Ali, M., Al-Anssari, S., Arif, M., Barifcani, A., Sarmadivaleh, M., Stalker, L., . . . Iglauer, S. (2019). Organic acid concentration thresholds for ageing of carbonate minerals: Implications for CO₂ trapping/storage. *Journal of Colloid and Interface Science*, 534, 88-94. doi:https://doi.org/10.1016/j.jcis.2018.08.106
- Amaya, J., Rana, D., & Hornof, V. (2002). Dynamic interfacial tension behavior of water/oil systems containing in situ-formed surfactants. *Journal of Solution Chemistry*, 31(2), 139-148, doi: 10.1023/A:1015201119955
- Anderson, W. G. (1986). Wettability Literature Survey. 3. The Effects of Wettability on the Electrical-Properties of Porous-Media. *Journal of Petroleum Technology*, 38(13), 1371-1378, doi: 10.2118/13934-PA
- Arif, M., Al-Yaseri, A. Z., Barifcani, A., Lebedev, M., & Iglauer, S. (2016a). Impact of pressure and temperature on CO₂-brine-mica contact angles and CO₂-brine interfacial tension: Implications for carbon geo-sequestration. *Journal of colloid and interface science*, 462, 208-215, doi: 10.1016/j.jcis.2015.09.076
- Arif, M., Barifcani, A., Lebedev, M., & Iglauer, S. (2016b). Structural trapping capacity of oil-wet caprock as a function of pressure, temperature and salinity. *International Journal of Greenhouse Gas Control*, 50, 112-120, doi: 10.1016/j.ijggc.2016.04.024

- Arif, M., Barifcani, A., & Iglauder, S. (2016)c. Solid/CO₂ and solid/water interfacial tensions as a function of pressure, temperature, salinity and mineral type: Implications for CO₂-wettability and CO₂ geo-storage. *International Journal of Greenhouse Gas Control*, 53, 263-273, doi: 10.1016/j.ijggc.2016.08.020
- Arif, M., Barifcani, A., & Iglauder, S. (2016)d. Solid/CO₂ and solid/water interfacial tensions as a function of pressure, temperature, salinity and mineral type: Implications for CO₂-wettability and CO₂ geo-storage. *International Journal of Greenhouse Gas Control*, 53, 263-273, doi: 10.1016/j.ijggc.2016.08.020
- Arif, M., Lebedev, M., Barifcani, A., & Iglauder, S. (2017)a. CO₂ storage in carbonates: Wettability of calcite. *International Journal of Greenhouse Gas Control*, 62, 113-121, doi: 10.1016/j.ijggc.2017.04.014
- Arif, M., Lebedev, M., Barifcani, A., & Iglauder, S. (2017)b. Influence of shale-total organic content on CO₂ geo-storage potential. *Geophysical Research Letters*, doi: 10.1002/2017GL073532
- Bennett, P. C., Siegel, D. E., Baedeker, M. J., & Hult, M. F. (1993). Crude oil in a shallow sand and gravel aquifer—I. Hydrogeology and inorganic geochemistry. *Applied Geochemistry*, 8(6), 529-549, doi: 10.1016/0883-2927(93)90012-6
- Bikkina, P. K. (2011). Contact angle measurements of CO₂–water–quartz/calcite systems in the perspective of carbon sequestration. *International Journal of Greenhouse Gas Control*, 5(5), 1259-1271, doi: 10.1016/j.ijggc.2011.07.001
