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Influence of shale-total organic content on CO_2 geo-storage potential

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Key Points:

- Shale total organic content (TOC) scales with CO_2 wettability
- Low TOC shales are water-wet at storage conditions (good for structural trapping)
- Organic-rich shales are CO_2-wet at storage conditions (good for adsorption trapping)

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Abstract Shale CO_2 wettability is a key factor which determines the structural trapping capacity of a caprock. However, the influence of shale-total organic content (TOC) on wettability (and thus on storage potential) has not been evaluated despite the fact that naturally occurring shale formations can vary dramatically in TOC, and that even minute TOC strongly affects storage capacities and containment security. Thus, there is a serious lack of understanding in terms of how shale, with varying organic content, performs in a CO_2 geo-storage context. We demonstrate here that CO_2-wettability scales with shale-TOC at storage conditions, and we propose that if TOC is low, shale is suitable as a caprock in conventional structural trapping scenarios, while if TOC is ultrahigh to medium, the shale itself is suitable as a storage medium (via adsorption trapping after CO_2 injection through fractured horizontal wells).

1. Introduction

CO_2 geo-storage (CGS) in underground geological formations is considered to be a promising approach to reduce anthropogenic CO_2 emissions [*Intergovernmental Panel on Climate Change (IPCC)*, 2005; *Lackner*, 2003]. In CGS, structural CO_2 trapping is the principal storage mechanism whereby shale (in its classical caprock role), if strongly water-wet, provides an efficient seal to the reservoir disallowing upward CO_2 migration [*Arif et al.*, 2016a; *Armitage et al.*, 2013; *Chaudhary et al.*, 2015; *Iglauer et al.*, 2015a]. However, rock material can be even strongly CO_2-wet [*Arif et al.*, 2016b; *Iglauer et al.*, 2015a; *Iglauer*, 2017]—which would massively reduce storage capacity [*Al-Menhali et al.*, 2016; *Chaudhary et al.*, 2013; *Iglauer et al.*, 2015a, 2015b]—and shale wettability has so far only been reported for low-total organic content (TOC) shales [*Chaudhary et al.*, 2015; *Iglauer et al.*, 2015b; *Roshan et al.*, 2016; *Shojai Kaveh et al.*, 2016] despite the fact that shales can be very rich in organic carbon, i.e., high TOC [*Vernik and Milovac*, 2011].

Furthermore, recently, there is a mounting interest in utilizing shale as a CO_2 storage medium itself (whereby CO_2 is injected through fractured horizontal wells), where CO_2 is stored by adsorption trapping [*Fernø et al.*, 2015; *Li and Elsworth*, 2015; *Kim et al.*, 2017] with the benefit of producing additional methane [*Busch et al.*, 2008; *Kang et al.*, 2011; *Li and Elsworth*, 2015].

In both scenarios (caprock role and large CO_2 sink), shale wettability relates to CO_2 storage capacity and containment security [*Arif et al.*, 2016b; *Saghafi et al.*, 2014; *Shojai Kaveh et al.*, 2012; *Iglauer et al.*, 2015b]. However, there is a serious lack of understanding in terms of how shale organic content (TOC) influences wettability, even though it has been shown that even minute TOC strongly affects storage capacities and containment security [*Iglauer et al.*, 2015b].

Here we thus systematically analyzed a broad range of shale TOC (from 0.16 wt % to 23.4 wt %) at in situ storage conditions, and we demonstrate that shale TOC clearly scales with the CO_2-wettability: a high TOC content clearly led to strongly CO_2-wet conditions, while low TOC contents led to water-wet conditions, and medium TOC content was in between. We conclude that for the conventional caprock role, shale should have minimum TOC content to maximize storage capacity, while shale formations with a high TOC content are potentially suitable as large CO_2 sinks via CO_2 adsorption trapping.

