Impact of Wettability Alteration on 3D Nonwetting Phase Trapping and Transport

Anna L. Herring^{1,2}, Adrian Sheppard², Linnéa Andersson¹, and Dorthe Wildenschild¹

¹*School of Chemical, Biological and Environmental Engineering, Oregon State University, Corvallis, OR 97331, USA*

²*Department of Applied Mathematics, Research School of Physics and Engineering, Australian National University, Canberra, ACT 2601, Australia*

Corresponding Author

Anna L. Herring

Department of Applied Mathematics

Research School of Physics & Engineering

The Australian National University

Garran Road, Building 58

Canberra ACT 2601, Australia

anna.herring@anu.edu.au

+61 2 612 51585

Abstract

We investigate capillary trapping and fluid migration via x-ray computed microtomography (x-ray CMT) of nonwetting phase (air) and wetting phase (brine) in Bentheimer sandstone cores which have been treated to exhibit different degrees of uniform wettability. X-ray CMT scans were acquired at multiple steps during drainage and imbibition processes, as well as at the endpoints; allowing for assessment of the impact of wettability on nonwetting phase saturation and cluster size distribution, connectivity, topology and efficiency of trapping. Compared with untreated (water-wet) Bentheimer sandstone, cores treated with tetramethoxysilane (TMS) were rendered weakly water-wet, and cores treated with octadecyltrichlorosilane (OTS) demonstrate intermediate-wet characteristics. As apparent contact angle increases, drainage flow patterns deviate from those derived for water-wet systems, total residual trapping and trapping efficiency decrease, and buoyancy plays a larger role during nonwetting phase mobilization; this has significant implications for CO₂ migration and trapping during CO₂ sequestration operations.

Keywords: wettability, drainage flow pattern, capillary trapping, residual trapping, pore scale, geologic CO₂ sequestration

1.0 Introduction

Multiphase flow in porous media has long been a subject of intensive research, traditionally with application to oil extraction. More recently, geologic CO₂ sequestration has been suggested as a potential climate change mitigation strategy, which has initiated renewed research efforts into multiphase flow processes. While some basic principles of multiphase flow can be immediately transferred between the two applications, the fluid properties of CO₂ (particularly density and viscosity) are dramatically different to those of oil, necessitating additional investigation of CO₂ flow processes. This study uses ambient condition air as a proxy for CO₂ to investigate how the wettability state of the porous medium impacts fluid flow behavior, and highlights consequences of potential wettability alteration during CO₂ sequestration operations.

Geologic sequestration of CO₂ in subsurface reservoirs is a climate change mitigation strategy which prevents carbon emissions to the atmosphere. Sequestration involves capture of CO₂ from the effluent of a large power production point source, transport to the storage reservoir in a dense liquid state, and then injection into a subsurface storage reservoir. The CO₂ will warm to the temperature of the geologic formation, resulting in a phase change to a supercritical state (we refer to supercritical CO₂ as scCO₂). During injection, the CO₂ phase displaces the resident brine of the geologic formation, i.e. a brine drainage process. Subsequently, upward travel of the buoyant CO₂ plume allows for brine imbibition as the brine re-enters the pore space. Accurate prediction of transport and trapping of subsurface CO₂ is necessary to ensure the safety, security, and effectiveness of a CO₂ sequestration operation. [IPCC, 2005]

Multiple trapping mechanisms have been identified which prevent CO₂ migration and release at the surface [IPCC, 2005]; one such mechanism is capillary (or residual) trapping, wherein CO₂ is held by capillary forces within the pore structure of the geologic matrix. Capillary trapping decreases the risk of inadvertent leakage of CO₂ due to cracks and faults (or other preferential pathways) of the geologic matrix; this mechanism also breaks up the injected CO₂ plume into small bubbles, increasing the surface area to volume ratio of the CO₂ and enhancing subsequent dissolution and precipitation reactions. Accordingly, understanding capillary trapping is critical for engineered geologic sequestration. The wettability state of a porous medium is a main factor influencing the strength of capillary forces (and thus, capillary trapping) during multiphase flow [Anderson, 1987b; Morrow, 1990; Iglaue et al., 2012; Wan et al., 2014].

Wettability is defined as the affinity of a solid surface for one fluid in the presence of other immiscible fluids. From a pore-scale perspective, wettability can be measured by the contact angle (θ) created by the intersection of the fluid-fluid and fluid-solid interfaces. As measured through the aqueous phase, a contact angle between 0-75° is considered water-wet, 75-105° is intermediate-wet, and measurements of 105-180° are oil/scCO₂-wet [Treiber and Owens, 1972; Anderson, 1987a]. The wettability of a porous medium affects the distribution of wetting and nonwetting fluids within the pore structure and can have a dramatic effect on permeability and connectivity of fluids. Depending on the saturation state of the medium, nonwetting phase fluid clusters tend to occupy the larger pores, while wetting fluid will exist in thin layers throughout the smallest throats and within crevices and roughness on the surface of the medium [Blunt and Scher, 1995; Kumar et al., 2009]. As fluids redistribute in a water-wet medium due to changes in saturation or capillary pressure, the nonwetting phase can become isolated and trapped via “snap-

off” [Roof, 1970]; this occurs during imbibition, when encroaching wetting fluid films surround a nonwetting fluid element in a pore body and the wetting fluid menisci touch as the pore throat constricts. This mechanism will be very different, and potentially completely absent if the system wettability is altered to be less strongly water-wet. Thus, wettability is a dominant factor controlling the occurrence of snap-off (as wetting films are only present in strongly-wetting systems), as well as the morphology and topology of fluid phases within the porous medium [Blunt, 1998]; it is therefore crucial to understand the degree to which wettability will affect residual trapping of the nonwetting phase for application in CO₂ sequestration scenarios.