- Birkholzer, J. T., Zhou, Q., & Tsang, C. F. (2009). Large-scale impact of CO₂ storage in deep saline aquifers: a sensitivity study on pressure response in stratified systems. *International Journal of Greenhouse Gas Control*, 3(2), 181-194, doi: 10.1016/j.ijggc.2008.08.002
- Blunt, M., Fayers, F. J., & Orr Jr, F. M. (1993). Carbon dioxide in enhanced oil recovery. *Energy Conversion and Management*, 34(9-11), 1197-1204, doi: 10.1016/0196-8904(93)90069-M
- Broseta, D., Tonnet, N., & Shah, V. (2012). Are rocks still water-wet in the presence of dense CO₂ or H₂S?. *Geofluids*, 12(4), 280-294, doi: 10.1111/j.1468-8123.2012.00369.x
- Busch, A., Alles, S., Gensterblum, Y., Prinz, D., Dewhurst, D. N., Raven, M. D., ... & Krooss, B. M. (2008). Carbon dioxide storage potential of shales. *International Journal of Greenhouse Gas Control*, 2(3), 297-308, doi: 10.1016/j.ijggc.2008.03.003
- Chaudhary, K., Bayani Cardenas, M., Wolfe, W. W., Maisano, J. A., Ketcham, R. A., & Bennett, P. C. (2013). Pore-scale trapping of supercritical CO₂ and the role of grain wettability and shape. *Geophysical Research Letters*, 40(15), 3878-3882, doi: 10.1002/grl.50658
- Chen, C., Wan, J., Li, W., & Song, Y. (2015). Water contact angles on quartz surfaces under supercritical CO₂ sequestration conditions: Experimental and molecular dynamics simulation studies. *International Journal of Greenhouse Gas Control*, 42, 655-665, doi: 10.1016/j.ijggc.2015.09.019
- Chiquet, P., Broseta, D., & Thibeau, S. (2007). Wettability alteration of caprock minerals by carbon dioxide. *Geofluids*, 7(2), 112-122, doi: 10.1111/j.1468-8123.2007.00168.x
- Davis, J. A. (1982). Adsorption of natural dissolved organic matter at the oxide/water interface. *Geochimica et Cosmochimica Acta*, 46(11), 2381-2393, doi: 10.1016/0016-7037(82)90209-5
- Dickson, J. L., Gupta, G., Horozov, T. S., Binks, B. P., & Johnston, K. P. (2006). Wetting phenomena at the CO₂/water/glass interface. *Langmuir*, 22(5), 2161-2170, doi: 10.1021/la0527238
- El-Maghraby, R. M., Pentland, C. H., Iglauder, S., & Blunt, M. J. (2012). A fast method to equilibrate carbon dioxide with brine at high pressure and elevated temperature including solubility measurements. *The Journal of Supercritical Fluids*, 62, 55-59, doi: 10.1016/j.supflu.2011.11.002
- Espinoza, D. N., & Santamarina, J. C. (2010). Water-CO₂-mineral systems: Interfacial tension, contact angle, and diffusion—Implications to CO₂ geological storage. *Water resources research*, 46(7), doi: 10.1029/2009WR008634

- Farokhpoor, R., Bjørkvik, B. J., Lindeberg, E., & Torsæter, O. (2013). Wettability behaviour of CO₂ at storage conditions. *International Journal of Greenhouse Gas Control*, 12, 18-25, doi: 10.1016/j.ijggc.2012.11.003
- Gaines, G. L. (1966). Insoluble monolayers at liquid-gas interfaces.
