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CO_2 Wettability of Sandstones: Addressing Conflicting Capillary Behaviors

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Key Points:

- Drainage capillary pressure measurements were repeated on a Berea core untreated, fired and then exposed to supercritical CO2
- Firing the rock core does not impact the strongly water wetting state of the system
- No wettability alteration is observed after the Berea core is exposed to supercritical CO2 for a month

Supporting Information:

- Supporting Information S1

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Abstract Understanding the capillary and wetting behavior of supercritical CO_2 ($scCO_2$) and brine in reservoir rocks is crucial for reliable predictions of geologic carbon storage, as it strongly impacts CO_2 migration and residual trapping in the reservoir. The wetting state of such systems can be assessed through laboratory measurements of the capillary pressure characteristic curve. However, while some studies reported consistent scaling with strongly water wet systems, some others observed deviations from hydrophilic conditions. We present core-flooding drainage capillary pressure measurements using $scCO_2$/water and N_2/water on a Berea sandstone, untreated, then fired, and then exposed to $scCO_2$ for 28 days. The purpose is to investigate the impact of firing and longer exposure to $scCO_2$, two potential sources for variability in experimental observations, on capillarity and wettability. The results show excellent agreement among all the core-flooding capillary pressure data, suggesting no change in wetting state due to firing or longer exposure.

Plain Language Summary Carbon capture and storage is a promising technology to limit anthropogenic greenhouse gas emissions responsible for global warming. It consists in capturing CO_2 from large point source emitters and transporting it to a site where it will be injected in deep geological formations for storage. One important property of a rock in the presence of two nonmiscible fluids (here CO_2 and formation brine) is the preference of one fluid over another to be in contact with the rock's surface, a property called wettability. Wettability directly impacts the way injected CO_2 will flow in the subsurface and will stay trapped in the rock. However, although considerable effort has been made in the past decade to determine the wettability of storage rocks with respect to CO_2 and brine, there is considerable variability in the reported data. This study focuses on two particular factors that could lead to the differences in experimental observations: the preparation of the rock sample used for measurements and the duration of exposure to CO_2. We observed no change of wettability and general conditions favorable for CO_2 trapping in the studied rock, a sandstone.

1. Introduction

Residual trapping is an important mechanism for CO_2 immobilization in geological formations. Following active injection, the plume of supercritical CO_2 ($scCO_2$) migrates upward, leaving behind CO_2 bubbles trapped in the pore space during brine imbibition. This mechanism plays a major role in the long-term security of a carbon storage project, as it provides an additional form of CO_2 trapping in addition to the primary trapping mechanism that relies on the efficiency and integrity of a stratigraphic seal to stop the migration of buoyant $scCO_2$ (Benson & Cole, 2008). Residual trapping is strongly controlled by both capillary and wetting forces. Displacement and equilibrium processes that occur at the pore scale and govern residual trapping are strongly controlled by capillary pressure P_c, which is conventionally described through the characteristic capillary pressure curve relating P_c to the saturation of the wetting fluid, S_w. Wettability, which is quantified by the angle between the fluid/fluid/solid phases referred to as the contact angle, is an important property, as it is directly related to the capillary pressure by the Young-Laplace equation.