The wettability state of a CO₂-brine-rock system is dependent on complex geochemical, ionic, and physical chemistry interactions, and there is currently no real consensus regarding how interaction with scCO₂ will impact rock surfaces in geologic systems. Transition to intermediate wettability after exposure to scCO₂ and brine has been reported for shale minerals [Chiquet *et al.*, 2005], silica micromodels [Kim *et al.*, 2012], sand columns [Plug and Bruining, 2007], and sandstones [Iglauer *et al.*, 2011; Akbarabadi and Piri, 2013; Berg *et al.*, 2013]. However, other studies investigating scCO₂ in Berea sandstone have reported relative permeability and capillary pressure-saturation curves similar to gas-phase fluids, indicative of a water-wet system [Pini and Benson, 2013], and significant residual trapping due to snap-off of scCO₂ during drainage-imbibition studies, also implying water-wet conditions [Pentland *et al.*, 2011; Krevor *et al.*, 2012; Pini and Benson, 2013]. Recently, Kaveh *et al.* [2014] showed that, in contrast to pure quartz, transition of CO₂ from subcritical to supercritical has no effect on the wettability of the Bentheimer sandstone/water system (despite the 90-96% quartz composition of Bentheimer sandstone). In carbonate rocks, Andrew *et al.* [2014] measured a scCO₂-brine *in-situ* average contact angle of approximately 45°. El-Maghraby and Blunt [2013] report that experiments with

Indiana Limestone show increased levels of residual trapping of CO₂ under supercritical conditions as compared to experiments conducted at subcritical pressure; they deduce that geochemical reactions force the system to a more strongly water-wet state than the same system at lower pressure. Wan et al. [2014] provide an overview of studies demonstrating the wide variation of contact angles reported for scCO₂-mineral systems and conclude that several factors contribute to the variation in reported contact angles: (1) nominally similar substrates can have different surface properties (i.e. reactivity or roughness) either intrinsically or due to cleaning methods; (2) contaminants may adsorb onto substrate surfaces and are difficult to avoid; (3) dissolution of CO₂ droplets due to non-equilibrium conditions affect contact angle measurements; and (4) the CO₂-substrate contact time, flow process order (i.e. which fluid first contacts the substrate), and contact repetition may affect water film/CO₂ stability. Given the range of observed wetting behavior, it seems prudent to further explore how wettability alteration affects CO₂ migration and capillary trapping.

A number of previous studies have investigated the impact of wettability on nonwetting phase trapping from the perspective of oil recovery. A pattern of minimum residual oil saturation at intermediate rock wettability and increased residual oil saturation at strongly water-wet and strongly oil-wet conditions is established in a review by Anderson [1987] (which presents the experimental results of Lorenz et al. [1974], Kennedy et al. [1955]; and Amott [1959]); as well as in more recent work by Morrow [1990]. This pattern is due to a combination of several factors. Snap-off dominates in water-wet conditions, leading to high residual oil saturations. Under intermediate-wet conditions, both fluids can easily flow through small constrictions; snap-off is suppressed [Mahmud and Nguyen, 2006], and oil can remain connected via smaller pore throats and drain to low residual saturation. Under oil-wet conditions, snap-off with respect to

the oil-phase does not occur, but oil resides in the small pore spaces and throats of the media, again resulting in relatively high residual oil saturations. Blunt [1998] performed numerical simulations which demonstrate a similar pattern to the experimental results described above, but also indicate reduced residual saturations in strongly oil-wet ($\theta > 135^\circ$) media due to the formation of oil films which allow oil to drain to very low saturations during water flooding.

However, results derived from oil-brine systems are not directly applicable to scCO₂-brine systems due to differences in fluid properties between oil and scCO₂. The viscosity of scCO₂ is lower than that of brine, resulting in an inverted viscosity ratio as compared to oil-brine systems. Such systems for which the invading phase is less viscous than the defending phase (e.g. CO₂, during a CO₂ injection) are said to have an “unstable” viscosity ratio, as the invading phase penetrates the medium via long fingers; this is in comparison to a “stable” displacement, where the invading phase moves through the medium as a solid front [Lenormand *et al.*, 1988]. In addition, gravity-buoyancy forces are generally stronger for scCO₂-brine systems compared to oil-brine systems due to the relatively large density difference between scCO₂ and brine; these differences in fluid properties between scCO₂-brine and oil-brine systems limit the applicability of oil recovery literature to scCO₂-brine systems. Drainage flow patterns (nonwetting fluid invading wetting fluid) have been studied in water-wet two dimensional (2D) systems for a wide range of viscosity ratios and capillary numbers [Lenormand *et al.*, 1988; Zhang *et al.*, 2011], as well as a function of gravitational force [Méheust *et al.*, 2002a; Chau and Or, 2006]. However, similar flow regimes are not well-defined for systems of intermediate wettability, or for three dimensional (3D) systems. In one of only a few supercritical condition CO₂-brine studies, Chaudhary *et al.* [2013] measured residual saturation of scCO₂ in glass (water-wet) and teflon (scCO₂-wet) bead cores, and found that residual trapping was greatly reduced in the scCO₂-wet

system; however, the bead systems used in that study had large pore spaces, the size of which impacts the relative importance of snap-off and fluid-solid adhesive forces, and thus may not be directly applicable to natural geologic systems.

The impact of wettability alteration on capillary trapping of scCO₂ during geologic sequestration operations is difficult to investigate due to the inherent difficulty involved in conducting and quantifying wettability during supercritical-condition experiments. In this work we use an ambient-condition system of air, brine, and Bentheimer sandstone. While absolute values of fluid properties (e.g. density, viscosity and interfacial tension with brine) differ widely between air and scCO₂, the ambient condition experimental system used in this study does approximate the capillary, gravitational, and viscous forces present in a scCO₂-brine-sandstone system [Herring *et al.*, 2015]. Further, compared to an oil-brine system, the air-brine system provides characteristics representative of scCO₂ injection scenarios, namely: (a) an unstable viscosity ratio during drainage (i.e. both air and scCO₂ are less viscous than brine), and (b) buoyancy driven flow due to significantly lower density of the nonwetting phase. To investigate different wettability states, Bentheimer sandstone cores were treated to produce three types of cores: water-wet (plasma cleaned, but otherwise untreated sandstone cores), weakly water-wet (cores treated with tetramethoxysilane, denoted “TMS”), and intermediate-wet (cores treated with octadecyltrichlorosilane, denoted “OTS”). For consistency, we refer to “drainage” as brine withdrawal from the core, “imbibition” as brine entering the core, and air is described as the nonwetting phase, regardless of the actual wettability state. Nonwetting phase (air) saturation and distribution is quantified via x-ray computed microtomography (x-ray CMT), and paired with capillary pressure measurements obtained during the scanning periods throughout the flow process.