- Gaus, I. (2010). Role and impact of CO₂-rock interactions during CO₂ storage in sedimentary rocks. *International journal of greenhouse gas control*, 4(1), 73-89, doi: 10.1016/j.ijggc.2009.09.015
- Golding, S. D., Uysal, I. T., Boreham, C. J., Kirste, D., Baublys, K. A., & Esterle, J. S. (2011). Adsorption and mineral trapping dominate CO₂ storage in coal systems. *Energy Procedia*, 4, 3131-3138, doi: 10.1016/j.egypro.2011.02.227
- Gomari, K. R., & Hamouda, A. A. (2006). Effect of fatty acids, water composition and pH on the wettability alteration of calcite surface. *Journal of petroleum science and engineering*, 50(2), 140-150, doi: 10.1016/j.petrol.2005.10.007
- Grate, J. W., Dehoff, K. J., Warner, M. G., Pittman, J. W., Wietsma, T. W., Zhang, C., & Oostrom, M. (2012). Correlation of Oil-Water and Air-Water Contact Angles of Diverse Silanized Surfaces and Relationship to Fluid Interfacial Tensions. *Langmuir*, 28(18), 7182-7188. doi:10.1021/la204322k
- Hamouda, A. A., & Rezaei Gomari, K. A. (2006, January). Influence of temperature on wettability alteration of carbonate reservoirs. In *SPE/DOE Symposium on Improved Oil Recovery*. Society of Petroleum Engineers, doi: 10.2118/99848-MS
- Hansen, G., Hamouda, A. A., & Denoyel, R. (2000). The effect of pressure on contact angles and wettability in the mica/water/n-decane system and the calcite+ stearic acid/water/n-decane system. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 172(1), 7-16, doi: 10.1016/S0927-7757(99)00498-7
- Heshmati, M., & Piri, M. (2014). Experimental investigation of dynamic contact angle and capillary rise in tubes with circular and noncircular cross sections. *Langmuir*, 30(47), 14151-14162, doi: 10.1021/la501724y
- Hobeika, N., Bouriat, P., Touil, A., Broseta, D., Brown, R., & Dubessy, J. (2017). Help from a Hindrance: Using Astigmatism in Round Capillaries To Study Contact Angles and Wetting Layers. *Langmuir*, 33(21), 5179-5187. doi:10.1021/acs.langmuir.7b01025
- Hoeiland, S., Barth, T., Blokhus, A. M., & Skauge, A. (2001). The effect of crude oil acid fractions on wettability as studied by interfacial tension and contact angles. *Journal of Petroleum Science and Engineering*, 30(2), 91-103, doi: 10.1016/S0920-4105(01)00106-1
- Iglauer, S. (2017). CO₂-Water-Rock Wettability: Variability, Influencing Factors, and Implications for CO₂ Geostorage. *Accounts of Chemical Research*, doi: 10.1021/acs.accounts.6b00602
- Iglauer, S., Al-Yaseri, A. Z., Rezaee, R., & Lebedev, M. (2015)a. CO₂ wettability of caprocks: Implications for structural storage capacity and containment security. *Geophysical Research Letters*, 42(21), 9279-9284, doi: 10.1002/2015GL065787
- Iglauer, S., Pentland, C. H., & Busch, A. (2015)b. CO₂ wettability of seal and reservoir rocks and the implications for carbon geo-sequestration. *Water Resources Research*, 51(1), 729-774, doi: 10.1002/2014WR015553
- Iglauer, S., Salamah, A., Sarmadivaleh, M., Liu, K., & Phan, C. (2014). Contamination of silica surfaces: impact on water-CO₂-quartz and glass contact angle measurements. *International Journal of Greenhouse Gas Control*, 22, 325-328, doi: 10.1016/j.ijggc.2014.01.006
- Iglauer, S., Paluszny, A., Pentland, C. H., & Blunt, M. J. (2011)a. Residual CO₂ imaged with X-ray microtomography. *Geophysical Research Letters*, 38 (21), doi: 10.1029/2011GL049680
- Iglauer, S., Wüilling, W., Pentland, C. H., Al-Mansoori, S. K., & Blunt, M. J. (2011)b. Capillary-trapping capacity of sandstones and sandpacks. *SPE Journal*, 16(4), 778-783, doi: 10.2118/120960-PA

- Iglauer, S. (2011)c. Dissolution trapping of carbon dioxide in reservoir formation brine - a carbon storage mechanism. INTECH Open Access Publisher.