2. Experimental Procedure

2.1. Materials

Four shale samples of low, medium, high, and ultrahigh TOC content were systematically analyzed; sample characteristics are summarized in Table 1. The samples were cut to cuboid shape (1 cm × 1 cm × 0.4 cm)

Table 1. Shale Sample Description, Characterization, and Mineralogy

Sample ID	Type of Shale	Location	TOC* (mg/kg)	Surface Roughness (nm)	Composition From XRD		Porosity Range (%)
					Mineral	wt %	
Shale A	Laminated shale (low TOC)	Little Falls, NY, USA	1,600 (0.16 wt %)	350	Quartz	37	0–18[a]
					Calcite	7	
					Albite	27	
					Microcline	4	
					Illite	24	
					Chlorite	1	
Shale B	Bituminous shale (medium TOC)	MT, USA	11,000 (1.1 wt %)	1,300	Quartz	17	3.5–8[b]
					Calcite	45	
					Ankerite	14	
					Albite	5	
					Pyrite	1	
					Illite	18	
Shale C	Oil shale (high TOC)	Garfield Co., CO, USA	117,000 (11.7 wt %)	770	Quartz	11	4.22–10.77[c]
					Calcite	16	
					Ankerite	38	
					Albite	18	
					Microcline	11	
					Pyrite	1	
					Illite	5	
Shale D	Oil shale ultrahigh TOC	Wessex Coast, southern England	234,000 (23.4 wt %)	290	Quartz	12	8–19.9[d]
					Calcite	28	
					Dolomite	28	
					Oligoclase	20	
					Microcline	4	
					Pyrite	1	
					Illite	7	

[a] *David et al.* [2004].
[b] *Manger* [1963].
[c] *Randolph* [1983].
[d] *Curtis et al.* [2012a].
[e] TOC was measured using high-temperature combustion and IR detection method at NMI, Australia.

with a diamond cutter. All the measurements were conducted using 1 M NaCl brine which was prepared by dissolving NaCl (purity ≥0.995 mass %) in deionized (DI) water (Ultrapure from David Gray; electrical conductivity = 0.02 mS/cm and de-gassed by vacuuming for 12 h). CO_2 used was 99.9 mol% (from BOC, gas code-082). Acetone (99.9 mol%, Rowe Scientific) was used to wash the sample surfaces.

2.2. Contact Angle Measurements

CO_2 wettability of the shale samples was measured with a pendant-drop tilted plate goniometric setup [*Lander et al.*, 1993]. The experimental configuration has been described elsewhere [*Arif et al.*, 2017]. Prior to each measurement, the samples were washed with acetone and then cleaned for 3 min using air plasma [*Iglauer et al.*, 2014; *Love et al.*, 2005].

The samples were then positioned inside the pressure cell on the tilted plate and the cell was heated to the desired temperature (323 K and 343 K). Subsequently, CO_2 pressure in the cell was raised to desired values (0.1 MPa, 5 MPa, 10 MPa, 15 MPa, and 20 MPa). The temperature of the cell was controlled by means of a wrapped heating tape. The fluids used were thermodynamically equilibrated with an equilibrium reactor (Parr 4848 reactor controller, John Morris Scientific [*El-Maghraby et al.*, 2012]). Note that CO_2 was in supercritical state at 10 MPa, 15 MPa, and 20 MPa, and in gaseous state at 0.1 MPa and 5 MPa. The surfaces used were dry, i.e., not presaturated with any fluid.

After pressure stabilization, a droplet of de-gassed brine was dispensed onto the substrate by a needle, and the advancing (θ_a) and receding (θ_r) water contact angles were measured simultaneously [*Lander et al.*, 1993] at the leading and trailing edge of the droplet, just before the droplet started to move. A high-resolution 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) was used to record movies of these whole processes, and θ_a and θ_r were measured on images extracted from the movie files. The standard deviation of the angle measurements was ±4°.

3. Results and Discussion

The influence of TOC on CO_2 wettability for the four shale samples (low, medium, high, and ultrahigh TOC shales) was comprehensively tested for a wide range of operating pressures (0.1–20 MPa) at 343 K; results are presented in Figure 1a as a 3-D plot. Moreover, the measurements were also conducted at a lower temperature 323 K (at pressures 15 MPa and 20 MPa) and are expressed in Figure 1b with few measurements at 343 K to allow a systematic evaluation of the temperature effect and a comparison with literature data (note that logarithmic *x* axis is used in Figure 1b in order to improve readability of the data in low-TOC range).