2.0 Materials and Methods

2.1 Sandstone Cores and Silane Treatment

All experiments are conducted on Bentheimer sandstone cores with a diameter of 4.9 mm and lengths ranging 8.5-10.0 mm, which were cleaned via radio-frequency plasma treatment for at least 5 minutes at 50 watts and approximately 0.15 torr [Liston, 1989]. This high-vacuum procedure removes excess water from the pore space surfaces and enhances subsequent depositional uniformity of the silanes; for a brief description of factors contributing to silane aggregation and heterogeneity, see Diebold and Clarke [2012]. TMS treatment was applied to cores via vapor-phase deposition, under low pressure conditions (between 0.15 and 760 torr), for a period of at least 12 hours. For liquid-phase deposition with OTS, cores were first saturated under vacuum with dodecane for 25 minutes; then approximately 15 pore volumes of a solution of 5% OTS/95% dodecane by mass was flushed through the core several times over a period of 24 hours. These timeframes are significantly longer than is generally required for diffusion-based deposition of silanes (for comparison, Silberzan et al. [1991] employed a 6 minute time period for OTS deposition onto silicon wafers), but should ensure complete coverage of silanes throughout the pore space of the Bentheimer cores. After the OTS/dodecane flushing stage was complete, 30 pore volumes of toluene was flushed through the core to remove the OTS/dodecane solution from the pore space, and the core was placed under vacuum to volatilize toluene from the core. In addition to these silane-treated cores, flow experiments were also conducted on non-silane treated (only plasma-cleaned) water-wet (WW) cores. For each treatment type, a glass slide was subjected to the same treatment for contact angle measurement, which was accomplished using the sessile drop method in a goniometer.

Brine-water contact angles were measured for the glass slides (two duplicate measurements per treatment type) and assumed to represent idealized conditions within the pore space of the rock; this assumption was checked subsequently via inspection of pressure-saturation curves and tomographic data. After treatment, rock cores were wrapped with one layer of Teflon tape, and stored in sealed vials filled with MilliQ water when not in use.

2.2 Core Holder Assembly and Flow Processes

All rock cores were imaged in a titanium core holder (manufactured in-house at the Australian National University, ANU) which allows for favorable x-ray penetration (wall thickness of 0.120 mm). The sandstone sample was wrapped in Teflon tape and inserted into the core holder onto a circular hydrophilic nylon membrane with pore size of 1.2 μm (General Electric Company, Fairfield CT, United States), which was mounted on top of a Buna-N nitrile o-ring. The semi-permeable hydrophilic membrane was flush to the bottom of the core, thus preventing air breakthrough through the core and into the lines below the sample. The brine flow lines (made of PEEK material) were connected in series to a Keller Series 35X pressure transmitter with a range of 0 - 1.2 bar and accuracy of 0.1 mbar (Keller America, Inc., Newport News, VA, United States) and a Harvard PHD2000 syringe pump (Harvard Apparatus, Holliston MA, United States).

During experiments, a Bentheimer sandstone core was first saturated under vacuum with brine (1 part potassium iodide (KI) to 6 parts deionized water, by mass) to establish conditions representative of a reservoir prior to injection (i.e. 100% brine saturation), and a scan was acquired to ensure complete brine saturation was achieved; all experiments began with an original nonwetting phase saturation ($S_{\text{NW},0}$) of 0%. A small flexible air-tight air reservoir (volume of approx. 2 ml) was connected to the top of the core holder to reduce evaporation from

the core and maintain the nonwetting air phase at atmospheric pressure. Brine was then withdrawn at 0.3 $\mu\text{l}/\text{min}$ (drainage) to a predetermined volume (equivalent to the approximate volume of the pore space, as estimated by the mass and volume of the core and assuming a solid phase density of 2.65 g/cm^3), while ambient air entered the sample from the top of the core to the initial nonwetting phase saturation endpoint ($S_{\text{NW,I}}$). Subsequently, the same volume of brine was pumped into the bottom of the core (imbibition) at 0.3 $\mu\text{l}/\text{min}$. The presence of excess brine at the top of the core, along with negative capillary pressure readings, indicated residual conditions ($S_{\text{NW,R}}$). Brine phase pressure measurements were collected continuously throughout pumping and scanning operations; capillary pressure was calculated as the pressure of the air phase (i.e. ambient) minus the measured brine phase pressure and is considered to be a “bulk phase” measure representing the total pressure difference over the core. Scans were collected at $S_{\text{NW,O}}$; $S_{\text{NW,I}}$; and $S_{\text{NW,R}}$ points; additionally, the pump was halted and intermediate scans were acquired at multiple points throughout the drainage and imbibition flow processes, providing information about fluid configurations at transitional points. The very low flow rate used in this study resulted in quasi-equilibrium conditions for the permeable Bentheimer sandstone, and relatively short equilibration time was required (approximately 1-2 minutes) before the start of scanning. Reported capillary pressure values for scanned data points represent the time-average pressure values measured over the course of the scans.

2.3 X-ray Microtomographic Imaging and Processing

X-ray CMT scans were acquired at the ANU μCT facility. X-rays are generated by a GE-Phoenix xs180nf micro-focus x-ray source, and radiographs are captured by a 2048 x 2048 pixel Perkin Elmer XRD 1621 CNES amorphous silicon flat-panel x-ray detector, coated with a cesium iodide scintillator. Depending on sample placement relative to the detector, each data set

had a slightly different voxel resolution value, ranging from 3.2 μm to 3.8 μm per voxel edge. X-ray tube settings were 80 kV and 110 μA for all scans except one OTS data set, which was erroneously imaged at a much lower accelerating voltage of just 30 kV (this difference in accelerating voltage did not produce an excessive difference in image quality, and the resulting data volumes were processed according to the same protocol as all other data sets). Depending on energy settings and height of the imaged section, scans typically required 1.5-2.5 hours to collect at least 6000 projection angles on a helical scanning trajectory at 0.14 degree angle spacing. The precise number of projections depended on the length of the core plug. Reconstruction was accomplished using helical cone-beam filtered backprojection [Varslot *et al.*, 2011]. Figure 1 provides an example of the data processing procedure: For each grayscale data volume (Figure 1a), a 6.1 mm tall and 3.65 mm diameter cylindrical subsection of the center of the core was chosen to exclude influence on flow and trapping from the core holder walls, and three iterations of a three-dimensional (3D) median filter were applied (Figure 1b). The segmentation threshold was set to the grayscale value corresponding to the local minimum separating the air and combined solid/brine phases in the grayscale histogram (Figure 1c). The resulting segmented volumes were denoised to exclude falsely-labeled air phase voxels by removing isolated air phase features smaller than the equivalent volume of a sphere with a radius of approximately 18 μm ; this is consistent with the pore size distribution of Bentheimer sandstone reported by Maloney *et al.* [1990]. All reported quantitative measures are calculated on this final binary image of air phase (Figure 1d).