- Intergovernmental Panel on Climate Change (IPCC) (2005), IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change, edited by B. Metz et al., Cambridge Univ. Press, Cambridge, United Kingdom, and New York, USA
- Jardine, P. M., McCarthy, J. F., & Weber, N. L. (1989). Mechanisms of dissolved organic carbon adsorption on soil. *Soil Science Society of America Journal*, 53(5), 1378-1385, doi: 10.2136/sssaj1989.03615995005300050013x
- Ji, X., & Zhu, C. (2015). CO₂ storage in deep saline aquifers. Chapter 10 in *Novel Materials for Carbon Dioxide Mitigation Technology*, 299-332, doi: 10.1016/B978-0-444-63259-3.00010-0
- Jones, D. M., Head, I. M., Gray, N. D., Adams, J. J., Rowan, A. K., Aitken, C. M., ... & Oldenburg, T. (2008). Crude-oil biodegradation via methanogenesis in subsurface petroleum reservoirs. *Nature*, 451(7175), 176, doi: 10.1038/nature06484
- Juanes, R., MacMinn, C. W., & Szulczewski, M. L. (2010). The footprint of the CO₂ plume during carbon dioxide storage in saline aquifers: storage efficiency for capillary trapping at the basin scale. *Transport in Porous Media*, 82(1), 19-30, doi: 10.1007/s11242-009-9420-3
- Karoussi, O., Skovbjerg, L. L., Hassenkam, T., Stipp, S. S., & Hamouda, A. A. (2008). AFM study of calcite surface exposed to stearic and heptanoic acids. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 325(3), 107-114, doi: 10.1016/j.colsurfa.2008.04.039
- Kharaka, Y. K., Thordsen, J. J., Hovorka, S. D., Nance, H. S., Cole, D. R., Phelps, T. J., & Knauss, K. G. (2009). Potential environmental issues of CO₂ storage in deep saline aquifers: geochemical results from the Frio-I Brine Pilot test, Texas, USA. *Applied Geochemistry*, 24(6), 1106-1112, doi: 10.1016/j.apgeochem.2009.02.010
- Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., & Nico, P. S. (2015). Chapter one-mineral-organic associations: formation, properties, and relevance in soil environments. *Advances in agronomy*, 130, 1-140, doi: 10.1016/bs.agron.2014.10.005
- Krevor, S., Pini, R., Zuo, L., & Benson, S. M. (2012). Relative permeability and trapping of CO₂ and water in sandstone rocks at reservoir conditions. *Water Resources Research*, 48(2), doi: 10.1029/2011WR010859
- Kuhn, H., & Möbius, D. (1971). Systems of monomolecular layers—Assembling and physico-chemical behavior. *Angewandte Chemie International Edition*, 10(9), 620-637, doi: 10.1002/anie.197106201
- Lander, L. M., Siewierski, L. M., Brittain, W. J., & Vogler, E. A. (1993). A systematic comparison of contact angle methods. *Langmuir*, 9(8), 2237-2239, doi: 10.1021/la00032a055
- Legens, C., Toulhoat, H., Cuiec, L., Villieras, F., & Palermo, T. (1998, January). Wettability change related to the adsorption of organic acids on calcite: Experimental and ab initio computational studies. In *SPE Annual Technical Conference and Exhibition*. Society of Petroleum Engineers, doi: 10.2118/49319-MS
- Love, J. C., Estroff, L. A., Kriebel, J. K., Nuzzo, R. G., & Whitesides, G. M. (2005). Self-assembled monolayers of thiolates on metals as a form of nanotechnology. *Chemical reviews*, 105(4), 1103-1170, doi: 10.1021/cr0300789
- Maboudian, R., & Howe, R. T. (1997). Critical review: Adhesion in surface micromechanical structures. *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*, 15(1), 1-20, doi: 10.1116/1.589247