Conventional wisdom in carbon storage holds that reservoir rocks are strongly water wet for the CO_2-brine system and that significant residual trapping is then possible (Juanes et al., 2006; Kumar et al., 2005; Saadatpoor et al., 2010). However, when reviewing all the available observations of CO_2 wettability of reservoir rocks, it is clear that there is considerable uncertainty regarding the wetting state of CO_2/brine/rock systems (Iglauer et al., 2015). Of primary concern is the wide range of contact angles reported in the literature for the $scCO_2$/brine/quartz system, which were measured using classical contact angle measurements, micromodels observations, X-ray microtomography imaging, or molecular dynamic simulations. The high variability and uncertainty of contact angle measurements suggest that using one value of contact angle taken from the literature to predict capillary pressures in the reservoir may be prone to significant error. Another method to assess the CO_2 wettability of sandstones is to directly measure the characteristic capillary pressure curve P_c-S_w by conducting experiments on sandstone rocks or quartz sand packs using CO_2 and brine at the reservoir conditions and compare with other fluid pairs of known wetting properties. Again, the reported data do not show a unique trend, and different wetting behaviors are observed. In the one hand, Plug and Bruining (2007), Tokunaga et al. (2013), and Wang et al. (2016) reported sand-pack experiments with significant deviations from capillary scaling predictions for hydrophilic interactions that were explained by a change of wettability from water-wet to mixed-wet in the presence of $scCO_2$. Partial dewetting of silica surfaces was also reported during CO_2/brine contact angle measurements by Dickson et al. (2006) and Jung and Wan (2012) and during microfluidic experiments conducted by T. W. Kim et al. (2012). In addition, Chiquet et al. (2007), Espinoza and Santamarina (2010), Broseta et al. (2012), and Al-Yaseri et al. (2016) observed a significant effect of reservoir conditions (pressure, temperature, and salinity) on the wetting properties of the CO_2/brine/rock system. On the other hand, Pentland et al. (2011), Pini et al. (2012), and Pini and Benson (2013) performed core-flooding experiments on Berea sandstone rock cores that all showed predictable water-wet capillary scaling behavior indicating no changes of the water-wet conditions in the presence of $scCO_2$. Recent work by Al-Menhali et al. (2015) investigated the impact of pressure, temperature, and brine salinity on the capillarity and wetting properties of CO_2 and brine in Berea sandstone, and the authors observed that the wettability of the CO_2-brine-sandstone system was insensitive to reservoir conditions and that the system was strongly water wet and could be characterized by analog fluids. Evidence against wettability alteration is also shown by X-ray fluorescence measurements of stable thick brine films on smooth and rough silica surfaces under reservoir $scCO_2$ conditions (Y. Kim et al., 2012). These experiments were conducted at relatively high ionic strength, indicating that the commonly reported decreased wettability with increased salinity was not a strong influence.

The discrepancy observed in the few studies reporting $scCO_2$/water capillary pressure curves with reservoir conditions is still unclear and needs further investigation, as it has major implications for predicting CO_2 residual trapping. Among the causes that could explain the differences in experimental results is the preparation of the sample and more specifically the firing of rock cores, which consists in heating the cores in an oven at very high temperature for a certain time before using it for experiment, as was done by Pini et al. (2012), Pini and Benson (2013), and Al-Menhali et al. (2015). Firing rock cores has been a common preliminary step in core preparation mostly to ensure reproducibility by burning off organic matter, hence ensuring water-wet mineral surfaces, stabilizing clay mineral to avoid swelling and fines migration, or reducing eventual ion exchange reactions (Ma & Morrow, 1994). Wu and Firoozabadi (2011) reported a comprehensive study on the use of Berea, both untreated and fired, in single- and two-phase flows, however with a focus on how firing effects the efficiency of chemical treatments. In general, one could assume that firing of the rock core ensures water-wet conditions, in comparison with an untreated sample, resulting in the different capillary behaviors observed in fired Berea cores and untreated quartz sands. Another difference between the experimental results reported in the literature is the method used to determine the P_c-S_w curves, and in particular the duration of the experiment associated with the method: Whereas it usually takes few weeks to obtain a curve using the porous plate method, it only takes few days using the steady state core-flooding method. One can hypothesize that the anomalous capillary behavior observed using the porous plate method (Tokunaga et al., 2013; Wang et al., 2016) only occurs when the sample is exposed to $scCO_2$ for a prolonged period of time.

The objective of this work is to investigate the effect of firing rock cores and longer exposure to $scCO_2$ on the capillary and wetting behavior of the scCO2/water/sandstone system by repeating measurements of the $scCO_2$/water drainage capillary pressure characteristic curve in a Berea sandstone (i) untreated, (ii) fired, and (iii) exposed to $scCO_2$ for 28 days. Experiments were also performed using N_2 and water in order to compare with a system that is known to be strongly water wet.

Table 1
Characteristics of the Experiments Conducted on the Berea Rock Core and Properties of the Fluids at the Experimental Conditions (9 MPa, 50 °C)

Experiments	B1	B2	BF1	BF2	BE
Berea core treatment	Untreated	Untreated	Fired	Fired	Exposed
Fluid pair	N_2/H_2O	$scCO_2/H_2O$	N_2/H_2O	$scCO_2/H_2O$	$scCO_2/H_2O$
Fluids	N_2	$scCO_2$	H_2O		
Density, ρ (kg/m^3)	92.6	285	992		
Viscosity, μ (10^5 Pa/s)	2.05	2.31	54.8		
IFT, γ (mN/m)[a]	64	34	—		

[a] Chow et al. (2016).