(a)

(b)

(c)

(d)

Figure 1. Data processing procedure for x-ray microtomographic data. The (a) raw 4.1 mm diameter grayscale data showing nonwetting phase (air, darkest gray phase) and wetting phase (brine, lightest gray) within Bentheimer sandstone (intermediate gray) is (b) filtered with three iterations of a three dimensional (3D) median filter and cropped to a diameter of 3.65 mm (original size shown with blue ring), after which the grayscale histogram minimum between the air phase and solid phase is determined (c). The minimum value separating the histogram peaks is set as the threshold value which defines which voxels represent air phase (blue in image) (d), upon which all subsequent quantitative measures are calculated.

2.4 Quantitative Connectivity Metrics

Two quantitative metrics were used to characterize nonwetting phase (air) connectivity from the binary data volumes. The Euler number (χ) is a topological invariant defined as the alternating sum of the first three Betti numbers ($\beta_0, \beta_1, \beta_2$):

$$\chi = \beta_0 - \beta_1 + \beta_2 \quad \text{Eqn. 1}$$

where β_0 is the number of individual objects present (i.e. individual, isolated air clusters), β_1 is the number of redundant loops or handles present (i.e. redundant pore throats through which air is connected within the air clusters), and β_2 is the number of inclusions within the object(s) (e.g. this would indicate a solid/brine particle floating within an air cluster in the system; this value is irrelevant for the porous medium system of this study). Herring et al. [2013, 2015] divide the Euler number of each data volume by the Euler number of the same medium at 100% nonwetting phase saturation (i.e. the Euler value of the pore space of the medium), resulting in a normalized Euler number ($\hat{\chi}_{NW}$) which ranges from negative values (indicating disconnected nonwetting phase) to a maximum value of 1.0 (indicating maximum interconnectivity of nonwetting phase, i.e. a completely filled pore space). Euler numbers have been used to quantify topology of a number of different types of networks and systems [Mecke and Wagner, 1991; Odgaard and Gundersen, 1993; Vogel, 2002; Renard and Allard, 2013; Wildenschild and Sheppard, 2013].

Similarly, $\Gamma(p)$ is a percolation metric defined as a function of permeable phase saturation, p [Renard and Allard, 2013]. Here, we define the permeable phase p to be nonwetting (NW) fluid [Herring et al., 2013, 2015]. $\Gamma(NW)$ is then the ratio of the sum of squares of all individual nonwetting phase cluster volumes to the square of the total volume of nonwetting phase in the

domain; from an image analysis perspective, nonwetting phase volume is equivalent to the voxel counts of the nonwetting clusters. Thus, $\Gamma(\text{NW})$ is defined as:

$$\Gamma(\text{NW}) = \frac{1}{n_{\text{NW}}^2} \sum_{i=1}^{N(X_{\text{NW}})} n_i^2 \quad \text{Eqn. 2}$$

where n_{NW} is the total number of NW phase voxels in the set X_{NW} , $N(X_{\text{NW}})$ is the number of distinct clusters in the set X_{NW} , and n_i is the number of NW voxels in cluster i . As $\Gamma(\text{NW})$ approaches 1.0, the fraction of the fluid that is associated with a single cluster increases.

3.0 Results

The results of these experiments are presented in terms of the apparent wettability state (section 3.1), drainage front patterns and the forces controlling displacement (sections 3.2 and 3.3), and capillary trapping amount (section 3.4) of the various cores. Flow patterns are difficult to resolve during imbibition, as the invading front is difficult to delineate from the drainage endpoint air-water interface; consequently, we focus on the drainage process only, in terms of describing connectivity and flow patterns, while both drainage and imbibition data are considered subsequently in order to describe nonwetting phase trapping.

3.1 Effect of Wettability Treatment

Representative capillary pressure-saturation (P_c - S) drainage curves for the three treatments are presented in Figure 2; nonwetting phase saturation values shown are the average saturation value of the entire imaged section of the x-ray CMT data and are paired with the capillary pressure of the bulk wetting and nonwetting phases measured during the time of the scan. We note here that the cores are each less than 10 mm tall, corresponding to a hydrostatic pressure gradient of 1 mbar; therefore the bulk capillary pressure values presented in Figure 2 represent the capillary

pressure along the entire vertical extent of the cores, to within approximately 1 mbar. Error bars shown represent the range of pressure recorded over the duration of the scan. Although multiple experiments were run for the various cores, each curve presented in Figure 2 consists of data points taken from a single experiment. As shown, for the drainage process (Figure 2) the bulk capillary pressure is relatively high for plasma-cleaned but otherwise untreated water-wet (WW) cores, while weakly water-wet (TMS) and intermediate wet (OTS) cores demonstrate significantly lower capillary pressures for intermediate saturation values (i.e. 50-90% nonwetting saturation). Additionally, TMS and OTS cores exhibit significantly higher water saturations at elevated capillary pressures (greater than 80 mbar) relative to the WW core. These characteristics are indicative of increased contact angle [Anderson, 1987a; McDougall and Sorbie, 1995; Bradford *et al.*, 1997; Chalbaud *et al.*, 2007]. Contact angles of the treated cores are estimated from drainage P_c -S curves using the Washburn equation:

$$P_c = \frac{2\sigma}{r} \cos\theta \quad \text{Eqn.3a}$$

$$\theta_i = \cos^{-1} \frac{P_{c,i}}{P_{c,ww}} \cos\theta_{ww} \quad \text{Eqn.3b}$$

where r is the radius of a channel in treated core i from which water is draining, P_c is the capillary pressure (the difference between the nonwetting and wetting phase pressure) at which the channel drains, σ is the interfacial tension between air and brine, and θ is the contact angle, measured through the aqueous phase. Values of estimated contact angle are presented in Table 1, these values are calculated from capillary pressure values at approximately 60% nonwetting phase saturation (40% brine saturation). This estimation assumes σ and r are constant for and

comparable between the cores, and that the water-wet contact angle for the sandstone cores, θ_{ww} , is approximately 5° , as measured on the plasma cleaned glass slide (Table 1). Also presented in Table 1 are the contact angle values measured from treated glass slides.

Figure 2. Curves of measured capillary pressure paired with x-ray tomographic image derived saturation values for the quasi-static brine drainage process in wettability-altered Bentheimer sandstone cores from three selected experiments. Wettability is classified as water-wet (WW), weakly water-wet (TMS), and intermediate-wet (OTS). The error bars represent the entire range of pressure recorded during the scan.

Table 1. Contact angle measurements for Bentheimer sandstone and glass slide surfaces treated with tetramethoxysilane (TMS) or octadecyltrichlorosilane (OTS), compared to plasma cleaned water-wet (WW) surfaces.