The shale/CO_2/brine system turned more CO_2-wet with increasing TOC, i.e., θ_a and θ_r, exhibited a clear increase with TOC throughout the tested experimental matrix (Figures 1a and 1b). A sharp increase in contact angle was observed when TOC increased from low to medium (i.e., 0.16 wt % to 1.1 wt %); however, with further TOC increase from high to ultrahigh (i.e., 11.7 wt % to 23.4 wt %), the corresponding increase dampened out. For instance, at 20 MPa and 343 K, θ_a increased from 78° to 125° and θ_r increased from 71° to 109° when sample TOC increased from 0.16 wt % to 1.1 wt % (low to medium), implying that the wettability of the system shifted from weakly water-wet to weakly CO_2-wet (refer to the classification by *Iglauer et al*. [2015a]). However, for the TOC increment from 11.7 wt % to 23.4 wt % (high to ultrahigh), at the same operating conditions (20 MPa and 343 K), θ_a only increased from 140° to 145° and θ_r increased from 130° to 134°; i.e., the system turned strongly CO_2-wet. Specifically, at any given operating pressure and temperature, the ultrahigh-TOC shale was found to be most nonwetting to water, while low-TOC shale was most water-wet. For instance, at 15 MPa and 343 K, θ_a measured 72°, 120°, 132°, and 142° and θ_r measured 63°, 104°, 123°, and 131° for the low, medium, high, and ultrahigh TOC shales, respectively. The results imply that low-TOC shale was weakly water-wet, medium-TOC shale was intermediate-wet, high-TOC shale was weakly CO_2-wet, and ultrahigh-TOC shale was strongly CO_2-wet at typical storage conditions. Similar trends are found for coal wettability; i.e., high-rank coal (anthracite/semianthracite) is strongly CO_2-wet, medium-rank coal (medium volatile bituminous) is weakly CO_2-wet, and low-rank coal (lignite) is weakly water-wet [cp. *Arif et al*., 2016c; *Shojai Kaveh et al*., 2012].

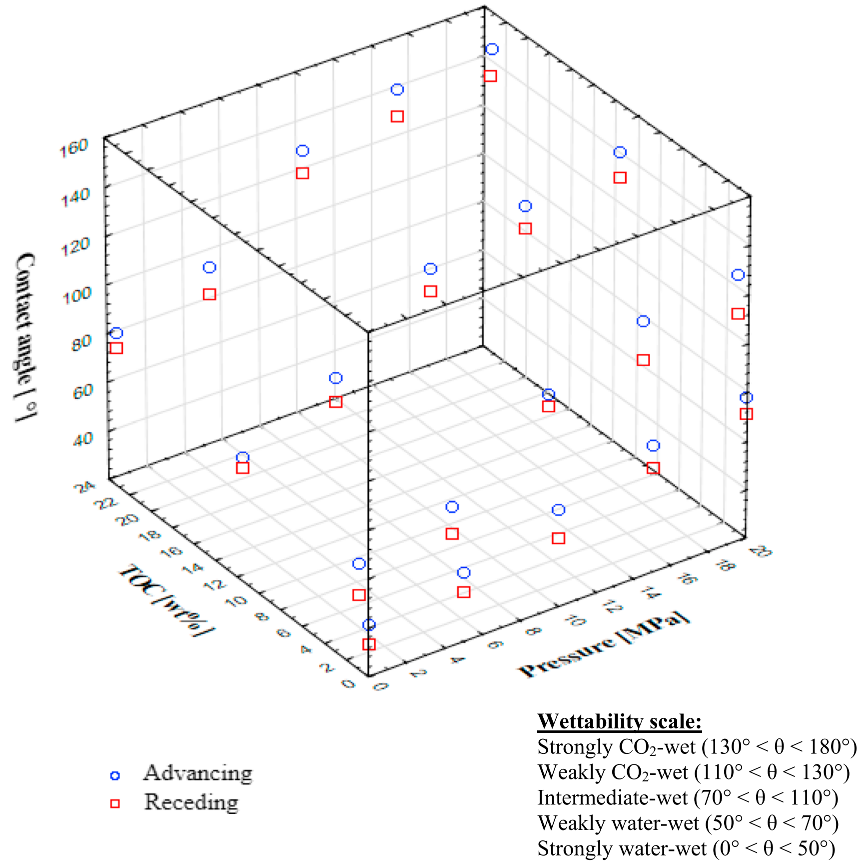
Further, an increase in pressure pronounced the effect of TOC on contact angle following a consistent trend at all pressures, suggesting that the influence of organic content on wettability depends on the formation depth. Overall, the measured contact angles followed a logarithmic variation with TOC and a linear variation with pressure. Consequently, the following fits described the relationship of advancing and receding water contact angles as a function of TOC and operating pressure (*P*) for the data presented in Figure 1a:

$$\theta_a = 54.33 + 3.14P + 25.4\,\log\mathrm{TOC} \tag{1}$$

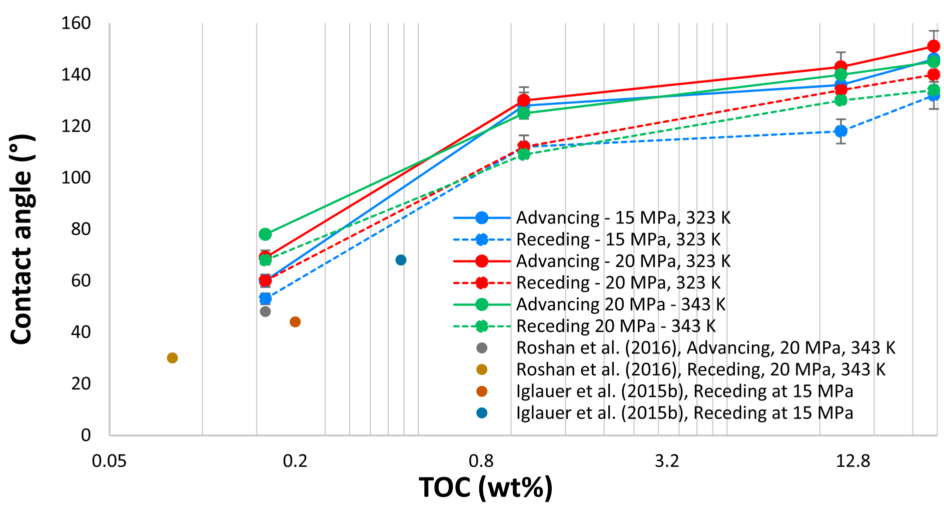
$$\theta_r = 46.025 + 2.98P + 25.67\log\mathrm{TOC} \tag{2}$$

In equations (1) and (2), TOC is in wt % and "*P*" is pressure in MPa, and these fits are based on data of four shales only. R^2 values for these multiple regression fits are 0.9135 for θ_a and 0.9215 for θ_r.

Mechanistically, shale pore networks comprise of (a) inorganic porosity (clay and nonclay minerals) and (b) organic matter porosity where the organic pores are hydrophobic while the inorganic pores are hydrophilic [*Curtis et al*., 2012b]. Thus, the composite wetting behavior of shale is controlled by the distribution and connectivity of organic and inorganic matter [*Hu et al*., 2016]. Consequently, the CO_2-wet nature of high-TOC samples (shales C and D) indicates that organic matter dominates the composite wetting behavior, while the water-wet behavior of low TOC shale indicates mineral dominance in pore spaces. The increase in contact angle with TOC can be attributed to the higher organic content of the shale sample, which leads to a more hydrophobic surface and surface de-wetting [cp. *Dickson et al*., 2006; *Arif et al*., 2016c; *Iglauer*, 2017]. Shale TOC can thus be regarded as a measure of the shale hydrophobicity in CO_2-water-shale systems, with high-TOC shale demonstrating more CO_2-wet behavior. Moreover, there is mounting evidence that shales become patchily oil-wet through in situ maturation of organic matter or exposure to organic compounds found in formation water [*Larter et al*., 1996].



a)



b)

Figure 1. Advancing and receding water contact angles of shale/CO_2/1 M NaCl brine systems as a function of TOC and operating pressure (at 343 K). (a) 3-D plot of contact angles versus TOC versus pressure and (b) 2-D plot of θ_a and θ_r as a function of TOC, also showing literature data (logarithmic *x* axis is used in Figure 1b in order to improve readability of the data in low-TOC range).

In addition, the increase in contact angle with pressure is also evident from previous work on low-TOC shales [*Iglauer et al*., 2015a; *Roshan et al*., 2016; *Shojai Kaveh et al*., 2016]. Physically, the increase in contact angle with pressure is attributed to a reduction in the solid/CO_2 interfacial tension with pressure which promotes de-wetting of the surface, resulting in higher water contact angles [*Arif et al*., 2016d] and an associated increase in CO_2-rock intermolecular interactions. Moreover, we found two distinct trends of wettability variation with temperature (Figure 1b). θ decreased with temperature for the medium, high, and ultrahigh-TOC shale samples, consistent with the reduction in CO_2 adsorption with increasing temperature [*Mosher et al*., 2013], while θ increased with temperature for the low-TOC sample consistent with *Iglauer et al*. [2015a] and *Roshan et al*. [2016]. We note that such distinct trends of shale wettability alteration with temperature are not clear so far and require further investigation.

4. Implications for CO_2 Geo-Storage

The shale wetting behavior can be related to the way shale is utilized in a storage project, as a function of shale-TOC.