2. Materials and Methods

2.1. Rock Sample, Fluids, and Experimental Conditions

All experiments were conducted on a same cylindrical rock sample of 5-cm diameter and 11.7-cm long cored in a Berea sandstone with bedding planes parallel to the flow. An average porosity of 0.163 was measured at the beginning of the first experiment conducted on the untreated Berea rock core using X-ray CT scans of the dry and water-saturated sample (Perrin & Benson, 2010), and a permeability of 32 mD was measured once the sample was saturated with water, before starting the first drainage experiment. Measurements of the grain density of the rock, ρ_g, and Mercury Intrusion Capillary Pressure (MICP) curve were also conducted on ~1-cm^3 sister samples (untreated and fired Berea) and sample drilled in the core after the last experiment (exposed to $scCO_2$) using a Helium pycnometer Micromeritics AccuPycII 1340 and a Micromeritics Autopore IV, respectively. After a set of two flow experiments, B1 and B2, the original core was fired at 700 °C for 4 hr, and a set of two additional flow experiments, BF1 and BF2, was conducted on the fired core. Two fluid pairs were used for the experiments: nitrogen and water (experiments B1 and BF1) and $scCO_2$ and water (experiments B2 and BF2). The rock core was then exposed to $scCO_2$ for 28 days by continuously flowing $scCO_2$ through the core at a low flow rate of 0.01 ml/min, and a last flow experiment, BE, was conducted using $scCO_2$ and water on the fired then exposed rock core. Before each experiment the core was vacuum dried at 50 °C for at least 24 hr. The entire sequence of experiments is summarized in Table 1. All flow experiments were conducted at 9 MPa and 50 °C, with a confining pressure of 10.3 MPa. The properties of the fluids at these conditions of pressure and temperature are listed in Table 1. The values of interfacial tension of 64 and 34 mN/m, for ($N_2 + H_2O$) and ($CO_2 + H_2O$), respectively, were calculated using correlations proposed by Chow et al. (2016).

2.2. Experimental Procedure

The drainage capillary pressure experiments were performed in a core-flooding setup detailed in Perrin and Benson (2010). For each experiment, the core was first fully saturated with water pre-equilibrated with the nonwetting phase (N_2 or $scCO_2$). Then the nonwetting phase, also pre-equilibrated with water, was injected for at least 5 pore volumes at constant flow rates, Q, ranging from 0.3 to 33 ml/min for the drainage experiments using N_2 and from 0.9 to 95 ml/min for the drainage experiments using $scCO_2$. In each case, capillary forces should dominate over viscous forces: Capillary numbers $N_C = Q\mu/A\gamma$, where A is the sample cross section, range between 9×10^{-10} and 9×10^{-8} for N_2/H_2O experiments and between 6×10^{-9} and 6×10^{-7} for $scCO_2/H_2O$ experiments. Increasing flow rates lead to increasing nonwetting phase saturations, measured using X-ray CT scans of the core, and for each flow rate we can measure the pressure drop across the core at steady state, which corresponds to the capillary pressure, P_c, at the inlet face of the core, as explained in Pini et al. (2012). A capillary pressure curve can then be constructed by associating each pressure drop measurement with the corresponding saturation computed at the inlet slice of the core. More details on the method and procedure can be found in Pini et al. (2012).

2.3. Core-Flooding Data Analysis

The core-flooding capillary pressure data obtained using the representative fluids can be compared to the MICP data converted from the mercury/air system to the system of interest (N_2/water or $scCO_2$/water) using the following equation:

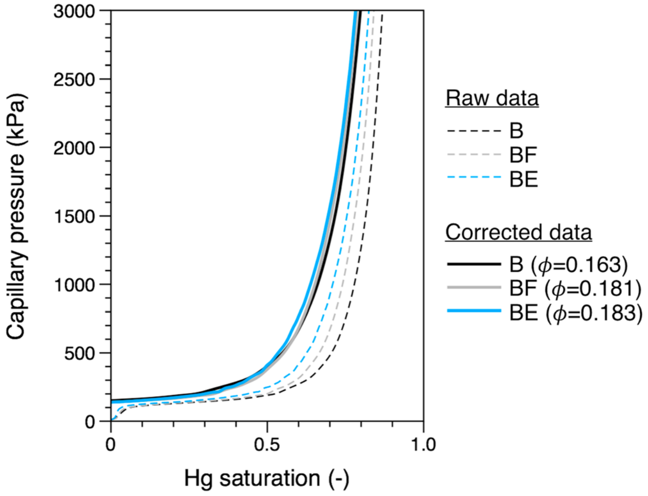

Figure 1. Mercury Intrusion Capillary Pressure curves measured on samples extracted from the Berea sandstone untreated (B), fired (BF), and then exposed to $scCO_2$ (BE): raw (dashed lines) and corrected (solid lines) data. The porosity value, ϕ, used to correct the raw data is given for each sample.

$$P_{c,i} = \frac{\gamma_i \cdot \cos\theta_i}{\gamma_{Hg} \cdot \cos\theta_{Hg}} \cdot P_{c,Hg}, \tag{1}$$

where $P_{c,\ i}$, γ_i, and θ_i are the capillary pressure, interfacial tension, and contact angle measured in the wetting phase for the i/water system (i referring to either N_2 or $scCO_2$) and $P_{c,\ Hg}$, γ_{Hg}, and θ_{Hg} are the capillary pressure, interfacial tension, and contact angle for the mercury/air system, respectively. The interfacial tensions γ_i at the experimental conditions are given in Table 1, γ_{Hg} and θ_{Hg} are assumed to be 485 mN/m and 140°, respectively, and θ_i is used as a fitting parameter.

Differences in wetting state for systems consisting of the same rock but different fluid pairs can be assessed by dividing the core-flooding capillary pressures by the appropriate value of interfacial tension. A good scaling of the data suggests that the contact angles of the two systems are similar (equation (1)). The N_2/water drainage experiments (B1/BF1) were performed in order to compare the $scCO_2$/water data (B2 and BF2) with a system known as strongly water wet in Berea sandstone using this approach.

The Brooks-Corey model, equation (2), is often used to describe drainage capillary pressure-saturation data,

$$P_c = P_e \cdot \left(\frac{S_w - S_{wirr}}{1 - S_{wirr}}\right)^{-1/\lambda}, \tag{2}$$

where P_e is the capillary entry pressure, S_{wirr} is the irreducible water saturation, and λ is a parameter reflecting the pore size distribution (Brooks & Corey, 1964).

3. Results and Discussion

3.1. MICP Curves

The mercury intrusion curves obtained for the untreated (B), fired (BF), and fired-exposed to $scCO_2$ (BE) samples are presented in Figure 1. The final curves (solid lines) were obtained by adjusting the raw data (dashed lines) using measurements of the sample grain density, ρ_g (2.676, 2.661, and 2.658 g/cm^3 for B, BF, and BE, respectively), and porosity, ϕ (0.163, 0.181, 0.183 for B, BF, and BE, respectively), to account for unresolved pore space and entry pressure effects (Pini & Benson, 2013). The porosity values for samples B and BF were taken as the mean porosity of the rock core used in the experiments computed using X-ray CT scans for experiments B1 and BF1. The data analysis shows indeed that the porosity of the Berea core is homogeneous (standard deviation of 0.001 for B1 and of 0.002 for BF1), validating use of the mean porosity for the sister samples used in the MICP tests. For sample BE, porosity was calculated using the voxels where the actual sample was drilled after experiment instead of taking the core-average value. The results suggest similar mercury/air drainage behavior for all tested samples. Assuming that analog fluids can be used to characterize the CO_2-water-sandstone system, as observed in previous studies (Al Menhali et al., 2015; Pentland et al., 2011; Pini & Benson, 2013), one could conclude that firing of Berea rock core and exposure of the core to $scCO_2$ for longer period of time do not change the capillary and wetting properties. However, since other studies reported different behavior for the $scCO_2$/water/sandstone system specifically, this assumption has to be verified by looking at the core-flooding capillary pressure data obtained using $scCO_2$ and water. Obtaining CO_2 drainage curves by scaling the MICP data using equation (1) requires indeed to know the value of the contact angle for the CO_2/water/rock system. It should also be noted that using the raw MICP curve instead of the corrected curve for applying the scaling method would yield significantly different results.