	Estimated from drainage P_c -S curve	Average measure from treated* glass slide		Wettability designation
		Advancing	Receding	
WW	-	5°	5°	Strongly water-wet
TMS	42°	73°	69°	Weakly Water-wet

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OTS	60°	108°	96°	Intermediate-wet
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*Treatment of WW glass slide consisted of radio-frequency plasma cleaning only

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342 The contact angles estimated from the Bentheimer P_c -S curves are shifted toward water-wet by
343 30° (for TMS) and 40° (for OTS) relative to the values measured on the treated glass slides.
344 Anderson [1987a] presents a review of studies which show similar behavior, and puts forth
345 several reasons for the observed insensitivity of capillary pressure measurements on contact
346 angle: (a) the porous medium cannot necessarily be approximated by a bundle of capillary tubes
347 as is implicitly assumed when using eqn. 3, (b) the presence of sharp edges in reservoir rocks
348 samples permit a wider range of contact angles than flat surfaces, and (c) surface roughness
349 diminishes the apparent contact angle for contact angles less than 90° . The inconsistency
350 between glass slide and core contact angle estimates could also be due to treatment constraints:
351 the silanization treatment is limited by transport throughout the complex network of pores and
352 throats of the sandstone pore-space, while the glass slide surface is easily accessible to the OTS
353 and TMS molecules. In addition, Bentheimer is not pure quartz (reported values for the bulk
354 material vary, e.g. 90-96% [Mayr and Burkhardt, 2006], 91.7% [van Hemert et al., 2013], 97.2%
355 [Tchistiakov, 2000]) and so the surfaces being coated are not exclusively silica. These factors
356 may result in reduced coverage of the sandstone pore surface with silane as compared to the
357 glass slides. The OTS glass slide contact angle measurements agree with a value of 106°
358 reported by Araujo et al. [1995], while the values estimated from the P_c -S curve is in good
359 agreement with values reported by Bradford and Leij [1995] (64.9° advancing and 38.0°
360 receding) who also estimated contact angle from P_c -S data of OTS treated sands. For further
361 interpretation of the data, contact angles of the sandstone cores are assumed to be equivalent to
362 those estimated from P_c -S curves; untreated cores are considered to represent water-wet

conditions (labeled WW), TMS treated cores are considered to be weakly water-wet (labeled TMS), and OTS treated cores represent intermediate-wet conditions (labeled OTS).

3.2 Enhancement of Buoyancy-Driven Flow by Wettability Alteration

Previous experimental work in 2D micromodels has led to the development of flow regimes as a function of viscosity ratio (ratio of invading to defending phase viscosities, $M = \mu_{INV}/\mu_{DEF}$) and capillary number (Ca) [Lenormand *et al.*, 1988; Zhang *et al.*, 2011]. Capillary number is sometimes defined to include contact angle (e.g. Jamaloei *et al.* [2012]):

$$Ca = \frac{\mu_{INV} v_{INV}}{\sigma \cos \theta} \quad Eqn.4$$

where μ_{INV} is the invading phase viscosity and v_{INV} is the invading phase velocity. Figure 3 shows the experiments of this study on the previously developed phase diagram, after Lenormand *et al.* [1988] and Zhang *et al.* [2011], using this definition of capillary number, and using contact angle values as estimated from the Pc-S curves (Figure 2 and Table 1). Values for capillary number (for both drainage and imbibition) of the various experiments are presented in Table 2. Based on the traditional “Lenormand Flow Regime” description of flow pattern regimes, the OTS, TMS, and WW data would be expected to exhibit similar flow patterns inherent to the capillary fingering regime.

Table 2. Wettability designation for Bentheimer sandstone drainage-imbibition experiments with resulting capillary and Bond number values (as calculated in Eqns. 4 and 5b, respectively). Corresponding nonwetting (NW) saturation values, derived from tomographic images, are presented for the *initial* stage at the end of drainage ($S_{NW,I}$) and *residual* stage at the end of imbibition ($S_{NW,R}$). Two duplicate experiments were run for each WW and TMS cores; one experiment was run for the OTS treated core for which results are presented in terms of whole core, top of core, and bottom of core values.

	Contact Angle	Wettability designation	Drainage Capillary Number	Imbibition Capillary Number	Bond Number	Experiment Designation	$S_{NW,I}$	$S_{NW,R}$
WW	5°	Strongly water-wet	6.7×10^{-11}	4.2×10^{-9}	5.3×10^{-3}	Duplicate 1	0.96	0.36
						Duplicate 2	0.91	0.37
TMS	42°	Weakly Water-wet	8.9×10^{-11}	5.6×10^{-9}	7.1×10^{-3}	Duplicate 1	0.91	0.26
						Duplicate 2	0.87	0.28
OTS	60°	Intermediate-wet	1.3×10^{-10}	8.3×10^{-9}	0.011	Whole Core	0.75	0.37
						Core Top	0.75	0.53
						Core Bottom	0.75	0.21

Figure 3. Classification of drainage flow regime in Bentheimer sandstone as a function of capillary number (as defined in equation 2) and viscosity (mobility) ratio during drainage, after Lenormand et al. [1988] and Zhang et al. [2011]. Wettability is classified as water-wet (WW), weakly water-wet (TMS), and intermediate-wet (OTS).

The experimental system investigated in this study is a 3D system, which necessitates additional investigation of the impact of gravitational forces. For injection of a relatively less dense fluid from the top of a sample into a more dense fluid (as was done in this study), previous 2D micromodel [Méheust et al., 2002] and numerical [Chau and Or, 2006] studies of drainage front patterns have shown that as gravity dominance increases, the invading phase displays a transition from a fingering flow regime to a stable displacement flow regime, as gravity acts to prevent downward finger formation of the less dense phase. In these previous studies, gravity was manipulated via *increase* in the *gravitational force* (i.e. by changing the tilt angle of the 2D micromodel, as by Méheust et al. [2002], or by changing the value for gravitational acceleration in the Lattice Boltzmann simulation, as by Chau and Or [2006]); this is in contrast to our study, where we have *decreased capillary forces* by changing the apparent contact angle of the system. These previous studies [Méheust et al., 2002; Chau and Or, 2006; Or, 2008] have quantified the transition from unstable fingering flow to gravity dominated flow using combinations of capillary number (sometimes modified to incorporate permeability; e.g. see Or [2008]) and Bond number, which is defined as:

$$Bo = \frac{\Delta\rho C_g C d^2}{\sigma} \quad Eqn.5a$$

where $\Delta\rho$ is the difference in density between fluids, g is the gravitational constant, and d is a representative length scale (e.g. mean pore radius, fracture aperture). In the current case we define d to be the average grain diameter of Bentheimer sandstone, as measured by Maloney et al. [1990], which provides an “order of magnitude” approximation of the length scale relevant to

the pore spaces of Bentheimer sandstone. None of the above studies have included the impact of medium wettability in their analysis; here we modify the definition of Bond number to do so:

$$Bo = \frac{\rho C_g C d^2}{\sigma \cos \theta} \quad (0^\circ \leq \theta < 90^\circ) \quad \text{Eqn.5b}$$