Low-TOC shale, which is strongly water-wet to weakly water-wet at storage conditions, is suitable for its classical caprock role as the stronger capillary forces in water-wet pores can outbalance higher CO_2 buoyancy forces (i.e., higher CO_2 column heights [*Naylor et al*., 2011; *Iglauer et al*., 2015a; *Iglauer*, 2017]). Note that the reported data also imply that the capillary sealing efficiency will be higher at lower pressure, salinity, and temperature (due to lower θ [cp. *Arif et al.*, 2016a, 2017; *Iglauer et al*., 2015b; *Broseta et al*., 2012]).

On the contrary, if the caprock is an organic-rich shale (high TOC), a pertinent risk would entail to the containment security due to the CO_2-wet characteristics of these shales; i.e., negative capillary pressure will prevail under such conditions and thus leakage can occur. However, such shales (i.e., medium, high, and ultrahigh TOC) can potentially be utilized as storage media themselves; i.e., they are potentially large CO_2 sinks due to their high CO_2 wettability which eases CO_2 adsorption on the organic matter in such shales [*Arif et al*., 2016c; *Saghafi et al*., 2014; *Shojai Kaveh et al*., 2012] and thus significant CO_2 adsorption trapping. CO_2 injection into such organic-rich shales is coupled with the additional benefit of enhanced methane recovery [*Busch et al*., 2008; *Zhang et al*., 2012]. As soon as CO_2 wets the pore spaces, it expels methane to flow through the fracture network and get produced while CO_2 gets stored within the process [*Gray*, 1987; *Saghafi et al*., 2014]. In summary, the reported data provide a guideline for the optimum caprock and shale formation selection for CO_2 storage.

Practically, however, there are certain challenges associated with CO_2 injection and subsequent storage in shales. First is the limited injectivity due to the extremely low permeability, which is currently an active area of research [*Fernø et al*., 2015; *Kim et al*., 2017]. Although it has been shown that CO_2 flooding through fractured horizontal wells overcomes this limitation and is field tested as well [*Eshkalak et al*., 2014; *Kim et al*., 2017], yet the diffusion induced CO_2/CH_4 exchange and the subsequent CO_2 transport and accessibility of shale micropores need to be evaluated [*Busch et al*., 2016].

Shale matrix swelling by CO_2 injection is another limiting factor; however, sorption-induced shale swelling is not confirmed and not well understood [*Busch et al*., 2016], compared to coal swelling which is well established [*Brochard et al*., 2012].

5. Conclusions

CO_2 geological sequestration (CGS) is a promising technology to reduce anthropogenic greenhouse gas emissions [*Intergovernmental Panel on Climate Change*, 2005]. In CGS, caprock wettability characterization is essential to elucidate the conditions that lead to safe storage conditions [*Iglauer et al*., 2015a, 2015b; *Iglauer*, 2017]. Thus, shale CO_2 wettability as a function of TOC at in situ conditions was reported here to evaluate the effective role shale can offer during CO_2 geo-sequestration. Water contact angles increased with TOC. This increase was sharp up to ~1 wt % TOC and almost flattened out above ~11 wt % TOC for all conditions tested. Thus, at typical storage conditions (e.g., 20 MPa and 343 K), the higher the TOC was, the greater was the tendency of CO_2 to wet the shale; i.e., ultrahigh-TOC shale was strongly CO_2-wet, high-TOC shale was weakly CO_2-wet, medium-TOC shale was intermediate-wet, and low-TOC shale was water-wet.

We thus conclude that low-TOC shale is more suitable as a classical caprock as it can render larger CO_2 columns immobile in structural trapping due to its water-wet behavior [*Iglauer et al.*, 2015a, 2015b]. However, if TOC is above 1.1 wt %, the shale is CO_2-wet. Although such shale may not be suitable as caprock, it may provide a large CO_2 sink via adsorption trapping [*Busch et al.*, 2008; *Chareonsuppanimit et al.*, 2012; *Zhang et al.*, 2012; *Kim et al.*, 2017].

It is clear, however, that in all cases precise knowledge of shale TOC and the associated CO_2 wettability is vital for accurate storage capacity and containment security predictions.

While the CO_2-wet behavior of organic-rich shales measured here is encouraging for CO_2-adsorption trapping, the influence of shale swelling, diffusion-driven CO_2 transport, and hydraulic fracturing requirements need further investigation to develop an overall framework of CO_2 sequestration in organic-rich shales.

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