- Madsen, L., & Ida, L. (1998). Adsorption of carboxylic acids on reservoir minerals from organic and aqueous phase. *SPE Reservoir Evaluation & Engineering*, 1(01), 47-51, doi: 10.2118/37292-PA

- Mahadevan, J. (2012). Comments on the paper titled "Contact angle measurements of CO₂-water-quartz/calcite systems in the perspective of carbon sequestration": A case of contamination?. *International Journal of Greenhouse Gas Control*, 7, 261-262, doi: 10.1016/j.ijggc.2011.07.001
- Masalmeh, S. K. (2003). The effect of wettability heterogeneity on capillary pressure and relative permeability. *Journal of Petroleum Science and Engineering*, 39(3-4), 399-408, doi: 10.1016/S0920-4105(03)00078-0
- Meredith, W., Kelland, S. J., & Jones, D. M. (2000). Influence of biodegradation on crude oil acidity and carboxylic acid composition. *Organic Geochemistry*, 31(11), 1059-1073, doi: 10.1016/S0146-6380(00)00136-4
- Morrow, N. R. (1970). Physics and thermodynamics of capillary action in porous media. *Industrial & Engineering Chemistry*, 62(6), 32-56
- Morrow, N. R. (1976). Capillary pressure correlations for uniformly wetted porous media. *Journal of Canadian Petroleum Technology*, 15(04), doi: 10.2118/76-04-05
- Nordbotten, J. M., Celia, M. A., & Bachu, S. (2005). Injection and storage of CO₂ in deep saline aquifers: analytical solution for CO₂ plume evolution during injection. *Transport in Porous media*, 58(3), 339-360, doi: 10.1007/s11242-004-0670-9
- Ochs, M., Čosović, B., & Stumm, W. (1994). Coordinative and hydrophobic interaction of humic substances with hydrophilic Al₂O₃ and hydrophobic mercury surfaces. *Geochimica et Cosmochimica Acta*, 58(2), 639-650, doi: 10.1016/0016-7037(94)90494-4
- Orr, F. M. (2009). Onshore geologic storage of CO₂. *Science*, 325(5948), 1656-1658, doi: 10.1126/science.1175677
- Paterson, L., Boreham, C., Bunch, M., Ennis-King, J., Freifeld, B., Haese, R., ... & Stalker, L. (2011). The CO₂CRC Otway stage 2B residual saturation and dissolution test: test concept, implementation and data collected. Milestone Report to ANLEC.
- Pearce, J. K., Kirste, D. M., Dawson, G. K., Farquhar, S. M., Biddle, D., Golding, S. D., & Rudolph, V. (2015). SO₂ impurity impacts on experimental and simulated CO₂-water-reservoir rock reactions at carbon storage conditions. *Chemical Geology*, 399, 65-86, doi: 10.1016/j.chemgeo.2014.10.028
- Pentland, C. H., El-Maghraby, R., Georgiadis, A., Iglauer, S., & Blunt, M. J. (2011). Immiscible displacements and capillary trapping in CO₂ storage. *Energy Procedia*, 4, 4969-4976, doi: 10.1016/j.egypro.2011.02.467
- Rahman, T., Lebedev, M., Barifcani, A., & Iglauer, S. (2016). Residual trapping of supercritical CO₂ in oil-wet sandstone. *Journal of colloid and interface science*, 469, 63-68, doi: 10.1016/j.jcis.2016.02.020
- Sarmadivaleh, M., Al-Yaseri, A. Z., & Iglauer, S. (2015). Influence of temperature and pressure on quartz-water-CO₂ contact angle and CO₂-water interfacial tension. *Journal of Colloid and Interface Science*, 441, 59-64, doi: 10.1016/j.jcis.2014.11.010
- Shafrin, E. G., & Zisman, W. A. (1962). Effect of progressive fluorination of a fatty acid on the wettability of its adsorbed monolayer. *The Journal of Physical Chemistry*, 66(4), 740-748