The incorporation of contact angle in this formulation is a necessary change for finite contact angles since the strength of capillary forces, which form the denominator, are proportional to $\sigma \cos \theta$: as contact angle increases to intermediate wet conditions (90°), Bond number increases, indicating reduced influence of capillary forces and a transition to buoyancy driven flow. For this definition of Bond number, the experiments performed in this study exhibit values ranging from 5.3×10^{-3} (WW) to 7.1×10^{-3} (TMS) to 0.011 (OTS), as detailed in Table 2.

3.3 Evolution of Topology and Connectivity of the Nonwetting Phase during 3D Drainage

Visualization of flow regimes in 3D is more complex than for 2D systems, as the fluid front can become obscured and difficult to delineate due to flow heterogeneities in the transverse dimension. Correspondingly, in this section both visualization and quantitative measures are presented to describe the flow regimes of the wettability-altered core samples.

The topology of the nonwetting phase after drainage has been shown to have a distinct impact on the mobilization (trapping) of nonwetting phase after imbibition [Herring *et al.*, 2013, 2015], and is also useful in describing dynamic nonwetting phase behavior during imbibition [Rücker *et al.*, 2015]. As described above (Section 2.3), the normalized Euler number ($\hat{\chi}_{NW}$) relates the number of individual, independent fluid clusters to the number of redundant connections (e.g. pore throats) within fluid clusters. A negative

433 $\hat{\chi}_{NW}$ value indicates the presence of multiple, relatively poorly connected nonwetting phase
434 clusters; as $\hat{\chi}_{NW}$ increases towards a value of 1.0 the system is approaching maximum
435 nonwetting phase connectivity as the air clusters become more interconnected via redundant pore
436 throat pathways. The relationship between nonwetting phase-normalized Euler number and
437 nonwetting phase saturation ($\hat{\chi}_{NW}$ -S) is shown in Figure 4. Data from all experimental runs,
438 including duplicates, are presented in this figure. We note that the shape of the $\hat{\chi}_{NW}$ -S
439 relationship measured in these experiments is in agreement with the $\hat{\chi}_{NW}$ -S relationship
440 measured previously by Herring et al. [2015], who investigated topology of nonwetting phase
441 after relatively fast drainage (flow rate of 3.3 $\mu\text{l}/\text{min}$, 10 times higher than this study) in untreated
442 Bentheimer sandstone.

443 The WW, TMS, and OTS data all demonstrate approximately the same $\hat{\chi}_{NW}$ -S relationship.
444 However, we note that the OTS data reaches a maximum $\hat{\chi}_{NW}$ value of only approximately 0.2
445 during drainage, indicating a poorly connected nonwetting phase, even though a relatively high
446 capillary pressure value is achieved (Figure 2). The behavior of the OTS $\hat{\chi}_{NW}$ -S relationship can
447 be attributed to the absence of water films in the intermediate-wet system, as all brine which
448 remains in the sandstone pore space is disconnected and lacks a path to drain from the sample.
449 Consequently, nonwetting phase is unable to invade the pore throats required to reach high $\hat{\chi}_{NW}$
450 values; resulting in the cluster of OTS points at approximately $\hat{\chi}_{NW}$ of 0.2 and 80% nonwetting
451 phase saturation at the end of the drainage process.

452 An alternative measure of nonwetting phase connectivity is Γ , defined in Section 2.3 and eqn. 2,
453 which describes the likelihood that a nonwetting-labeled fluid voxel is connected to all other

nonwetting fluid voxels [Renard and Allard, 2013; Herring et al., 2015]. As Γ approaches 1.0, the likelihood that all nonwetting fluid clusters are connected to each other increases. Figure 5 presents Γ as a function of nonwetting phase saturation during drainage. Data from all experimental runs, including duplicates, are presented in this figure. As shown, for low to moderate (0-60%) nonwetting phase saturation, air invasion in the cores follows a trend in Γ where $\text{OTS} > \text{TMS} > \text{WW}$. Indeed, the intermediate wet core (OTS) reaches a relatively high nonwetting phase connectivity of $\Gamma \approx 0.9$ at a significantly lower nonwetting phase saturation (12%) than the weakly water-wet (TMS) and water-wet (WW) cores (approx 55%). The difference in nonwetting phase connectivity during drainage, quantified by Γ , shows that the nonwetting phase in the intermediate wet core (OTS) can more easily permeate the sandstone than in the weakly-wet (TMS) and water-wet (WW) cores. This indicates that the nonwetting phase in the OTS core is connected through pathways (throats) not accessible to the nonwetting phase in the TMS and WW cores until higher capillary pressures have been reached. This connectivity analysis quantitatively demonstrates that nonwetting fluid migration patterns are affected by changes in wettability. Two data points which exemplify early drainage conditions are circled in Figure 5 and are investigated further in Figures 6 and 7.

In Figure 6, we present 2D vertical cross-sections of nonwetting phase intrusion in the cores at 12% and 13% overall nonwetting phase saturation for OTS and TMS cores respectively, the 2D grayscale images are overlain with the vertical saturation profiles of the cores. Unfortunately, since the exact saturation at which the tomographic snapshot were taken depended on difficult-to-control experimental parameters, no tomographic images of similar low saturation levels were obtained for WW cores. Both of these profiles represent an early-stage drainage regime where the nonwetting phase has not yet percolated throughout the core. It is necessary to investigate

477 low nonwetting phase saturation data (i.e. early drainage conditions) because visualization of
478 high nonwetting phase saturation data is very cluttered, rendering flow pattern identification
479 impractical. Furthermore, we base our comparisons on a saturation basis (rather than a capillary
480 pressure basis) due to the fact that for low to moderate nonwetting phase saturation values,
481 capillary pressure for a given core does not vary significantly due to the “plateau” region of the
482 P_c -S curve, so similarly valued P_c data points can have dramatically different saturation values;
483 for visualization purposes this is undesirable. Visually, nonwetting phase flow in the OTS core is
484 more compact and restricted to the top of the core, while the TMS data volume exhibits longer
485 fingering. In comparison to the bulk (overall) saturation values, the z-slice averaged vertical
486 distributions of nonwetting phase saturation for these treated cores are also shown in Figure 6; in
487 order to reduce noise, each point on the vertical profiles (plotted in 0.003 mm increments)
488 represents the average nonwetting phase saturation value of the neighboring 0.5 vertical mm of
489 the core. The OTS volume exhibits a sharp decrease in nonwetting phase saturation
490 approximately 2.5 mm from the top of the core, while the TMS core demonstrates a relatively
491 linear nonwetting phase profile, due to the presence of the multiple longer fingers.