3.2. Effect of Firing Rock Core

The impact of firing the Berea rock core on the capillary and wetting behavior of the $scCO_2$/water/Berea system is investigated by comparing capillary pressure-saturation curves obtained experimentally for the untreated core and the fired core for two different fluid pairs, N_2/water (experiments B1 and BF1) and

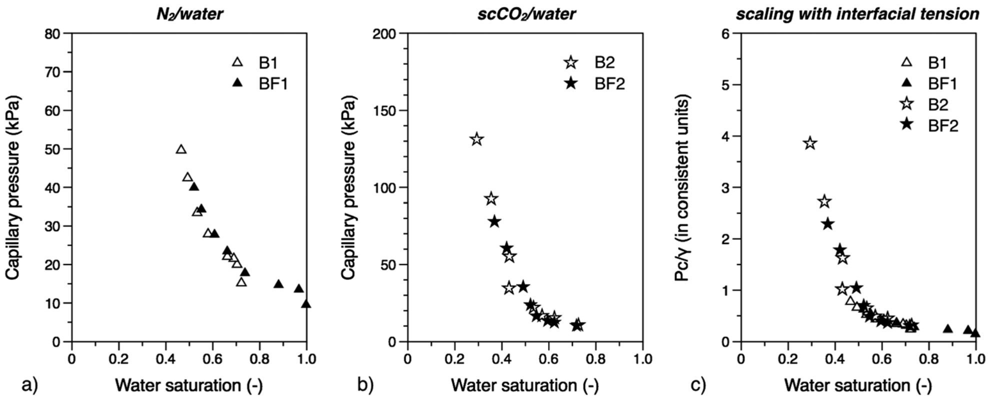

Figure 2. Capillary pressure curves measured experimentally on the untreated and then fired Berea core for (a) the N_2/water system (B1 and BF1, respectively) and (b) the $scCO_2$/water system (B2 and BF2, respectively). (c) The experimental data for the different fluid pairs are scaled with respect to interfacial tension (64 mN/m for N_2/water and 34 mN/m for $scCO_2$/water at 50 °C and 9 MPa).

$scCO_2$/water (experiments B2 and BF2). The data show no difference in between the untreated and fired core for both the N_2/water system (Figure 2a) and the $scCO_2$/water system (Figure 2b). Moreover, all the core-flooding capillary pressure data scale well without any adjustment of the contact angle (Figure 2c). This suggests that there is no noticeable change in the wetting state after firing the rock core and that the $scCO_2$/water/Berea sandstone system presents the same wettability as the N_2/water/Berea system, which has been previously characterized as strongly water wet (Wu & Firoozabadi, 2010). The contact angle for these two systems can be estimated by scaling the MICP curves (B and BF) to the experimental data (equation (1)). For all cases, the best fit was achieved for a contact angle of about 52°. Recall that the accuracy of this method relies strongly on the MICP data used for the scaling: The correction of the raw MICP curves is sensitive to the porosity value used, and even a difference in porosity of 0.001 (as estimated for BF1) results in a difference in contact angle estimation of 2°.

3.3. Effect of Longer Exposure to $scCO_2$

The $scCO_2$/water capillary pressure-saturation data obtained experimentally on the fired Berea rock core (BF2) and on the same core after it was exposed to $scCO_2$ for about a month (BE) are displayed in