- ShojaiKaveh, N., Wolf, K. H., Ashrafizadeh, S. N., & Rudolph, E. S. J. (2012). Effect of coal petrology and pressure on wetting properties of wet coal for CO₂ and flue gas storage. *International Journal of Greenhouse Gas Control*, 11, S91-S101, doi: 10.1016/j.ijggc.2012.09.009
- ShojaiKaveh, N., Barnhoorn, A., & Wolf, K. H. (2016). Wettability evaluation of silty shale caprocks for CO₂ storage. *International Journal of Greenhouse Gas Control*, 49, 425-435, doi: 10.1016/j.ijggc.2016.04.003
- Stalker, L., Varma, S., Van Gent, D., Haworth, J., & Sharma, S. (2013). South West Hub: a carbon capture and storage project. *Australian Journal of Earth Sciences*, 60(1), 45-58, doi: 10.1080/08120099.2013.756830

- Standnes, D. C., & Austad, T. (2003). Wettability alteration in carbonates: Interaction between cationic surfactant and carboxylates as a key factor in wettability alteration from oil-wet to water-wet conditions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 216(1), 243-259, doi: 10.1016/S0927-7757(02)00580-0
- Tabrizy, V. A., Denoyel, R., & Hamouda, A. A. (2011). Characterization of wettability alteration of calcite, quartz and kaolinite: Surface energy analysis. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 384(1), 98-108, doi: 10.1016/j.colsurfa.2011.03.021.
- Thurman E. M. (1985). *Organic geochemistry of natural waters*. Springer Netherlands, (pp. 151-180)
- Ulrich, H. J., Stumm, W., & Cosovic, B. (1988). Adsorption of aliphatic fatty acids on aquatic interfaces. Comparison between two model surfaces: the mercury electrode and δ - Al_2O_3 colloids. *Environmental science & technology*, 22(1), 37-41
- Wan, J., Tokunaga, T. K., Ashby, P. D., Kim, Y., Voltolini, M., Gilbert, B., & DePaolo, D. J. (2018). Supercritical CO_2 uptake by nonswelling phyllosilicates. *Proceedings of the National Academy of Sciences*, 201710853, doi: 10.1073/pnas.1710853114
- Wang, S., & Tokunaga, T. K. (2015). Capillary pressure–saturation relations for supercritical CO_2 and brine in limestone/dolomite sands: Implications for geologic carbon sequestration in carbonate reservoirs. *Environmental science & technology*, 49(12), 7208-7217, doi: 10.1021/acs.est.5b00826
- Watson, J. S., Jones, D. M., Swannell, R. P. J., & Van Duin, A. C. T. (2002). Formation of carboxylic acids during aerobic biodegradation of crude oil and evidence of microbial oxidation of hopanes. *Organic Geochemistry*, 33(10), 1153-1169, doi: 10.1016/S0146-6380(02)00086-4
- White, C. M., Strazisar, B. R., Granite, E. J., Hoffman, J. S., & Pennline, H. W. (2003). Separation and capture of CO_2 from large stationary sources and sequestration in geological formations—coalbeds and deep saline aquifers. *Journal of the Air & Waste Management Association*, 53(6), 645-715, doi: 10.1080/10473289.2003.10466206
- Yang, L., Xu, T., Wei, M., Feng, G., Wang, F., & Wang, K. (2015). Dissolution of arkose in dilute acetic acid solution under conditions relevant to burial diagenesis. *Applied Geochemistry*, 54, 65-73, doi: 10.1016/j.apgeochem.2015.01.007
- Zasadzinski J. A., Viswanathan R., Madsen L., Garnaes J., & Schwartz D. K. (1994). Langmuir-Blodgett films, *Science* (Washington, D.C.), 263, 1726 – 1733
- Zullig, J. J., & Morse, J. W. (1988). Interaction of organic acids with carbonate mineral surfaces in seawater and related solutions: I. Fatty acid adsorption. *Geochimica et Cosmochimica Acta*, 52(6), 1667-1678, doi: 10.1016/0016-7037(88)90235-9