492 We suggest that the observed flow patterns during drainage (Figures 5-6) are due to a decrease in
493 capillary forces and relative increase in viscous/gravitational forces as contact angle increases,
494 resulting in stable displacement of the nonwetting (air) phase into the core and elevated
495 nonwetting phase saturations in the upper section of the OTS core. Due to the density difference
496 between the fluid phases, buoyancy forces cause a capillary pressure gradient along the length of
497 the core, and this effect is accentuated for the cores of altered contact angle as described by eqn.
498 3a. The vertical gradient in capillary pressure results in a vertical gradient in saturation within the
499 cores, indicating that buoyancy forces need to be considered in the equilibrium description of

fluid distributions. Even though the hydrostatic gradient in these cores is relatively small (cores are only approx. 1 cm tall), the resulting saturation gradient is significant; this indicates that buoyancy forces are relevant for the wettability altered systems, even at the pore scale.

The apparent transition from fingering type flow demonstrated by the TMS core to a stable displacement regime in the OTS core agrees well with analysis by Or [2008], who showed that the transition between these two displacement types occurs at $Bo \approx 0.05$. This finding also agrees with recent studies by Trojer et al. [2015] who demonstrated a transition from viscous fingering flow to stable displacement with contact angle increases for a less viscous fluid invading a more viscous fluid in horizontally oriented 2D micromodels.

Conceptually, this shift in invasion pattern from fingering to uniform displacement can be attributed to the reduction of capillary forces associated with an increased contact angle. For a water-wet (or weakly water-wet) medium, wetting fluids exist in films on the grain surfaces and fill small pore spaces, while nonwetting fluid preferentially travels through larger pore bodies and throats, causing fingering; however, in an intermediate-wet medium (e.g., our OTS core), flow is less dependent on the pathway size as the solid surface displays equal affinity to either fluid phase. Additionally, in the 3D system investigated in this study, increases in contact angle result in higher Bond number values, causing gravity separation and contributing to the relatively sharp delineation between the more buoyant air phase and the aqueous brine phase below.

3.4 Trapping Trends

The effect of wettability state on (a) residual nonwetting saturation and (b) trapping efficiency (residual nonwetting saturation, $S_{NW,R}$, normalized by initial nonwetting saturation, $S_{NW,I}$) is presented in Figure 7. As was found in the drainage experiments, nonwetting phase distribution

in OTS cores is strongly dependent on vertical position within the core. Thus, the single OTS data volume is presented as air saturation of the top 2 mm of the core, bottom 2 mm, and whole core (the whole core is 6.1 mm tall). Residual saturation and trapping efficiency is highest in the upper 2 mm of OTS treated cores, followed by WW untreated cores and TMS treated cores, with the bottom 2 mm of OTS treated cores showing the lowest trapping efficiency. Duplicates of the WW and TMS experiments demonstrate that these experiments are highly repeatable, however, only one OTS experiment was completed through the full drainage and imbibition cycle due to experimental complications. Vertical distributions of residual (trapped) nonwetting phase saturation in WW and TMS experiments are uniform with depth; however, the vertical distribution of nonwetting phase in the OTS core is highly variable and depth dependent (Figure 8). The relative uniformity of residual nonwetting phase in WW and TMS cores, compared to the nonuniformity of nonwetting phase distribution of the OTS core is also visible in nonwetting phase isosurfaces of the residual state (Figure 9).

Figure 7. (a) Residual trapping ($S_{NW,R}$), and (b) trapping efficiency (residual saturation normalized by initial saturation, $S_{NW,I}$) of nonwetting (NW) phase (air) as a function of contact

angle (estimated from the capillary pressure-saturation curves of drainage, see Table 1) of Bentheimer sandstone cores of intermediate wettability (OTS), weakly water-wet wettability (TMS), and water-wet wettability (WW). The data from the OTS experiment is shown as the saturation calculated from the upper 2 mm of the core, the bottom 2 mm of the core, and the whole core (unlabeled). WW and TMS data are whole core values and include values of duplicate experiments.

Figure 8. Vertical distribution of air saturation measured at the end of imbibition for a water-wet WW core (overall air saturation of 36%), a weakly water-wet TMS core (overall air saturation of 26%), and an intermediate-wet OTS core (overall air saturation of 37%). For clarity, data is coarsened such that each point on each profile represents the average saturation of 0.5 vertical mm.

552 **Figure 9.** Isosurfaces of residual air clusters in Bentheimer sandstone cores at the end of
 553 imbibition for (a) a water-wet WW core (overall air saturation of 36%), (b) a weakly water-wet
 554 TMS core (27% overall air saturation), and (c) an intermediate-wet OTS core (overall air
 555 saturation of 53%).

556 The imbibition endpoint for the OTS experiment was reached based on visual confirmation of
 557 brine above the sample and from P_c -S data, indicating that the observed vertical distribution of
 558 nonwetting phase was stable for the OTS system. We have not found a clear explanation for the
 559 elevated nonwetting phase saturation of the upper 2 mm of the OTS core. Evaporation of water
 560 from the top of the core during scanning is possible, but unlikely, as measures were taken to
 561 prevent evaporation in these experiments. Nonuniformity of the OTS layer is also possible;
 562 however, deposition procedures were designed to ensure uniform and complete silane deposition
 563 during OTS treatment (as previously discussed in Section 2.1). We therefore conclude that the
 564 elevated nonwetting phase saturation present at the top of the OTS core must be due to enhanced
 565 boundary condition effects resulting from the increased contact angle of the core. In order to

neglect these boundary condition effects, only data from the lower 2 mm of the OTS experiment is considered to be representative of trapping behavior in wettability altered systems. Using the lower 2 mm the data indicate reduced trapping as contact angle increases (Figure 7), very similar to trends reported in oil recovery literature [Kennedy *et al.*, 1955; Amott, 1959; Lorenz *et al.*, 1974; Morrow, 1990], and to scCO₂-brine experiments conducted in water-wet and scCO₂-wet bead pack [Chaudhary *et al.*, 2013].