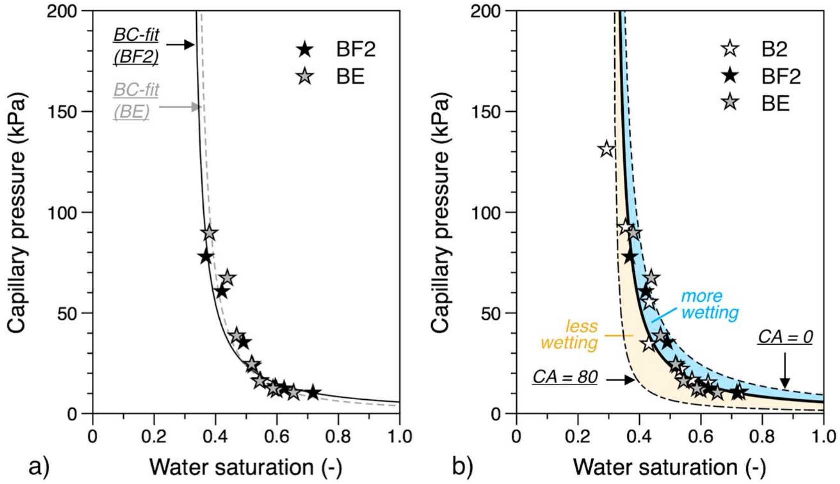

Figure 3. (a) Capillary pressure-saturation curves measured experimentally for the $scCO_2$/water system on the fired and then exposed Berea core (BF2 and BE, respectively). Brooks-Corey curves fitted to the data (BC-fit) are displayed in solid lines for BF2 ($P_e = 5.70$ kPa, $S_{w,irr} = 0.31$, $\lambda = 0.89$) and dashed lines for BE ($P_e = 3.81$ kPa, $S_{w,irr} = 0.31$, $\lambda = 0.7$). (b) Comparison of all experimental data for the $scCO_2$/water system (B2, BF2, and BE) with capillary pressure-saturation curves for a contact angle of 0 and 80 (dashed lines) derived from the BC-fit of BF2 (black solid line) assuming a contact angle of 52°.

Figure 3a, together with Brook-Corey fits. The data show good agreement, suggesting that no significant change resulted from exposure of the rock core to $scCO_2$ for 28 days. The Brooks-Corey fit for the data of experiment BF2 ($scCO_2$/water drainage in fired core) can be used to obtain the capillary pressure-saturation curves that would be expected for a contact angle of 0 and of 80, assuming a contact angle of 52°, as estimated in section 3.2. The results are presented in Figure 3b, and the core-flooding capillary pressures data for all the experiments performed with $scCO_2$ and water on the Berea core (B2, BF2, and BE) are also plotted on the graph for comparison. The figure allows a clear visualization that (i) the $scCO_2$/water/rock system is not specifically more water wetting for the fired Berea sandstone than for the untreated rock and that (ii) there is no noticeable dewetting after the core was exposed to $scCO_2$ for an extended period of time. In summary, no deviation from the water wetting state such as reported by Tokunaga et al. (2013) is observed when using an untreated Berea core instead of a fired core and after the core had been in contact with $scCO_2$ for 28 days.

4. Conclusions

Core-flooding capillary pressure measurements were performed on a Berea sandstone core at reservoir conditions (9 MPa and 50 °C) and were repeated after the core was fired and after the core was exposed to supercritical CO_2 for 28 days, in order to assess the impact of firing and longer exposure on the $scCO_2$/water drainage capillary pressure characteristic curve. The purpose of this work was to investigate if these two specific conditions could be responsible for the conflicting behaviors reported by previous authors for the $scCO_2$/water/quartz system: predictable capillary behavior of water wet systems (Al Menhali et al., 2015; Pentland et al., 2011; Pini & Benson, 2013) and deviation from hydrophilic conditions suggesting dewetting in the presence of supercritical CO_2 (Y. Kim et al., 2012; Tokunaga et al., 2013; Wang et al., 2016).

Our data show that the $scCO_2$/brine/Berea system is water wet with no change in wettability due to firing or longer exposure to $scCO_2$, suggesting that other factors contribute to the difference in experimental observations. One potential factor is a change in interfacial tension rather than a change in wettability. The $scCO_2$/water interfacial tension could indeed be significantly lowered by the presence of organic matter (Wan et al., 2017) that was present in the sand used for the experiments by Tokunaga et al. (2013) and Wang et al. (2016). Another factor is the fundamental difference in the experimental method used to characterize the capillary pressure-saturations curves (porous plate or core flooding), beside the duration of the experiment and contact to $scCO_2$, and, in particular, the difference in flow rate. While the core-flooding experiments were done at reasonably low capillary numbers, the porous-plate results reflect even lower, essentially zero, capillary numbers. It should also be noted that wettability alteration for the $scCO_2$/water system has mostly been observed in sand packs, micromodels, and flat surfaces but not in real rocks. Finally, most experimental studies of the capillary and wetting behaviors of the $scCO_2$/water/sandstone system using real rocks were performed in a Berea sandstone, and it would be valuable to extend this work to other types of sandstone rock.

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