The cluster size distributions of the residually trapped nonwetting phase are shown in Figure 10. Residual nonwetting phase clusters in the OTS sample occupy smaller pore spaces relative to those in the WW and TMS samples. Additionally, there is a higher frequency of small clusters in the lower 2 mm of the OTS core compared to the upper 2 mm of the same core, despite a much higher nonwetting phase saturation in the upper section; this is due to the presence of one large cluster which comprises most of the nonwetting phase volume (approx. 5 mm³, not shown in Figure 10) in the upper 2 mm of the OTS core. This distribution of cluster sizes as a function of wettability state is supported by the imaging studies of Iglauer *et al.* [2012] who reported that there are more small clusters of residual oil under oil-wet vs. water-wet conditions.

Figure 10. Representative histograms of frequency of residual air clusters present for a given cluster volume in a water-wet (WW) Bentheimer sandstone core, weakly water-wet (TMS) core, and three sections of an intermediate-wet (OTS) core. The OTS data is displayed as whole core (full 6.1 mm), lower 2 mm, and upper 2 mm, depending on which vertical section of the core was analyzed.

4.0 Conclusions

We have qualitatively and quantitatively investigated the impact of wettability on drainage flow patterns and residual trapping of a nonwetting phase (air), as a proxy for CO₂, in an air-brine-Bentheimer sandstone system, using cores of 4.9 mm diameter and 8.5-10.0 mm height. Capillary pressure-saturation curves, measured concurrently with x-ray CMT imaging studies (conducted on 3.65 mm diameter and 6.1 mm tall subsections of the cores), indicate that TMS vapor-phase treatment renders the (originally water-wet) sandstone cores to be weakly water-wet (contact angle of 42° as measured through the aqueous phase), while OTS liquid-phase treatment produces intermediate-wet cores (60°). Apparent contact angle values are estimated using the Washburn equation (Eqn. 3b).

Visual investigation of the nonwetting phase distribution in OTS and TMS cores and quantified vertical nonwetting phase distribution (Figure 6), along with quantitative analysis of the nonwetting phase connectivity during drainage (Figure 5), imply that different wettability states produce distinctly different drainage flow regimes: the weakly water-wet TMS core displays a fingering-type nonwetting phase invasion, while the intermediate-wet OTS core shows nonwetting phase invasion via a more compact, stable displacement pattern. Further, the flow regimes are distinct from those predicted by studies of water-wet systems of Lenormand et al. [1988] and Zhang et al. [2011], since these prior 2D micromodel studies neglect the role of gravity and wettability. The flow patterns observed in this study are however supported by the studies of Méheust et al. [2002], Chau and Or [2006], and Or [2008], who have shown the same flow regime transition as gravity forces become stronger over viscous or capillary forces in a system; a similar transistion in flow regimes has also been recently reported by Trojer et al. [2015] as a result of increasing contact angle in 2D horizontal micromodels. In our 3D experimental system, we find that as contact angle increases, capillary effects decrease (resulting in reduced fingering during drainage) and buoyancy effects dominate flow patterns and residual distribution. Further research is needed to clearly delineate flow regimes in 3D, intermediate-wet systems.

Residual nonwetting phase saturation was highest in the upper imaged section (2 mm of the total 6.1 mm long data volume) of the intermediate-wet OTS core (Figure 7); however, this effect is likely due to enhanced boundary condition effects due to the increased contact angle compared to the other cores, and is not expected to be representative of overall trapping behavior. We observe that residual nonwetting phase saturation is highest in WW cores (average $S_{NW,R}$ of 36% and $S_{NW,R}/S_{NW,I}$ of 39%), followed by weakly water-wet TMS cores (average $S_{NW,R}$ of 27%, average

$S_{NW,R}/S_{NW,I}$ of 30%), with the lowest 2 mm region of intermediate-wet OTS cores demonstrating reduced trapping ($S_{NW,R}$ of 21%, $S_{NW,R}/S_{NW,I}$ of 28%). Trapped nonwetting phase clusters in WW and TMS cores are present as larger clusters relative to the OTS trapped cluster distribution (Figure 10), in agreement with results from existing literature.

For application to residual trapping of $scCO_2$ in geologic sequestration operations, this study indicates that further research is needed to develop accurate models for the flow of CO_2 in media of different wettability; especially in flow regimes where buoyancy forces are important. The range of Bond numbers of these experiments (5.3×10^{-3} to 1.1×10^{-2} as calculated by eqn. 5b, see Table 2) is similar to that of $scCO_2$ -brine-sandstone systems (e.g. Bond number values of 2.5×10^{-4} to 3.0×10^{-3} , assuming water-wet sandstone with 0° contact angle as per analysis by Herring et al. [2015]), indicating that potential wettability changes could have a surprisingly large effect on CO_2 migration; an increase in contact angle could greatly enhance buoyancy effects and significantly influence pore scale displacement patterns for intermediate-wet systems, if medium wettability is indeed susceptible to alteration due to exposure to $scCO_2$. Furthermore, systems that exhibit a wettability change to higher contact angle due to exposure to $scCO_2$ will likely demonstrate reduced residual trapping efficiency. However, even under intermediate-wet conditions, significant trapping (e.g. $S_{NW,R}$ of 21% and $S_{NW,R}/S_{NW,I}$ of approximately 28%) was still evident for our low capillary-number imbibition experiments at ambient conditions.

Acknowledgements

This material is based upon work supported by the National Science Foundation under Grant No. IIA-1209476, as part of the East Asia and Pacific Summer Institute (EAPSI); as well as the U.S. Department of Energy, Basic Energy Sciences, Geosciences Program under award number DE-FG02-11ER16277. The EAPSI program is supported by the Australian Government and

managed by the Australian Academy of Science. Adrian Sheppard is the recipient of an Australian Research Council Future Fellowship (project number FT100100470). We also wish to thank Vince Craig and Andrew Fogden for assistance with silanization treatment.

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- 787 • Bentheimer sandstone cores were treated to achieve different wettability states
- 788 • 3D x-ray microtomography experiments characterize air and brine flow in the cores
- 789 • Flow patterns during air invasion (drainage) are a function of wettability state
- 790 • Residual trapping of air (after imbibition) is reduced in intermediate-wet cores
- 791 • Buoyancy-driven flow becomes important for cores with altered wettability
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